7.4; N, 9.8. Found: C, 33.6; H, 7.2; N, 9.7.

[3-(Dimethylamino)butyl-*C*,*N*](dimethylamine)palladium(II) Trifluoromethanesulfonate (11). To a solution of complex 10 (10 mg, 0.035 mmol) in 3 mL of THF was added a solution of CF_3SO_3Ag (9 mg, 0.035 mmol) in 1 mL of THF at 0 °C under argon. After being stirred for 0.5 h, the solution was filtered and evaporated to give 11 (13 mg, 95%) as a pale yellowish oil.

[3-(Dimethylamino)butyl-*C*,*N*](ethylenediamine)palladium(II) Trifluoromethanesulfonate (12). Complex 4 (15 mg, 0.036 mmol) was dissolved in $CHCl_3$ (5 mL) and left at room temperature for 3 days. After filtration the solvent was removed under reduced pressure to give a crude product (14 mg). Crystallization from CH_2Cl_2/pentane afforded white crystals of product 12 (12 mg, 80%). Anal. Calcd for $C_9H_{22}N_3SO_3F_3Pd$: C, 26.0; H, 5.33; N, 10.1. Found: C, 25.4; H, 5.26; N, 10.1.

Decomposition of Palladium Complexes with Trifluoroacetic Acid. (1) Decomposition of Chloro[2-(dimethylamino)-1-methylpropyl-*C*,*N*](dimethylamine)palladium(II) (2) with Trifluoroacetic Acid. To a solution of complex 2 (28.7 mg, 0.1 mmol) in $CDCl_3$ (1 mL) was added trifluoroacetic acid (15 μL, 0.2 mmol) at 0–5 °C after degassing under argon. The cold bath was removed, and the reaction mixture was stirred for 0.5 h at room temperature. After addition of Na_2CO_3 (23 mg, 0.22 mmol) and stirring for 2 h, the reaction mixture was filtered. Benzene (4.4 μL, 0.05 mmol) was added into the filtrate as an internal NMR standard. On the basis of ^1H NMR and ^{13}C NMR spectra, the products were assigned as 3-(*N*,*N*-dimethylamino)-1-butene (13) (81%) and dichlorobis(dimethylamino)palladium (18%). ^1H NMR ($CDCl_3$) of 3-(dimethylamino)-1-butene: δ 1.36 (d, J = 6.8 Hz, 3 H, CH_3), 2.58 (s, 3 H, N–CH_3), 2.61 (s, 3 H, N–CH_3), 3.69 (dq, J_1 = 6.8, J_2 = 8.1 Hz, 1 H, CH–N), 5.37 (dt, J_1 = 17.0, J_2 = 0.8 Hz, 1 H, C=CH_Z), 5.43 (dt, J_1 = 10.4, J_2 = 0.8 Hz, 1 H, C=CH_E), 5.77 (ddd, J_1 = 8.1, J_2 = 10.4, J_3 = 17.0 Hz, 1 H, C=CH–C). ^{13}C NMR of 3-(*N*,*N*-dimethylamino)-1-butene: δ 15.22, 34.68, 42.11, 63.69, 123.81, 130.84. ^1H NMR ($CDCl_3$) of dichlorobis(dimethylamino)palladium: δ 2.38 (d, J = 6.1 Hz, 6 H). ^{13}C NMR of dichlorobis(dimethylamino)palladium: δ 42.11.

(2) Decomposition of Other Compounds. The compounds [2-(dimethylamino)-1-methylpropyl-*C*,*N*](ethylenediamine)palladium(II) trifluoromethanesulfonate (4), chloro[3-(dimethylamino)butyl-*C*,*N*](dimethylamine)palladium(II) (10), and [2-(dimethylamino)-1-methylpropyl-*C*,*N*](dimethylamine)palladium(II) trifluoromethanesulfonate (3) were subjected to the same procedure as the decomposition of chloro[2-(dimethylamino)-1-methylpropyl-*C*,*N*](dimethylamine)palladium(II) (2) above. For results, see Table V.

Determination of Decomposition Temperatures of Palladium Complexes 2, 4, 5, 6, 7, 8a, 8b, 9, 10, and 12. Decompositon temperature was measured on a Büchi 510 melting point apparatus in an open capillary. The starting temperature was 20 °C and the heating rate was 2 °C/min in all cases. The results are listed in Table II. Compound 9 turned dark before any heating could be applied.

Acknowledgment. The financial support from Neste Chemicals and the Nordic Fund for Industrial and Technological Development is gratefully acknowledged. We are very thankful to Professor Björn Åkermark for fruitful discussions.

Reaction of 1-Silyl Dienol Silyl Ethers with Palladium(II) Complexes: Novel Formation of Several Types of (η^3-Allyl)palladium(II) Complexes via the Versatile Complex (η^3-1-(Silylcarbonyl)allyl)palladium Chloride

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Reaction of the 1-silyl dienol silyl ethers 1 with Pd(II) salts gave various (η^3-allyl)palladium complexes depending on the type of Pd(II) salts, solvents, and the acidity of the medium. Treatment of 1 with Li_2PdCl_4 in the presence of Li_2CO_3 in MeOH resulted in simple transmetalation to give the (η^3-1-(silylcarbonyl)allyl)palladium chloride compound 2. Reaction of 1 with $PdCl_2(PhCN)_2$ in benzene led to formation of the (η^3-1-silylallyl)palladium chloride compound 4, a formal decarbonylation product of 2. Reaction of 1 with $PdCl_2(PhCN)_2$ in MeOH gave the (η^3-1-methoxy-3-methyl-1-silylallyl)palladium chloride compound 5. The key complex 2 was transformed into 4 by decarbonylation or into 5 by two-electron reduction. The complex 2 afforded (η^3-1-(methoxycarbonyl)allyl)palladium chloride (3) when treated with a stoichiometric amount of $PdCl_2(PhCN)_2$ in MeOH in the presence of Li_2CO_3 and also the (η^3-1-methoxy-3-(methoxymethyl)-1-silylallyl)palladium chloride compound 8 on treatment with a catalytic amount of HCl in MeOH. Possible reaction sequences connecting all of these η^3-allyl complexes are proposed.

Introduction

Extensive studies have been done on the reactions of (η^3-allyl)metal complexes.[1] In contrast, however, the chemistry of the (η^3-allyl)metal complexes in which a functional group is attached to the allyl moiety still remains to be studied. In view of this, the studies on the carbonyl groups attached at terminal carbons of an η^3-allyl system are very interesting. However, there have been only a few examples of the utilization of such carbonyl groups, i.e. those in (η^3-allyl)molybdenum[2] and (η^3-allyl)ruthenium complexes.[3] No such utilization in (η^3-allyl)palladium has yet been reported.

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[1] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. In *Principles and Applications of Organotransition Metal Chemistry*; University Science Books; Mill Valley, CA, 1987; Chapter 19.

[2] (a) Benyunes, S. A.; Green, M.; Grimshire, M. J. *Organometallics* **1989**, *8*, 2268. (b) Vong, W.; Peng, S.; Liu, R. *Organometallics* **1990**, *9*, 2187. Uong, W.; Lin, S.; Liu, R.; Lee, G.; Peng, S. *J. Chem. Soc., Chem. Commun.* **1990**, 1285.

[3] Benyunes, S. A.; Day, J. P.; Green, M.; Al-Saadoon, A. W.; Waring, T. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1416.

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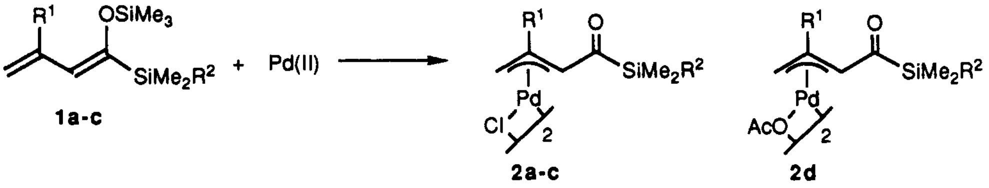
Table I. Simple Transmetalation of Dienol Silyl Ethers with Pd(II) Salts



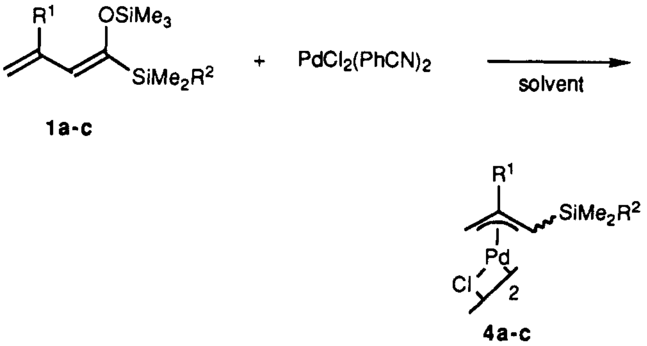
dienol silyl ether	Pd(II) salt	additive	solvent	product	yield,[a] %
1a: R^1 = H, R^2 = Me	Li_2PdCl_4	Li_2CO_3	MeOH	**2a**	85[b] (syn)
1b: R^1 = H, R^2 = Ph	Li_2PdCl_4	Li_2CO_3	MeOH	**2b**	33[c] (syn)
1c: R^1 = Me, R^2 = Me	Li_2PdCl_4	Li_2CO_3	MeOH	**2c**	72 (syn/anti = 27/73)
1a	Li_2PdCl_4	Li_2CO_3	THF	**2a**	42[d] (syn)
1a	Li_2PdCl_4		THF	**2a**	41[e] (syn)
1a	$Pd(OAc)_2$		C_6H_6	**2d**	51 (syn)

[a] All yields refer to isolated yields. [b] A small amount of **3** (4%) was obtained. [c] A small amount of **3** (2%) was obtained. [d] A small amount of **4a** (2%) was obtained. [e] A small amount of **4a** (7%) was obtained.

We thought it very interesting to study reactions of Pd(II) salts with the 1-silyl dienol silyl ethers **1**, since these reactions may provide a new entry to (η^3-allyl)palladium complexes bearing carbonyl functionalities.[4] In addition, the dienol silyl ether **1** contains various functional groups such as diene, dienol, enol silyl ether, and vinylsilane as well as the latent functionality of ketone, acyl silane, and enone. These multiple functionalities, when coupled with the oxidation/reduction properties of Pd(II) salts, would bring about a unique opportunity to find a variety of new reactions.

We have reported the preliminary finding that the reaction of dienol silyl ethers **1** with Pd(II) salts gives not only silylcarbonyl-substituted (η^3-allyl)palladium species but also their decarbonylation products.[6] We wish to report more detailed aspects of these reactions giving various (η^3-allyl)palladium complexes, which heavily depend on the type of Pd(II) salts, solvents, and the acidity of the medium, and the possible mechanisms of all reactions.

Table II. Decarbonylative Reactions of Dienol Silyl Ethers with $PdCl_2(PhCN)_2$



dienol silyl ether	solvent	product	yield,[a] % (syn/anti)
1a	THF	**4a**	44 (80/20)
1a	C_6H_6	**4a**	76 (73/27)
1b	C_6H_6	**4b**	57 (85/15)
1c	C_6H_6	**4c**	41 (33/67)

[a] All yields refer to isolated yields.

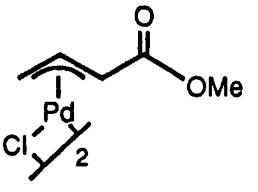
Table III. Decarbonylation of 2a–c Catalyzed by $PdCl_2(PhCN)_2$[a]

compd	time, h	product	yield,[b] % (syn/anti)
2a	12	**4a**	86 (71/29)
2b	24	**4b**	43 (83/17)
2c	70	**4c**	43 (59/41)

[a] Reaction conditions: **2** (0.1 mmol), $PdCl_2(PhCN)_2$ (0.01 mmol), C_6D_6 (1 mL), 25 °C. [b] NMR yields.

Results and Discussion

Simple Transmetalation. In the reaction of 1-silyl dienol silyl ethers with Pd(II) salts, a simple transmetalation to give (η^3-1-(silylcarbonyl)allyl)palladium complexes occurred under only limited conditions. Thus, the reaction of dienol silyl ethers **1a–c** with Li_2PdCl_4 in the presence of Li_2CO_3 in MeOH gave (η^3-1-(silylcarbonyl)allyl)palladium chlorides **2a–c** (85%, 33%, 72%) together with a small amount of (η^3-1-(methoxycarbonyl)allyl)palladium chlorides **3**[7] (4% from **2a**, 2% from **2b**) (Table I). The same reaction occurred in THF to give **2a** (42%) together with small amounts of (η^3-1-silylallyl)palladium chloride **4a** (2%), which is a formal decarbonylation product of **2a**. The reaction of **1a** with $Pd(OAc)_2$ in benzene also involved simple transmetalation to give **2d**. The use of Li_2PdCl_4 or $Pd(OAc)_2$ is essential to the simple transmetalation, for the analogous reactions employing $PdCl_2(PhCN)_2$ resulted in different products (see below).



3

Decarbonylation. In the reaction of **1a** in THF, changing the Pd(II) salt from Li_2PdCl_4 to $PdCl_2(PhCN)_2$ led to the exclusive formation of **4a** (44%). Moreover, similar treatment of **1a–c** with $PdCl_2(PhCN)_2$ in benzene also afforded (η^3-1-silylallyl)palladium chlorides **4a–c** (76%, 57%, 41%; Table II). The nature of the solvent is important here, for the reaction of $PdCl_2(PhCN)_2$ with **1** *in MeOH* took a still different course (see below).

When treated with a catalytic amount of $PdCl_2(PhCN)_2$ in benzene, **2a–c** underwent decarbonylation to give **4a–c** (85%, 43%, 43%; Table III). It then may well be that,

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(4) It is actually known that the reaction of an enol silyl ether with Pd(II) salts gave an (oxo-η^3-allyl)palladium intermediate,[5] and the reaction of a dienol silyl ether with $[M(NCMe)_2(CO)(\eta^5\text{-}C_5H_5)][BF_4]$ (M = Mo, Ru)[2a,3] gave an (η^3-1-formylallyl)metal complex.

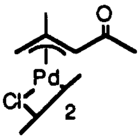
(5) (a) Ito, Y.; Aoyama, H.; Hirao, T.; Mochizuki, A.; Saegusa, T. *J. Am. Chem. Soc.* **1979**, *101*, 494. (b) Kende, A. S.; Roth, B.; Sanfilippo, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 1784.

(6) Ogoshi, S.; Ohe, K.; Chatani, N.; Kurosawa, H.; Kawasaki, Y.; Murai, S. *Organometallics* **1990**, *9*, 3021.

(7) Tsuji, J.; Imamura, S. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 197.

in the decarbonylation reaction of dienol silyl ether 1 with $PdCl_2(PhCN)_2$ in benzene (Table II), the formation of 2 is slow so that the decarbonylation catalyst $PdCl_2(PhCN)_2$ is always present to force most of the 2 formed to undergo decarbonylation.

This reaction is the first example of decarbonylation from formal homoacyl metal complexes. However, when 6[8] and 7,[9] analogous to **2a**, were treated with a catalytic amount of $PdCl_2(PhCN)_2$, decarbonylation did not occur. Thus, the decarbonylation needs the trimethylsilyl group attached to the carbonyl carbon.



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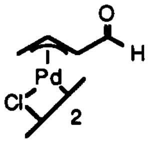

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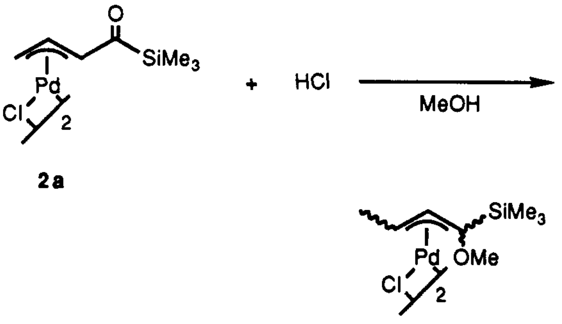
Two-Electron Reduction. The reaction of excess amounts of dienol silyl ethers **1a–c** with $PdCl_2(PhCN)_2$ (1/Pd = 2/1) in MeOH afforded the unexpected complexes (η^3-1-methoxy-3-methyl-1-silylallyl)palladium chloride (**5a–c**; 96%, 41%, 25%), no **2a–c** and **4a–c** being obtained (Table IV). These complexes were composed of some syn–anti isomers on the basis of ^{1}H NMR spectroscopy (see Experimental Section). However, we could not determine the exact disposition of the substituents with respect to the syn and anti sites. Note that the complex **5** is derived by a formal two-electron reduction of **2**. Similar reactions occurred also in EtOH and in benzyl alcohol to give the corresponding complexes **5d** and **5e** (95%, 47%; Table IV). There are only a small number of such complexes known that contain a terminal η^3-allyl carbon–oxygen bond (M = Pd, Ni, Fe).[10]

It is conceivable that the reaction of Table IV initially generated the complex **2** and Me_3SiCl, the latter of which might have reacted with MeOH to give HCl. Thus, we treated **2a** with 1 equiv of HCl (from Me_3SiCl) in MeOH resulting in formation of the complex **5a** (33%; eq 1).



2a

5a

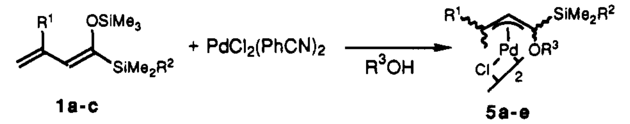
33%

(1)

However, the complexes **6** and **7**, analogous to **2a–c**, did not undergo the same reaction. Thus, the two-electron reduction of the η^3-allyl moiety also occurred only in **2**, in which silyl groups are attached at the carbonyl carbon.

Mechanistic Study. The decarbonylation reaction may be explained by a few mechanisms. The most plausible mechanism involves a palladium–silicon interaction.

Table IV. Reactions in Alcohol of Dienol Silyl Ethers with $PdCl_2(PhCN)_2$



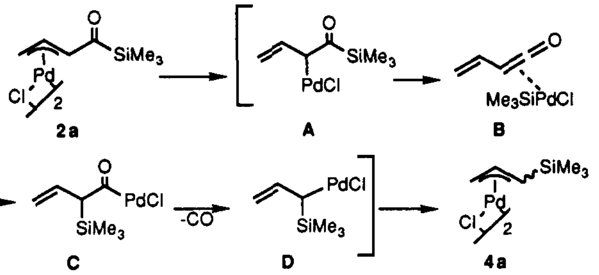
1a-c

5a-e

dienol silyl ether	solvent (R^3OH)	product	yield,[a] %
1a	MeOH	5a	96
1b	MeOH	5b	41
1c	MeOH	5c	25
1a	EtOH	5d	94
1a	$PhCH_2OH$	5e	47

[a] All yields refer to isolated yields.

Scheme I. Plausible Mechanism of Decarbonylation



Scheme I outlines a possible mechanism of the decarbonylation reaction.

The silylcarbonyl-substituted complex **2a** is converted to the η^1-allyl complex A, in which β-elimination of the trimethylsilyl group[11] affords the vinyl ketene complex intermediate B. No intermolecular exchange of the coordinated ketene would be occurring, because treatment of a mixture of **2b** and **2c** with a catalytic amount of $PdCl_2(PhCN)_2$ afforded only **4b** and **4c**, but no crossover products. Subsequent addition of the silyl–palladium moiety to the ketene in the reverse direction affords acylpalladium complex C, from which decarbonylation gives rise to the (η^1-allyl)palladium species D[12] and then (η^3-allyl)palladium complex **4a**. As an alternative, fragmentation of the vinylketene ligand in B into vinylcarbene and CO ligands, followed by insertion of the carbene into Si–Pd leading to D, can be envisaged.[13] A possible role of $PdCl_2$ species in catalyzing decarbonylation is to convert **2a** to the η^1-allyl intermediate.

Formation of **5** from **2** may be explained also by a few mechanisms. Any satisfactory mechanism must involve a source of electrons in order to be compatible with the apparently imbalanced stoichiometry of eq 1. Scheme II assumes MeOH as a reductant. In this scheme, the initial protonation converts **2a** to the dienol palladium complex E.[14] A similar conversion has been observed in the (η^3-allyl)molybdenum complex.[2a] An attack of the methoxy group on the palladium cation center gives the methoxy

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(8) Parshall, G. W.; Wilkinson, G. *Chem. Ind.* **1962**, 261.

(9) Andri, M. K.; Krylov, A. V.; Averochkin, N. E.; Belov, A. P. *Koord. Khim.* **1984**, *10*, 540.

(10) Sonoda, A.; Mann, B. E.; Maitlis, P. M. *J. Organomet. Chem.* **1975**, *96*, C16. Krysan, D. J.; Mackenzie, P. B. *J. Am. Chem. Soc.* **1988**, *110*, 6273. Goddard, R.; Green, M.; Hughes, R. P.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1976**, 1890. Ito, K.; Nakanishi, S.; Otsuji, Y. *Chem. Lett.* **1987**, 2103. Ito, K.; Nakanishi, S.; Otsuji, Y. *Chem. Lett.* **1988**, 473.

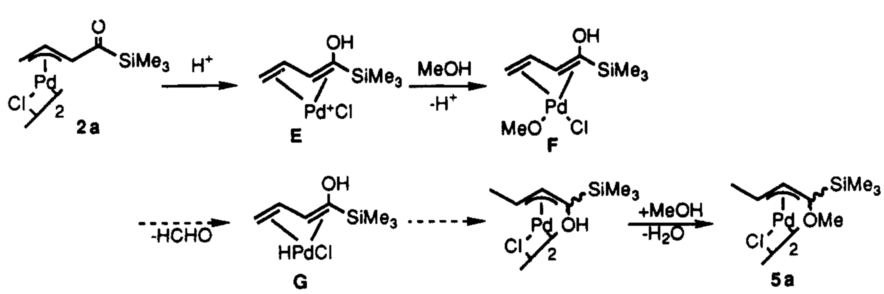
(11) Karabelas, K.; Hallberg, A. *J. Org. Chem.* **1989**, *54*, 1773.

(12) The 3-butenoylpalladium complexes analogous to C underwent decarbonylation to afford (η^3-allyl)palladium complexes: Ozawa, F.; Son, T.; Osakada, K.; Yamamoto, A. *J. Chem. Soc., Chem. Commun.* **1989**, 1067.

(13) Trost, B. M.; Self, C. R. *J. Am. Chem. Soc.* **1983**, *105*, 5942. Tsuji, J.; Watanabe, H.; Minami, I.; Shimizu, I. *J. Am. Chem. Soc.* **1985**, *107*, 2196. In a recent report on a vinylketene–iron to vinylketenimine–iron exchange, formation of a vinylcarbene–iron intermediate by decarbonylation is proposed; see: Richards, J. D.; Thomas, S. E. *J. Chem. Soc., Chem. Commun.* **1990**, 307. Alcock, N. W.; Richards, C. J.; Thomas, S. E. *Organometallics* **1991**, *10*, 231.

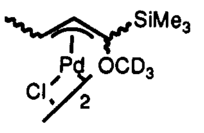
(14) It has been reported that acetyltrimethylsilane is converted to the enol isomer more easily than ordinary ketones are: Kresge, A. J.; Tobin, J. B. *J. Am. Chem. Soc.* **1990**, *112*, 2805.

Scheme II. Unlikely Mechanism



palladium species F. Subsequent β-elimination from the methoxy group[15] gives the key intermediate G, which can be converted to **5a**. According to this mechanism, **2a** would afford **5a** even with a catalytic amount of HCl. We assert below that this is not the case.

First, the reaction of **2a** (0.1 mmol) and benzyl alcohol (0.3 mmol) with 1 equiv of HCl in $CDCl_3$ gave **5e** and no benzaldehyde. Moreover, treatment of **1a** with $PdCl_2(PhCN)_2$ in CD_3OH resulted in **9**, where only the CH_3O– group was changed to the CD_3O– group and no deuterium incorporation in the rest of the allyl ligand was detected. From these results, it is clear that MeOH is not a source of electrons.



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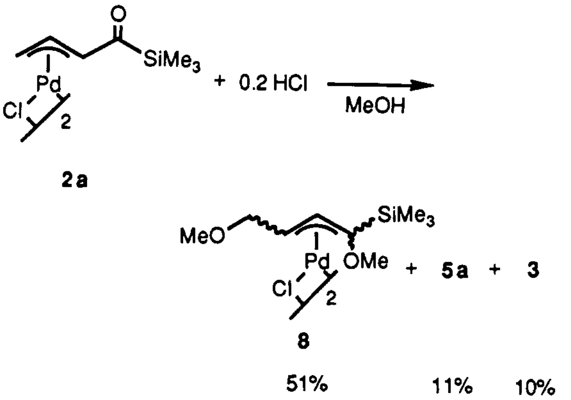
Second, when treated with a catalytic amount of HCl in MeOH, **2a** unexpectedly afforded the (η^3-1-methoxy-3-(methoxymethyl)-1-silylallyl)palladium chloride complex **8** (51%), together with a smaller amount of **5a** (11%) and the (η^3-1-(methoxycarbonyl)allyl)palladium chloride compound **3** (10%; eq 2).

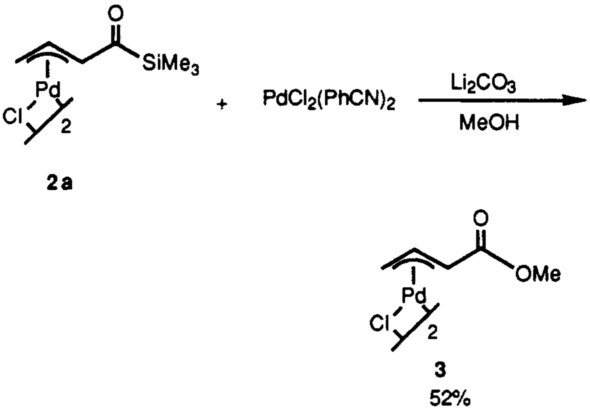


(2)

The complex **8** was transformed into **5a** (27%) with a stoichiometric amount of HCl in MeOH. The complex **8** was also transformed into **5d** with a stoichiometric amount of HCl in EtOH (11%). These facts suggest that in the presence of HCl the formation of **8** from **2a** was reversible. The formation of **8** may be explained by the attack of methanol directly at the diene of E,[16] rather than the Pd atom of E. In any case, it is clear that 1 equiv of HCl is necessary for the formation of **5a**.

Scheme III shows a more plausible mechanism. In the presence of HCl, **2a** could generate $PdCl_2$ and the α,β-unsaturated acylsilane H. As suggested above, this Pd(II) species would catalytically convert **2a** to the ketene–palladium complex intermediate B. The intermediate B might react with MeOH to give the key species HPdCl. Coordination of the dienol of E or H to HPdCl gives G, which is eventually transformed into **5a** by hydride attack and subsequent alcohol exchange. In this mechanism, HCl is not regenerated and the η^3-(silylcarbonyl)allyl ligand is a source of electrons. However, we failed to detect any product expected to be derived from vinylketene or any other intermediate in the reactions of both Table IV and eq 1.

When the reaction of **2a** with 1 equivalent of $PdCl_2(PhCN)_2$ in MeOH was carried out in the presence of Li_2CO_3, a considerable amount of **3** was obtained (52%; eq 3). The formation of **3** could arise via the generation of methyl crotonate through trapping of vinylketene intermediate B by MeOH.



(3)

Experimental Section

General Procedures. ^1H NMR spectra were recorded on JEOL JNM-GSX 270 (270 MHz), JEOL JNM-GSX 400 (400 MHz), and Bruker AM600 (600 MHz) spectrometers as solutions in $CDCl_3$ with reference to $CHCl_3$ (δ 7.26). IR spectra were recorded on a Hitachi 270-50 infrared spectrophotometer as KBr pellets. Melting points were determined on a Mitamura Riken Kogyo micro melting point apparatus and are uncorrected.

Representative Synthesis of 1-(Trimethylsilyl)-1-(trimethylsiloxy)butadiene (1a). An *n*-hexane solution of *n*-BuLi (30 mL; 1.6 M, 48 mmol) was added to a solution of 3.8 g (33.3 mmol) of allyltrimethylsilane in 13.3 mL of dry TMEDA and 56 mL of dry THF at 0 °C under an atmosphere of argon. The solution was stirred for 6 h. After three evacuations of argon gas under vacuum followed by substitution with carbon monoxide, the reaction mixture was warmed to 25 °C and stirred under an atmosphere of carbon monoxide for 12 h. Then 7.0 mL (6.0 g, 55 mmol) of Me_3SiCl was added to the mixture at 0 °C and the mixture was stirred for 1 h. The mixture was poured into 200 mL of saturated aqueous sodium bicarbonate solution. The aqueous layer was extracted with three 100-mL portions of Et_2O and the ether solution dried over anhydrous magnesium sulfate. The solvents were removed under reduced pressure to provide the mixture of TMEDA and dienol silyl ether **1a**. TMEDA was

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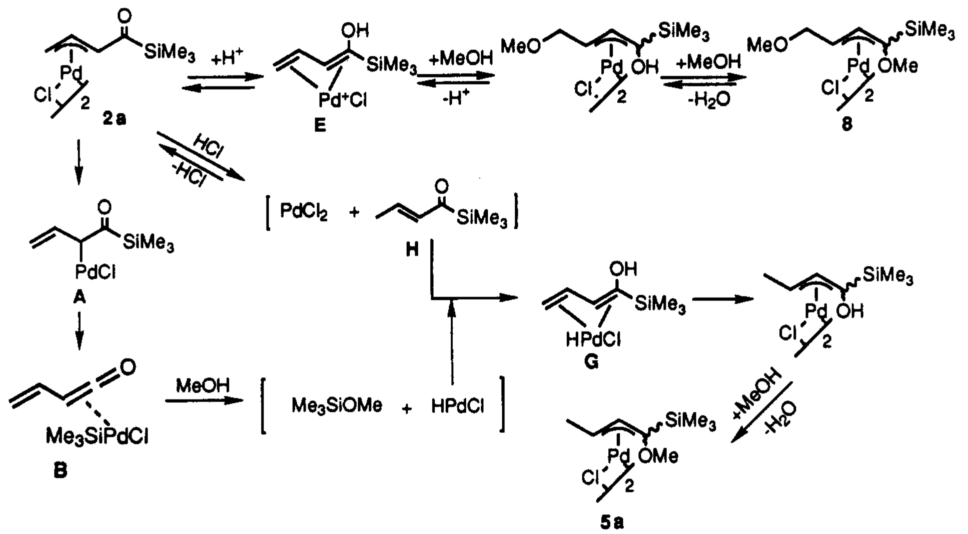
[15] A similar reaction has been observed in Ir–OR species: Vaska, L.; Diluzio, J. W. *J. Am. Chem. Soc.* **1962**, *84*, 4989.

[16] Bäckvall, J. E.; Nordberg, R. E.; Wilhelm, D. *J. Am. Chem. Soc.* **1985**, *107*, 6892.

Scheme III. Plausible Mechanism



distilled off from dienol silyl ether **1a** at 760 mmHg very carefully. Then the dienol silyl ether **1a** was obtained by distillation (50 mmHg, 100 °C) in 70% isolated yield: IR (neat) 1630, 1570 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.15 (s, SiMe$_3$), 0.23 (s, SiMe$_3$).

Reaction of 1-(Trimethylsilyl)-1-(trimethylsiloxy)butadiene (1a) with Li$_2$PdCl$_4$. Preparation of (η^3-1-((Trimethylsilyl)carbonyl)allyl)palladium Chloride (2a-syn). A suspension of 885 mg (5 mmol) of PdCl$_2$, 440 mg (10 mmol) of anhydrous LiCl, and 370 mg (5 mmol) of Li$_2$CO$_3$ in 25 mL of anhydrous MeOH was stirred for 2 h under an atmosphere of argon at 25 °C. Then, 1500 mg (7 mmol) of dienol silyl ether **1a** was added to the suspension and the mixture was stirred for 12 h. The reaction mixture was filtered under an atmosphere of argon. The filtrate was concentrated in vacuo (5 mmHg), and the concentrate was separated with use of a column (Florisil, 15 mm i.d. × 300 mm length, CH$_2$Cl$_2$). Orange fractions were concentrated under reduced pressure (5 mmHg) to afford an orange oil. Into this oil was poured 50 mL of hexane, and the mixture was cooled to -10 °C. After 20 h, the orange solids obtained were washed with three 10-mL portions of hexane. The complex **2a** was obtained with a small amount of **3** in 85% (1203 mg, **2a**/**3** = 95/5) isolated yield: mp 113–115 °C dec; IR (KBr) 1608 cm^{-1}; ^{1}H NMR (CDCl$_3$, J in Hz) δ 0.25 (s, 9 H), 3.22 (d, J = 12.7, 1 H), 4.08 (d, J = 10.7, 1 H), 4.21 (d, J = 6.8, 1 H), 5.95 (ddd, J = 12.7, 10.7, 6.8, 1 H). Anal. Calcd for $C_7H_{13}OClPdSi$: C, 29.70; H, 4.63; Cl, 12.52. Found: C, 29.42; H, 4.42; Cl, 12.39.

(η^3-1-((Dimethylphenylsilyl)carbonyl)allyl)palladium Chloride (2b-syn) was prepared with use of the procedure for **2a**: yield 33%; mp 124–125 °C dec; IR (KBr) 1605 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.52 (s, 3 H), 0.59 (s, 3 H), 3.22 (d, J = 12.7, 1 H), 3.95 (d, J = 11.0, 1 H), 4.12 (d, J = 7.1, 1 H), 5.84 (ddd, J = 12.7, 11.0, 7.1, 1 H), 7.41 (m, 3 H), 7.61 (m, 2 H). Anal. Calcd for $C_{12}H_{15}OClPdSi$: C, 41.75; H, 4.38. Found: C, 41.55; H, 4.44.

(η^3-1-((Trimethylsilyl)carbonyl)-2-methylallyl)palladium Chloride (2c-syn,anti) was prepared with use of the procedure for **2a**: yield 72% syn/anti = 27/73); mp 97–99 °C dec; IR (KBr) 1602 cm^{-1}; ^{1}H NMR (CDCl$_3$) **2c**-syn δ 0.23 (s, 9 H), 2.45 (s, 3 H), 2.98 (s, 1 H), 3.86 (s, 1 H), 3.94 (s, 1 H), **2c**-anti δ 0.27 (s, 9 H), 2.13 (s, 3 H), 3.90 (s, 1 H), 4.05 (s, 1 H), 5.19 (s, 1 H). Anal. Calcd for $C_8H_{15}OClPdSi$: C, 32.34; H, 5.09; Cl, 11.93. Found: C, 31.79; H, 5.13; Cl, 11.72.

Reaction of 1-(Trimethylsilyl)-1-(trimethylsiloxy)butadiene (1a) with PdCl$_2$(PhCN)$_2$. Preparation of (η^3-1-(Trimethylsilyl)allyl)palladium Chloride (4a-syn,anti). Under an atmosphere of argon, 214 mg (1 mmol) of dienol silyl ether **1a** was added to a suspension of 384 mg (1 mmol) of PdCl$_2$(PhCN)$_2$ in 10 mL of anhydrous benzene and the mixture stirred for 6 h at 25 °C. The reaction mixture was filtered, and the yellow solution was concentrated in vacuo (5 mmHg) to give yellow solids. These were washed with three 10-mL portions of hexane. The complex **4a** was obtained in 76% (183 mg, syn/anti = 73/27) isolated yield: mp 165–170 °C dec; IR (KBr) no absorption at 1600–1800 cm^{-1}; ^{1}H NMR (CDCl$_3$) **4a**-syn δ 0.20 (s, 9 H), 2.96 (d, J = 11.3, 1 H), 3.05 (d, J = 13.4, 1 H), 4.07 (d, J = 6.1, 1 H), 5.30 (ddd, J = 11.3, 13.4, 6.1, 1 H), **4a**-anti δ 0.23 (s, 9 H), 3.09 (d, J = 12.2, 1 H), 3.97 (d, J = 7.2, 1 H), 4.07 (d, J = 9.8, 1 H), 5.75 (ddd, J = 12.2, 7.2, 9.8, 1 H). Anal. Calcd for $C_6H_{13}ClPdSi$: C, 28.25; H, 5.14. Found: C, 28.66; H, 5.06.

Reaction of 1-(Trimethylsilyl)-1-(trimethylsiloxy)butadiene (1a) with Pd(OAc)$_2$. Preparation of (η^3-1-((Trimethylsilyl)carbonyl)allyl)palladium Acetate (2d-syn). The Pd(II) salt in the preparation of **4a** was changed from Pd$_2$Cl$_2$(PhCN)$_2$ to Pd(OAc)$_2$ to give (η^3-1-((trimethylsilyl)carbonyl)allyl)palladium acetate in 51% isolated yield: mp 130 °C dec; IR (KBr) 1610, 1571 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.19 (s, 9 H), 1.94 (s, 3 H), 3.30 (d, J = 12.5, 1 H), 3.84 (d, J = 7.1, 1 H), 4.21 (d, J = 11.0, 1 H), 6.39 (ddd, J = 12.5, 7.1, 11.0, 1 H). Anal. Calcd for $C_9H_{16}O_3PdSi$: C, 35.24; H, 5.26. Found: C, 35.02; H, 5.22.

(η^3-1-(Dimethylphenylsilyl)allyl)palladium Chloride (4b-syn,anti) was prepared with use of the procedure for **4a**: yield 57% (syn/anti = 85/15); mp 87–88 °C; IR (KBr) no absorption at 1600–1800 cm^{-1}; ^{1}H NMR (CDCl$_3$) **4b**-syn δ 0.50 (s, 3 H), 0.52 (s, 3 H), 3.02 (d, J = 11.5, 1 H), 3.17 (d, J = 13.7, 1 H), 4.09 (d, J = 6.4, 1 H), 5.32 (ddd, J = 11.5, 13.7, 6.4, 1 H), 7.37 (m, 3 H), 7.60 (m, 2 H). **4b**-anti δ 0.55 (s, 3 H), 0.59 (s, 3 H), 2.91 (d, J = 12.5, 1 H), 3.91 (d, J = 7.3, 1 H), 4.12 (d, J = 9.3, 1 H), 5.82 (ddd, J = 12.5, 7.3, 9.3, 1 H), 7.37 (m, 3 H), 7.60 (m, 2 H). Anal. Calcd for $C_{11}H_{15}ClPdSi$: C, 41.65; H, 4.77; Cl, 11.12. Found: C, 41.52; H, 4.78; Cl, 11.10.

(η^3-1-(Trimethylsilyl)-2-methylallyl)palladium Chloride (4c-syn,anti) was prepared with use of the procedure for **4a**: yield 41% (syn/anti = 33/67); mp 108–109 °C; IR (KBr) no absorption at 1600–1800 cm^{-1}; ^{1}H NMR (CDCl$_3$) **4c**-syn δ 0.24 (s, 9 H), 2.12 (s, 3 H), 2.75 (s, 1 H), 2.81 (s, 1 H), 3.76 (s, 1 H), **4c**-anti δ 0.21 (s, 9 H), 2.17 (s, 3 H), 2.92 (s, 1 H), 3.87 (s, 1 H), 3.87 (s, 1 H). Anal. Calcd for $C_7H_{15}ClPdSi$: C, 31.24; H, 5.62; Cl, 13.17. Found: C, 31.55; H, 5.63; Cl, 13.31.

Crossover Experiment. A mixture of 17.3 mg of **2b** (0.05 mmol), 29.7 mg of **2c** (0.1 mmol), and 5.7 mg of PdCl$_2$(PhCN)$_2$ (0.015 mmol) was dissolved in 1 mL of C$_6$D$_6$. After 24 h at 25 °C, the reaction mixture was examined by ^{1}H NMR (**2b**, 9%; **4b**, 77% (syn/anti = 83/17); **2c**, 70%; **4c**, 29% (syn/anti = 59/41)).

Reaction of 1-(Trimethylsilyl)-1-(trimethylsiloxy)butadiene (1a) with PdCl$_2$(PhCN)$_2$. Preparation of (η^3-1-Methoxy-3-methyl-1-(trimethylsilyl)allyl)palladium Chloride (5a). Under an atmosphere of argon, 428 mg (2 mmol) of dienol silyl ether **1a** was added to a suspension of 384 mg (1 mmol) of PdCl$_2$(PhCN)$_2$ in 5 mL of anhydrous MeOH and the mixture was stirred for 12 h at 25 °C. The reaction mixture was filtered, and the red solution was concentrated in vacuo (5 mmHg). The concentrate was separated with use of a column (Florisil, 15 mm i.d. × 200 mm length, CH$_2$Cl$_2$). The yellow fraction was concentrated in vacuo (0.5 mmHg) to give yellow solids of **5a** in 96% (292 mg) isolated yield: mp 145–150 °C dec; IR (KBr) no absorption at 1600–1800 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.31 (s, 9 H), 1.23 (d, J = 6.1, 3 H), 3.47 (dq, J = 6.1, 11.2, 1 H), 3.57 (s, 3 H), 5.30

(d, J = 11.2, 1 H). The peaks at δ 0.31 and 3.57 split into four peaks (0.273, 0.300, 0.312, 0.324; 3.538, 3.562, 3.573, 3.560), respectively, at −30 °C. Anal. Calcd for $C_8H_{17}OClPdSi$: C, 32.12; H, 5.73; Cl, 11.85. Found: C. 32.31; H, 5.74; Cl, 11.70.

(η^3-1-Methoxy-3-methyl-1-(dimethylphenylsilyl)allyl)-palladium Chloride (5b) was prepared with use of the procedure for **5a**: yield 41%; mp 142 °C dec; IR (KBr) no absorption at 1600–1800 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.56 (s, 3 H), 0.81 (s, 3 H), 1.12 (d, J = 5.6, 3 H), 3.13 (dq, J = 11.0, 5.6, 1 H), 3.61 (s, 3 H), 5.34 (d, J = 11.2, 1 H), 7.38 (m, 3 H), 7.74 (m, 2 H). The peak at δ 0.81 splits into four peaks (0.723, 0.740, 0.825, 0.838) at −40 °C. Anal. Calcd for $C_{13}H_{19}OClPdSi$: C, 43.22; H, 5.30; Cl, 9.81. Found: C, 43.44; H, 5.29; Cl, 9.72.

(η^3-1-Methoxy-3,3-dimethyl-1-(trimethylsilyl)allyl)palladium Chloride (5c) was prepared with use of the procedure for **5a**: yield 25% (major/minor = 67/33); mp 119–123 °C dec: IR (KBr) no absorption at 1600–1800 cm^{-1}; ^{1}H NMR ($CDCl_3$) (major) δ 0.45 (s, 9 H), 1.24 (s, 3 H), 1.39 (s, 3 H), 3.51 (s, 3 H), 5.00 (s, 1 H), (minor) δ 0.31 (s, 9 H), 1.44 (s, 3 H), 1.58 (s, 3 H), 3.57 (s, 3 H), 4.24 (s, 1 H). Anal. Calcd for $C_9H_{19}OClPdSi$: C, 34.51; H, 6.11. Found: C, 34.60; H, 6.31.

(η^3-1-Ethoxy-3-methyl-1-(trimethylsilyl)allyl)palladium Chloride (5d) was prepared with use of the procedure for **5a**: yield 94%; mp 150–155 °C dec; IR (KBr) no absorption at 1600–1800 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.33 (s, 9 H), 1.21 (d, J = 6.1, 3 H), 1.24 (t, J = 6.4, 3 H), 3.43 (dq, J = 11.2, 6.8, 1 H), 3.83 (m, J = 6.4, 2 H), 5.26 (d, J = 11.2, 1 H). The peak at δ 0.33 splits into four peaks (0.260, 0.282, 0.290, 0.317) at −40 °C. Anal. Calcd for $C_9H_{19}OClPdSi$: C, 34.51; H, 6.11; Cl, 11.32. Found: C, 34.67; H, 6.11; Cl, 11.30.

(η^3-1-Benzyloxy-3-methyl-1-(trimethylsilyl)allyl)palladium Chloride (5e) was prepared with use of the procedure for **5a**: yield 47% (major/minor = 54/46); mp 155–157 °C dec; IR (KBr) no absorption at 1600–1800 cm^{-1}; ^{1}H NMR ($CDCl_3$) (major) δ 0.36 (s, 9 H), 1.25 (d, J = 5.6, 3 H), 3.51 (dq, J = 10.0, 5.6, 1 H), 4.79 (d, J = 11.2, 1 H), 4.96 (d, J = 11.2, 1 H), 5.37 (d, J = 10.0, 1 H), 7.33 (m, 5 H), (minor) δ 0.34 (s, 9 H), 1.23 (d, J = 5.6, 3 H), 3.51 (dq, J = 10.0, 5.1, 1 H), 4.77 (d, J = 11.0, 1 H), 4.94 (d, J = 11.0, 1 H), 5.37 (d, J = 10.0, 1 H), 7.33 (m, 5 H). Anal. Calcd for $C_{14}H_{21}OClPdSi$: C, 44.81; H, 5.64. Found: C, 45.45; H, 5.63.

Reaction of 2a with a Stoichiometric Amount of HCl. Under an atmosphere of argon, 109 mg (1 mmol) of Me_3SiCl was added to a suspension of 285 mg (1 mmol) of **2a** in 10 mL of anhydrous MeOH and the reaction mixture was stirred for 24 h at 25 °C. The reaction mixture was filtered, and the filtrate was concentrated in vacuo (5 mmHg). The concentrate was separated with use of a column (Florisil, 15 mm i.d. × 100 mm length, CH_2Cl_2). Yellow fractions were concentrated under reduced pressure (1 mmHg) to give crude **5a** in 32% NMR yield.

Reaction of 1a with $PdCl_2(PhCN)_2$ in CD_3OH. Preparation of 9. The solvent in the preparation of **5a** was changed from CH_3OH to CD_3OH. The complex **9** was obtained in 65% isolated yield.

Reaction of 2a with a Catalytic Amount of HCl. Preparation of (η^3-1-Methoxy-3-(methoxymethyl)-1-(dimethylphenylsilyl)allyl)palladium Chloride (8). Under an atmosphere of argon, 17 mg (0.16 mmol) of Me_3SiCl was added to a suspension of 227 mg (0.8 mmol) of **2a** in 4 mL of anhydrous MeOH and the reaction mixture stirred for 12 h at 25 °C to generate yellow precipitates. The reaction mixture was filtered, and the yellow solids were dissolved in CH_2Cl_2. This solution was concentrated in vacuo to give yellow oily solids. The oily solids were separated with use of a column (Florisil, 15 mm i.d. × 100 mm length, CH_2Cl_2). Yellow fractions were concentrated in vacuo (1 mmHg) to give **8** (129 mg) in 52% isolated yield: mp 128–130 °C dec; IR (KBr) no absorption at 1600–1800 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.34 (s, 9 H), 3.37 (m, 2 H), 3.38 (s, 3 H), 3.56 (s, 3 H), 3.59 (m, 1 H), 5.42 (d, J = 10.3, 1 H). The peaks at 0.34, 3.38, and 3.56 split into three peaks (0.281, 0.303, 0.323; 3.366, 3.385, 3.404; 3.504, 3.541, 3.572), respectively, at −50 °C. Anal. Calcd for $C_9H_{19}O_2ClPdSi$: C, 32.84; H, 5.82; Cl, 10.77. Found: C, 32.80; H, 5.78; Cl, 10.66. The MeOH filtrate was concentrated in vacuo (5 mmHg), and the residue was separated with use of a column (Florisil, 15 mm i.d. × 100 mm length, CH_2Cl_2). Yellow fractions were concentrated to give a mixture of **5a** (11%) and **3** (8%).

Transformation of 8 into 5a. Under an atmosphere of argon, 3.0 mg (0.028 mmol) of trimethylsilyl chloride was added to a suspension of 9.1 mg (0.028 mmol) of **8** in 0.4 mL of anhydrous MeOH. After 12 h at 25 °C, the reaction mixture was evaporated under reduced pressure (5 mmHg) and the residue was separated by column chromatography (Florisil, 8 mm i.d. × 70 mm length, CH_2Cl_2). Yellow fractions were concentrated to give **5a** in 27% isolated yield.

Transformation of 8 into 5d. Under an atmosphere of argon, 94.1 mg (0.86 mmol) of trimethylsilyl chloride was added to a suspension of 283 mg (0.86 mmol) of **8** in 5 mL of anhydrous EtOH and the mixture was stirred for 12 h at 25 °C. The reaction mixture was concentrated in vacuo (5 mmHg), and the concentrate was separated by column chromatography (Florisil, 15 mm i.d. × 100 mm length, CH_2Cl_2). Red fractions were concentrated in vacuo (5 mmHg) to give red oily solids, which were washed with three 3-mL portions of *n*-hexane to give **5d** in 11% isolated yield.

Trapping of the Vinylketene Intermediate with MeOH. Under an atmosphere of argon, 113 mg (0.4 mmol) of **2a**, 153 mg (0.4 mmol) of $PdCl_2(PhCN)_2$, and 30 mg (0.4 mmol) of Li_2CO_3 were suspended in 2 mL of anhydrous MeOH. After 12 h, the reaction mixture was filtered and the filtrate was concentrated in vacuo (5 mmHg). The residue was dissolved in CH_2Cl_2 and dried over anhydrous magnesium sulfate. The drying agent was filtered out and the filtrate was concentrated in vacuo (1 mmHg) to give **3** in 52% isolated yield.

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