Novel Decarbonylation of a Formal Homoacyl–Palladium Linkage, $PdCH(CR{=}CH_2)C(O)SiR'_3$, Affording a $PdCH(CR{=}CH_2)SiR'_3$ Moiety[†]

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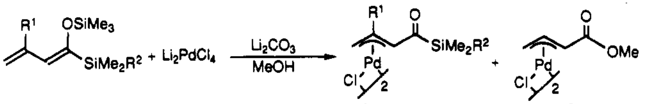
Summary: Reaction of dienol silyl ethers **1a–c** with Li_2PdCl_4 in the presence of Li_2CO_3 in MeOH gave [η^3-1-(silylcarbonyl)allyl]palladium chlorides **2a–c**, which have a formal homoacyl–palladium linkage, $PdCH(CR{=}CH_2)C(O)SiR'_3$. When treated with $PdCl_2(PhCN)_2$, complexes **2a–c** underwent decarbonylation to give (η^3-1-silylallyl)palladium chlorides **4a–c**. This reaction is the first example of the decarbonylation of homoacyl–metal complexes.

We wish to report a novel decarbonylation of the formal homoacyl–palladium linkage $Pd{-}CR_2C(O)R'$ in [η^3-1-(silylcarbonyl)allyl]palladium complexes, which we have found during our study aimed at developing a new entry to (η^3-1-acylallyl)palladium complexes from dienol silyl ethers and palladium(II) complexes.[1] Although decarbonylation of acylmetals $M{-}C(O)R'$, together with its reversal, carbonylation of alkylmetals, very often constitute a reaction sequence or a catalytic cycle for accomplishing transition-metal-mediated organic transformation, the decarbonylation described here is a new process. We also will show that the silyl substituent attached to the carbonyl group plays a unique role in this reaction.

The reaction of dienol silyl ether **1a** (7 mmol) with Li_2PdCl_4 (5 mmol) in the presence of Li_2CO_3 (5 mmol) in MeOH (25 mL) at 25 °C for 2 h gave the [η^3-1-(silylcarbonyl)allyl]palladium chloride **2a** (85%)[2] together with a small amount of the byproduct **3**[3] (eq 1). The analogous reaction of **1b** and **1c** with Li_2PdCl_4 also afforded **2b** (33%) and **2c** (72%), respectively.[4] Complex **2a** was also obtained from $PdCl_2(PhCN)_2$ and the mercury compound $Me_3SiC(O)CH{=}CHCH_2HgOAc$, prepared from **1a** and $Hg(OAc)_2$, in benzene.



1a-c **2a-c** **3**

a: R^1=H R^2=Me a: (85 %, syn) (4 %)
b: R^1=H R^2=Ph b: (33 %, syn) (2 %)
c: R^1=Me R^2=Me c: (72 %, syn/anti = 27/73) —

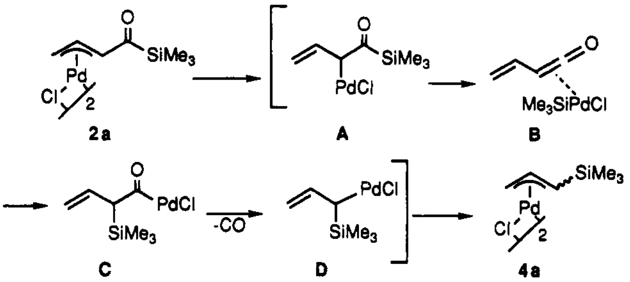
(1)

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

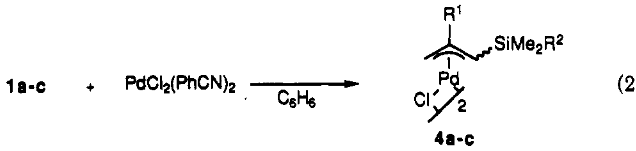
compd	time, h	product	yield, %[b]	syn/anti
2a	12	**4a**	86	71/29
2b	24	**4b**	43	83/17
2c	70	**4c**	43	59/41

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

Scheme I. Plausible Mechanism for Decarbonylation



Somewhat unexpectedly, direct treatment of **1a–c** (1 mmol) with $PdCl_2(PhCN)_2$ (1 mmol) in benzene (10 mL) at 25 °C gave none of **2a–c** but (η^3-1-silylallyl)palladium complexes **4a–c** (76%, 57%, 41%),[5] products from decarbonylation within the substituent of the η^3-allyl ligand in **2a–c** (eq 2). Next we examined this new decarbonylation under several conditions by employing isolated complexes **2** and their analogues.



(2)

4a-c

a: (76 %, syn/anti = 73/27)
b: (57 %, syn/anti = 85/15)
c: (41 %, syn/anti = 33/67)

As shown in Table I, treatment of **2a** with 0.1 equiv of $PdCl_2(PhCN)_2$ in C_6D_6 at 25 °C resulted in clean decarbonylation to afford **4a** (85%). Similar decarbonylation

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[†] Dedicated to the memory of the late Prof. J. K. Stille.

(1) Only a limited number of acyl-substituted allylic complexes of palladium are known: (a) Takahashi, M.; Urata, H.; Morooka, Y. *J. Organomet. Chem.* **1984**, *226*, 327. (b) Andri, M. K.; Krylov, A. V.; Averochkin, N. E.; Belov, A. P. *Koord. Khim.* **1984**, *10*, 540. (c) Parshall, G. W.; Wilkinson, G. *Chem. Ind.* **1962**, 261. (d) Faller, J. W.; Blankenship, B.; Whitmore, B.; Sena, S. *Inorg. Chem.* **1985**, *24*, 4483. (e) Yanase, N.; Nakamura, Y.; Kawaguchi, S. *Inorg. Chem.* **1980**, *19*, 1575.

(2) Typical procedure of reaction of 1-(trimethylsilyl)-1-(trimethylsiloxy)butadiene (**1a**) with Li_2PdCl_4: A suspension of 885 mg (5 mmol) of $PdCl_2$, 440 mg (10 mmol) of anhydrous LiCl, and 370 mg (5 mmol) of Li_2CO_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 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 by column chromatography (Florisil, 15 mm i.d. × 300 mm length, CH_2Cl_2). Orange fractions were concentrated under reduced pressure (5 mmHg) to afford an orange oil. Onto 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.

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

(4) The reaction of enol silyl ethers with $PdCl_2(PhCN)_2$ is known to afford oxo(π-allyl)palladium complexes: (a) Ito, Y.; Aoyama, H.; Hirao, T.; Mochizuki, A.; Saegusa, T. *J. Am. Chem. Soc.* **1979**, *101*, 495. (b) Kende, A. S.; Roth, B.; Sanfilippo, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 1784.

(5) Typical procedure of reaction of 1-(trimethylsilyl)-1-(trimethylsiloxy)butadiene (**1a**) with $PdCl_2(PhCN)_2$: 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. 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**[6] was obtained in 76% (183 mg, syn/anti = 73/27) isolated yield.

(6) Complex **4a** was prepared in a different way: Pannell, K. H.; Lappert, M. F.; Stanley, K. J. *J. Organomet. Chem.* **1976**, *37*, 112.

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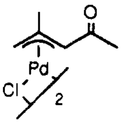
was also observed for **2b** and **2c**. It then may well be that in the decarbonylation reaction of dienol silyl ether 1 with $PdCl_2(PhCN)_2$ in benzene (eq 2) the formation of **2** is slow so that the decarbonylation catalyst $PdCl_2(PhCN)_2$ is always present to force most of **2** formed to undergo the 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 groups affords the vinylketene complex intermediate B.[7] No intermolecular exchange of the coordinated ketene occurs, 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.[8] Subsequent addition of the silylpalladium moiety to the ketene in the reverse direction affords acylpalladium complex C, from which decarbonylation gives rise to the (η^1-allyl)palladium complex D[9] and then (η^3-allyl)palladium complex **4a**.

Treatment of the complex **5**[1c] or **6**[1b] containing methyl or hydrogen attached to the carbonyl carbon, respectively, instead of the silyl group, with a catalytic amount of $PdCl_2(PhCN)_2$ resulted in no decarbonylation reaction.



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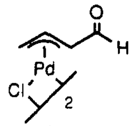

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Thus, the decarbonylation needs the trimethylsilyl group attached to the carbonyl carbon, and the step from A to B in Scheme I appears to be the key to the overall decarbonylation. A facile syn elimination of (trimethylsilyl)palladium iodide from (β-silylalkyl)palladium iodide has been reported.[10] Such an interaction between palladium and a silyl group is also important in other new transformations of the complexes of type **2**, which we will report in the near future.

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Supplementary Material Available: Typical experimental procedures and spectral data for all compounds prepared (3 pages). Ordering information is given on any current masthead page.

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[7] It is possible that in eq 1 3 is formed by the reaction of $PdCl_2$ with methyl crotonate, which may have been generated by trapping of vinylketene by MeOH. The reaction of **1a** with 2 equiv of $PdCl_2(PhCN)_2$ in MeOH with Li_2CO_3 gave a larger amount of **3** (39%) together with **2a** (30%).

[8] 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_6D_6. After 24 h, the reaction mixture was examined by ^1H NMR spectroscopy (**2b**, 9%; **4b**, 77% (syn/anti = 83/17); **2c**, 70%; **4c**, 29% (syn/anti = 59/41)).

[9] The (3-butenoyl)palladium 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.

[10] Karabelas, K.; Hallberg, A. *J. Org. Chem.* **1989**, *54*, 1773.

Stereoselective Formation of Dimethylcyclopentanes through Intramolecular Ziegler–Natta Alkene Insertion[†]

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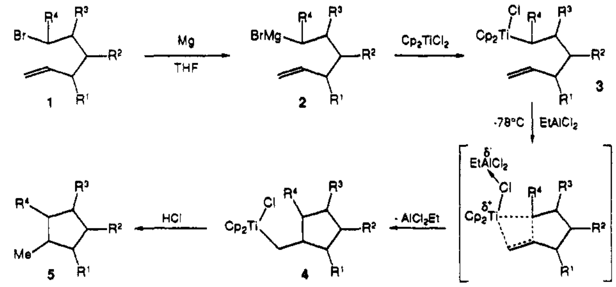
Summary: The intramolecular olefin insertion into titanium–carbon bonds results in efficient five-membered ring formation from 5-hexen-1-yl ligands. Cyclization of substrates having methyl groups on the alkyl tether proceeds with high diastereoselectivity (>94:6) in the formation of dimethylcyclopentane products.

The multitude of early transition-metal/Lewis acid complexes known as Ziegler–Natta catalysts includes some of the most efficient and selective reagents for organic reactions.[1] In 1955, Natta first reported the polymerization of propylene using a titanium catalyst ($TiCl_4/AlEt_3$), which sequentially formed hundreds of C–C bonds prior to chain termination.[1c,2] Each insertion of propylene into the metal–polymer bond occurred with high regioselectivity and was accompanied by the formation of a new asym-

Scheme I. Lewis Acid Promoted Intramolecular Alkene Insertion



	R^1	R^2	R^3	R^4
a	H	H	H	H
b	Me	H	H	H
c	H	Me	H	H
d	H	H	Me	H
e	H	H	H	Me

[†] Dedicated to the memory of John K. Stille, a colleague, mentor, friend, and father whose loss has been felt very deeply by so many people.

[1] For reviews in Ziegler–Natta polymerization and the catalysts used, see: (a) *Catalytic Polymerization of Olefins*; Keii, T., Soga, K., Eds.; Kodenska: Tokyo, 1986. (b) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99. (c) Pino, P.; Mulhaupt, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *18*, 99. (d) Boor, J., Jr. *Ziegler–Natta Catalysts and Polymerization*; Academic Press: New York, 1979. (e) Reichert, K. H. In *Transition Metal Catalyzed Polymerizations. Alkenes and Dienes*; Quirk, R. P., Ed.; Harwood Academic: New York, 1983; Part B, p 465.

[2] Natta, G.; Pino, P.; Corradini, F.; Danusso, F.; Mantica, E.; Mazzanti, G.; Moraglio, G. *J. Am. Chem. Soc.* **1955**, *77*, 1708.