An Unprecedented Dimerization of 1,2,3-Butatriene Catalyzed by Palladium Complexes

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Dehydrogenative dimerization of (*Z*)-1,4-bis(trimethylsilyl)-1,2,3-butatriene was catalyzed by Pd complexes in the presence of allyl halides to give predominantly an acyclic conjugated enyne, while addition of methylaluminoxane (MAO) instead of allyl halides produced an unprecedented dimer that has an alkynyl-substituted cyclopentadienyl structure.

1,2,3-Butatrienes, which are examples of cumulative unsaturated hydrocarbons, have attracted organometallic chemists because of their varying reactivities towards transition-metal complexes.[1] For example, we recently reported that 1,4-disubstituted-1,2,3-butatrienes form η^2-π-complexes with Rh,[2] while they form a 1-metallacyclopent-3-yne compound with a zirconocene unit.[3] There have also been some examples of transition metal-catalyzed reactions in which 1,2,3-butatrienes are involved. Iyoda reported Ni-catalyzed cyclodimerization and cyclotrimerization of 1,2,3-butatrienes that give radialene compounds.[4] Rh-catalyzed hydrosilation of butatriene has also been reported.[2,5] However, transition metal-catalyzed C–C bond formation reactions of 1,2,3-butatrienes are still rare.

One of the authors recently reported the efficient synthesis of (*Z*)-1,4-bis(trimethylsilyl)-1,2,3-butatriene (**1**) using a Ru catalyst.[6] Because a trimethylsilyl group can be transformed into various functional groups, compound **1** is potentially useful. Thus, the development of carbon–carbon bond forming reaction using **1** is intriguing. Herein we wish to describe the unprecedented dimerization reactions of **1** catalyzed by palladium complexes.[7]

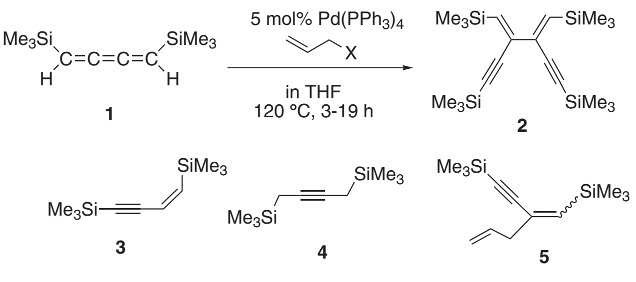
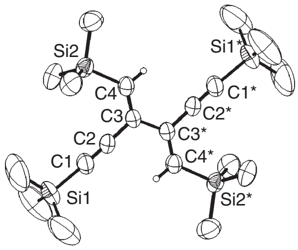


Figure 1. Dehydrogenative dimerization of **1** catalyzed by Pd in the presence of allyl halides and the minor products.

The reaction of **1** and a catalytic amount of $Pd(PPh_3)_4$ in a THF solution, with no additives, gave a mixture of unidentified products, although the starting material was consumed. Judging from gas chromatogram (GC) and mass spectrum, it is likely that some of the products consisted of dimeric compounds of **1**, albeit in low yields.

Therefore, we investigated the effect of additives. When a reaction was carried out in the presence of one equiv of allyl bromide, to our surprise, a conjugated acyclic enyne **2** was predominantly obtained accompanied by a small amount (typically 3–5%) of **3**, **4**, and **5** (Figure 1). Although the reaction has not been optimized yet, the yield amounted to 44% (isol.) when it was conducted in THF at 120 °C for 19 h. The starting material **1** disappeared at this stage.



Selected bond lengths (Å)
and angles (deg):

C1-C2	1.194(3)
C2-C3	1.450(3)
C3-C3*	1.505(4)
C3-C4	1.339(3)
Si1-C1-C2	177.6(3)
C1-C2-C3	178.0(3)
C2-C3-C3*	115.8(3)
C2-C3-C4	120.4(2)
C3*-C3-C4	123.7(3)
Si2-C4-C3	127.5(2)

Figure 2. Molecular structure of **2**. Drawn with 50% probability. Hydrogen atoms are in part omitted for clarity.

The dimer **2** was fully characterized by NMR and mass spectrometry, and its structure was confirmed by X-ray analysis (Figure 2).[8] Besides allyl bromide, allyl chloride (Y. 38%) and methallyl chloride (Y. 34%) were also effective. Benzyl bromide gave **2** in 14% yield, but the formation of numerous by-products was observed. Employing normal alkenes such as 1-hexene, in place of allyl halides, resulted in a low yield and selectivity.

It is to be emphasized that the reaction is dehydrogenative dimerization of butatriene. Pd-catalyzed dimerization of 1,3-diynes producing (*E*)-1,2-divinyl-1,2-diethynylethene has been reported,[9] in which the products lose no hydrogens overall. There must be a compound that accepts hydrogen atoms in this reaction system. Allyl bromide decreased with an increase of **2**. The formation of propyl bromide, however, was not observed by GC. Taking account of the moderate yield of **2** and the formation of **4**, a proportion of **1** might accept hydrogen atoms. The low yield of **4** may be rationalized by the formation of polymeric products. GPC analysis showed that the reaction mixture contained polymers whose molecular weight was in 800–4200 (M_w) range.

Although details of the reaction pathway are still vague, a plausible mechanism is as follows: the formation of palladacycle[10] and subsequent double β-hydrogen elimination results in liberation of **2** (Scheme 1). The role of allyl bromide is still a puzzle. Since a small amount of propylene was detected by GC (ca. 1–3%), it might at first form a π-allylpalladium species. Indeed, using $[(\pi\text{-allyl})PdCl]_2$ as a catalyst produced **2** in 20% yield although the selectivity was not excellent. When catalytic amount (0.1 equiv.) of allyl bromide was used, **2** was obtained in 8% yield. In the presence of $CuCl_2$, **2** was not obtained at all. Addition of NEt_3 retarded the reaction. The reaction from **3**, which

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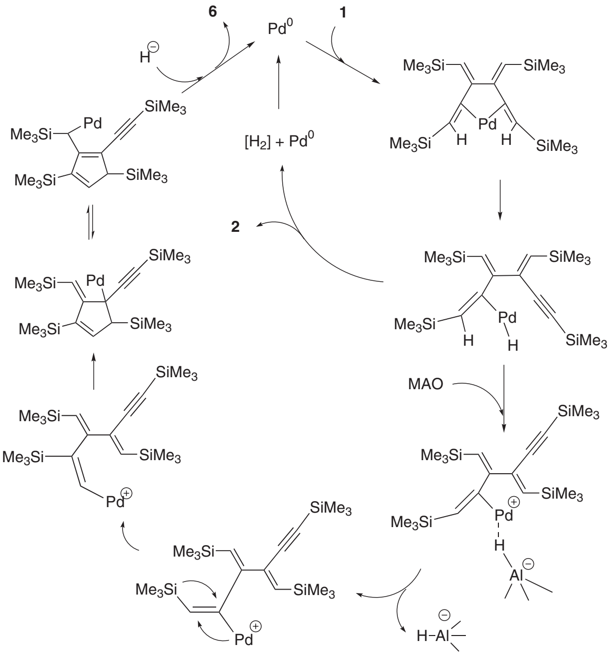
is an isomer of **1**, under the same conditions did not give **2**. Thus, the possibility that **1** initially isomerized to **3** and was then involved in the reaction to give **2** is ruled out. It is noteworthy that using allyl esters instead of allyl halide predominantly gave the allylated product **5** in ca. 30% yield. The reaction using (*Z*)-2,2,7,7-tetramethylocta-3,4,5-triene, [(*Z*)-*t*-Bu-CH=C=C=CH-*t*-Bu],[6b] under the same conditions gave a mixture of products in low yields. GC-MS analysis showed that a few of the products had $M^+ = 328$ (164 × 2), and no dehydrogenated dimers were found.



Scheme 1. Plausible mechanism for dimerization of **1**.

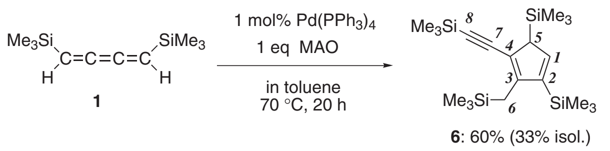


Figure 3. Pd-catalyzed dimerization of **1** in the presence of MAO.

The result above prompted us to study further the possibility of dimerization reaction of **1**. Methylaluminoxane (MAO) is well known as an activator in olefin polymerization. It reacts with catalyst precursors to form and stabilize cationic species in the reaction system. When **1** was reacted in the presence of catalytic amount of $Pd(PPh_3)_4$ and MAO that contained one equiv of Al atoms, the cyclopentadienyl compound **6** was predominantly obtained in moderate yield (60%, Figure 3). The structure of **6** was fully characterized by ^1H, ^{13}C and ^{29}Si NMR, HMQC, and HMBC.[11] All of the C–Si bonds were confirmed by the ^{29}Si satellites observed in ^{13}C NMR. It is surprising that **6** has a Me_3Si group at the 2-position instead of the 1-position. The reaction path of this dimerization is thus more puzzling. One possible route is proposed in Scheme 1. After a β-hydrogen elimination from the palladacycle, MAO reacts with Pd–H to form cationic species. The 1,2-shift of silicon and palladium atoms (or β-Si elimination–reinsertion) occurs, and intramolecular carbopalladation on the alkenyl silane results in a five-membered ring. An example of the 1,2-shift of silicon and a transition metal around a double bond has been reported,[12] although it would be uncommon. The butatriene with *tert*-butyl groups, (*Z*)-2,2,7,7-tetramethylocta-3,4,5-triene, did not give cyclopentadienyl compounds under the same conditions.

Both dimeric products **2** and **6** have π-conjugated enyne structures, and are of interest as building blocks for electronic and optical materials as well as ligands for organometallics.

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References and Notes

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8 **2.** ^1H NMR ($CDCl_3$): δ 0.14 (s, 18H), 0.15 (s, 18H), 6.69 (s, 2H). ^{13}C NMR ($CDCl_3$): δ −1.23, −0.24, 101.79, 102.34, 136.49, 141.27. HRMS Calcd for $C_{20}H_{38}Si_4$ 390.2051, Found 390.2057. Crystal Data: $C_{20}H_{38}Si_4$, $M_r = 390.86$, triclinic, $a = 6.212(1)$, $b = 10.747(3)$, $c = 11.430(3)$ Å, $\alpha = 109.947(4)$, $\beta = 97.206(5)$, $\gamma = 99.890(4)°$, $V = 692.6(3)$ Å^3, $P\bar{1}$ (# 2), $Z = 1$, $R_1 = 0.055$, $wR = 0.133$, GOF = 0.90. The crystallographic data have been deposited (CCDC 242990).

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10 Although it seems sterically crowded, it may be possible taking account of the formation of a Rh-(*Z*)-**1** complex. See Ref. 2.

11 **6.** ^1H NMR ($CDCl_3$): δ 0.00 (s, 9H), 0.02 (s, 9H), 0.18 (s, 18H), 2.15 (d, $J = 13$ Hz, 1H, CH_2), 2.19 (d, $J = 13$ Hz, 1H, CH_2), 3.41 (br, 1H, CH), 6.57 (br, 1H, CH). ^{13}C NMR ($CDCl_3$): δ −1.94, 0.34, 0.38, 0.50, 20.93 ($^1J_{CSi} = 47$ Hz, $J_{CH} = 119.3$ Hz, CH_2), 56.10 ($^1J_{CSi} = 34$ Hz, $J_{CH} = 135.8$ Hz, CH), 99.92 (q, $^1J_{CSi} = 87$ Hz), 104.88 (q, $^2J_{CSi} = 17$ Hz), 119.84 (q), 145.45 (q), 146.08 (CH), 154.92 (q). ^{29}Si NMR (C_6D_6): δ −19.0, −10.0, 3.5, 5.0. HRMS Calcd. for $C_{20}H_{40}Si_4$ 392.2207, Found 392.2212.

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