Palladium-Catalyzed Reactions of Di-*tert*-butylsiliranes with Electron-Deficient Alkynes and Investigations of the Catalytic Cycle

Wylie S. Palmer and K. A. Woerpel*

Department of Chemistry, University of California, Irvine, California 92697-2025

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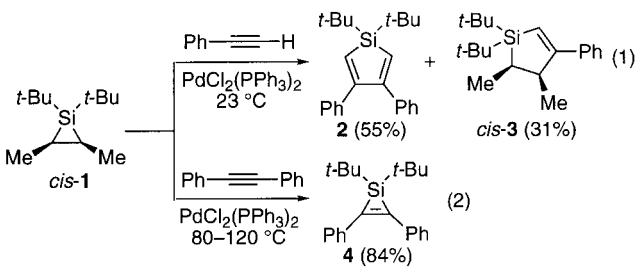
Siliranes undergo palladium-catalyzed reactions with alkynes to give a variety of silacycles depending upon the alkyne. When terminal and electron-poor alkynes (DMAD and methyl 2-butynoate) are employed, silole formation is favored. Silirenes are formed preferentially when more electron-rich internal alkynes are involved. Control experiments provide evidence that palladium(0) species are the active catalysts. By evaluation of product distributions in these reactions, a catalytic cycle that accounts for the production of all silacycles can be proposed.

Introduction

The study of metal-mediated reactions of organosilanes represents an important field of organosilicon chemistry.[1] A wide variety of silacycles, such as siloles,[2] disilacyclohexadienes,[3] and silirenes,[4] have been synthesized using metal-mediated transformations. Although many of these transformations, including oligosilane rearrangements,[5] disproportionations,[6] formation of a platinasilacylcohexadiene,[7] and the degradations of trisilanes to disilanes,[8] have been proposed to occur through metal−silylene complexes $(R_3P)_2M{=}SiR_2$ (M = Pd, Pt),[9] in many cases these intermediates have yet to be unambiguously demonstrated.

Our investigations of the palladium-catalyzed chemistry of di-*tert*-butylsiliranes[10] with alkynes have allowed for the synthesis of 3,4-disubstituted siloles,[11] trisubstituted siloles,[12] silacyclopentenes,[11] and silirenes[12] depending upon the type of alkyne employed. When a terminal alkyne, such as phenylacetylene, was employed in the reactions with *cis*-**1** and ≤3 mol % of $PdCl_2(PPh_3)_2$ at ambient temperature, silole **2** and silacyclopentene *cis*-**3** were produced (eq 1).[13] The reactions of siliranes with internal alkynes, on the other hand, gave neither of these products: when *cis*-**1** was treated with diphenylacetylene and $PdCl_2(PPh_3)_2$ at 110 °C, silirene **4** was isolated as the exclusive product (eq 2).



Because the transformations shown in eqs 1 and 2 might proceed via metal−silylene complexes, we have studied these transformations to determine their scope and to identify the reactive intermediates in the catalytic cycle. One issue that needed to be addressed was the influence of steric and electronic effects on the nature of the products obtained. To gain this information, we studied the reactions of siliranes with electron-deficient alkynes such as DMAD (dimethyl acetylenedicarboxylate), which has been employed in the palladium-catalyzed insertions into neopentylidenesiliranes[14] and silacyclobutanes.[15] Stoichiometric reactions of $PdCl_2(PPh_3)_2$ with siliranes were performed to elucidate the structure of the active catalyst and to discover how it was generated. These experiments suggest a catalytic cycle that accounts for the production of all silacycles obtained in the reactions of siliranes with alkynes. We conclude that a silylene complex (*t*-$Bu_2Si{=}PdL_n$) is not an intermediate in these transformations.

(1) Horn, K. A. *Chem. Rev.* **1995**, *95*, 1317−1350.
(2) For a review of group 14 metalloles, see: Dubac, J.; Laporterie, A.; Manuel, G. *Chem. Rev.* **1990**, *90*, 215−263.
(3) Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1977**, 352.
(4) Ohshita, J.; Ishikawa, M. *J. Organomet. Chem.* **1991**, *407*, 157−165.
(5) Tamao, K.; Sun, G.-R.; Kawachi, A. *J. Am. Chem. Soc.* **1995**, *117*, 8043−8044.
(6) Yamamoto, K.; Okinoshima, H.; Kumada, M. *J. Organomet. Chem.* **1971**, *27*, C31−C32.
(7) Yamashita, H.; Tanaka, M.; Goto, M. *Organometallics* **1992**, *11*, 3227−3232.
(8) Tamao, K.; Tarao, Y.; Nakagawa, Y.; Nagata, K.; Ito, Y. *Organometallics* **1993**, *12*, 1113−1120.
(9) Isolation of the first neutral silylene complex has recently been reported: Feldman, J. D.; Mitchell, G. P.; Nolte, J.-O.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 11184−11185, and references therein.
(10) Boudjouk, P.; Samaraweera, U.; Sooriyakumaran, R.; Chrusciel, J.; Anderson, K. R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1355−1356.
(11) Palmer, W. S.; Woerpel, K. A. *Organometallics* **1997**, *16*, 1097−1099.
(12) Palmer, W. S.; Woerpel, K. A. *Organometallics* **1997**, *16*, 4824−4827.
(13) The reaction of *trans*-**1** proceeded in a similar manner producing mostly silole **2** (83%) and a trace amount of *trans*-**3** (1%), demonstrating that the insertion of alkyne proceeded with stereospecific retention of configuration.
(14) Saso, H.; Ando, W. *Chem. Lett.* **1988**, 1567−1570.
(15) Sakurai, H.; Imai, T. *Chem. Lett.* **1975**, 891−894.

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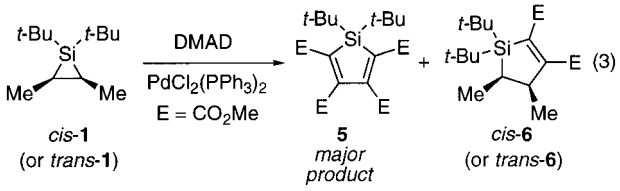
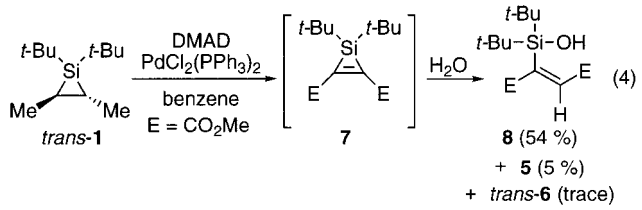
Results and Discussion

Reactions with Electron-Deficient Alkynes. The palladium-catalyzed reactions of siliranes **1** with the electron-deficient alkyne DMAD provided only silylene transfer and insertion products, and the product distribution depended upon reaction conditions (eq 3).[16] When the reactions of siliranes *cis*- and *trans*-**1** with DMAD were carried out at ambient temperatures over 2 days (1−3 mol % of $PdCl_2(PPh_3)_2$, 2−3 equiv of DMAD), both silole **5** (14% from *cis*-**1**, 23% from *trans*-**1**) and silacyclopentenes **6** (21% of *cis*-**6** from *cis*-**1**, and 2% of *trans*-**6** from *trans*-**1**) were isolated in low yields along with a large amount of unidentified decomposition products. Consistent with the reactions with terminal alkynes,[11] the formation of silacyclopentenes **6** occurred stereospecifically. When *cis*- and *trans*-**1** were heated (108−112 °C) with DMAD and $PdCl_2(PPh_3)_2$ in sealed NMR tubes, only silole **5** was obtained (76% and 65% yields, respectively).

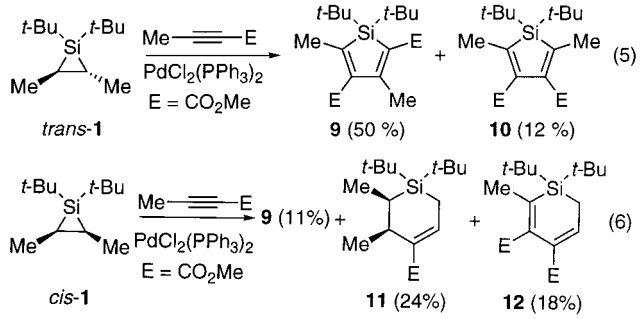


Whereas other reactions of siliranes **1** with internal alkynes provided silirenes,[12] no silirene product **7** was observed in the reaction with DMAD (eq 4). If **7** were a fleeting intermediate, its presence might be demonstrated by intercepting it by a hydrolysis process.[17] When the reaction of *trans*-**1** with DMAD and $PdCl_2(PPh_3)_2$ was carried out in the presence of water, the (*Z*)-vinylsilanol **8** (54%) was isolated as a single stereoisomer[18,19] along with the silole **5** (5%) and a trace amount of *trans*-**6**. The stereochemistry of **8**, which was determined by evaluating NOE data,[20] was the opposite of what has been observed during hydrolysis of other silirenes (i.e., retention of configuration).[18,19] The isolation of hydrolysis product **8** implicates the presence of silirene **7** in the formation of silole product **5** in the palladium-catalyzed reaction of siliranes **1** with DMAD (eq 3). The ability to intercept this product suggests that the insertion of the second equivalent of alkyne in the formation of siloles is the rate-limiting step.

The reactions of siliranes with an unsymmetrical internal alkyne, such as methyl 2-butynoate, provided data on the factors affecting the regioselectivity of alkyne insertion. The reaction of *trans*-**1** with 3 equiv



of methyl 2-butynoate and 1 mol % of $PdCl_2(PPh_3)_2$ produced a mixture of siloles **9** (50%) and **10** (12%, eq 5). The fact that **10** was isolated, and not the other possible symmetrical silole with both methyl groups placed away from silicon, suggests the electronic preference for ester placement away from silicon is nominally stronger than the slightly higher steric requirements for a methyl versus an ester group as suggested by their conformational A-values.[21] When a similar reaction was performed with *cis*-**1**, silole **9** (11%), alkyne insertion product **11** (24%), and silacyclohexadiene[22] **12** (18%) were isolated (eq 6). The two unusual products **11** and **12** must result from activation of the acetylenic methyl group of methyl 2-butynoate. The ability to functionalize this position provides valuable information about intermediates in the catalytic cycle (vide infra).



Because the reactions of siliranes **1** with methyl 2-butynoate may involve a silirene intermediate as suggested for DMAD, we investigated the regioselectivity of insertion of an unsymmetrical alkyne into a silirene. We have previously demonstrated that phenylacetylene inserts into silirene **13** regioselectively to produce silole **14** (eq 7).[12] When silirene **13** was treated with methyl 2-butynoate in the presence of $PdCl_2(PPh_3)_2$, the unsymmetrical silole **9** (75%) was isolated. None of the expected silole **15** or its regioisomer was observed by ^1H NMR spectroscopy. This experiment was the first demonstration we had of an alkyne exchange in our systems,[23,24] consistent with re-entry of silirenes into the catalytic cycle (vide infra). Even though this result prevented us from determining the regioselectivity for alkyne insertions into silirenes, it demonstrated that electron-deficient alkynes inserted in preference to electron-rich alkynes.

(16) A related reaction of allene episulfides with DMAD produced a variety of different thiacycles depending upon the conditions employed: Choi, N.; Kabe, Y.; Ando, W. *Tetrahedron Lett.* **1991**, *32*, 4573−4576.

(17) Unreported results in our laboratories have demonstrated that di-*tert*-butylsiliranes are resistant to hydrolysis with water or protic sources unless a nucleophilic catalyst is present, and silirenes are rapidly protolyzed in a stereoselective manner upon treatment with water, alcohol, or a carboxylic acid.

(18) Conlin, R. T.; Gaspar, P. P. *J. Am. Chem. Soc.* **1976**, *98*, 3715−3716.

(19) Seyferth, D.; Anarelli, D. C.; Vick, S. C. *J. Organomet. Chem.* **1984**, *272*, 123−139.

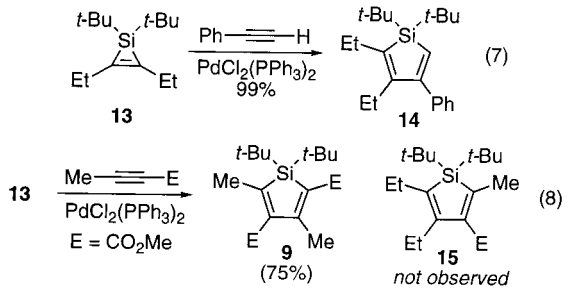
(20) We believe that the kinetically formed (*E*)-alkene isomerized during the course of this reaction.

(21) Eliel, E. L.; Wilen, S. H.; Mander, L. N. *Stereochemistry of Organic Compounds*; Wiley: New York, 1994; pp 696−697.

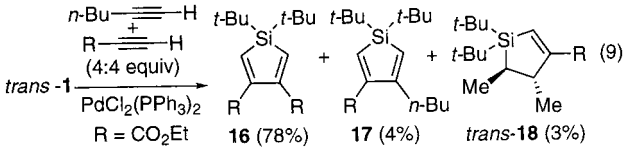
(22) A control experiment demonstrated that **10** was not on the pathway to **12**. Silole **10** was treated with a catalytic amount of $Pd(PPh_3)_2$, and no evidence for formation of **12** was observed by ^1H NMR spectroscopy.

(23) Seyferth, D.; Shannon, M. L.; Vick, S. C.; Lim, T. F. O. *Organometallics* **1985**, *4*, 57−62.

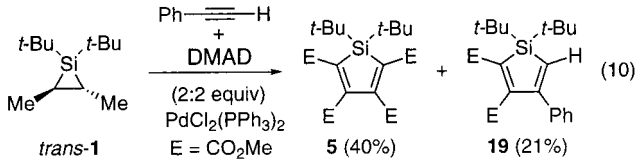
(24) Seyferth, D.; Vick, S. C.; Shannon, M. L. *J. Organomet. Chem.* **1977**, *135*, C37−C44.



The favored insertion of alkynes containing electron-withdrawing groups was also reflected in competition experiments performed with various alkynes. When *trans*-**1** was treated with 4 equiv each of 1-hexyne and ethyl propiolate in the presence of $PdCl_2(PPh_3)_2$, electron-deficient silole **16**[11] (78%) was produced in preference to mixed silole **17** (4%) and insertion product *trans*-**18** (3%, eq 9). None of the electron-rich silole (corresponding to **16** where R = *n*-Bu)[11] was observed by ^{1}H NMR spectroscopy.

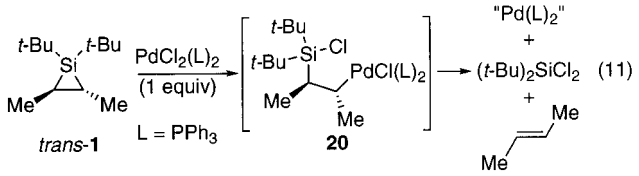


The preference for insertion of a more electron-deficient alkyne can also override the steric inhibition of inserting an internal alkyne. When *trans*-**1** was treated with 2 equiv each of DMAD and phenylacetylene in the presence of $PdCl_2(PPh_3)_2$, siloles **5** (40%) and **19** (21%) were isolated (eq 10). This experiment demonstrated that a more sterically demanding alkyne (DMAD) was inserted preferentially over the less sterically demanding alkyne (phenylacetylene). Electronic factors play a larger role than steric factors in the insertion of alkynes.



Nature of the Catalyst. Changing the structure of the palladium catalyst did not substantially influence the reactions of *cis*-**1** with phenylacetylene (eqs 1 and 2). A wide variety of Pd(0)[25] and Pd(II)[26] catalysts gave similar product distributions of products. These experiments suggested that Pd(II) catalysts were being reduced in situ to give a catalytically active Pd(0) species.[23,27]

Experiments employing stoichiometric quantities of palladium complexes confirmed that the Pd(II) catalyst was reduced by siliranes **1**. When silirane *trans*-**1** was treated with 1 equiv of $PdCl_2(PPh_3)_2$ in a sealed vessel, clean reduction occurred to produce "$Pd(PPh_3)_2$",[23,28] *trans*-2-butene, and di-*tert*-butyldichlorosilane[29] (48% isolated yield, eq 11).[30] Silirane *cis*-**1** reacted in a similar manner, producing *cis*-2-butene instead. The "$Pd(PPh_3)_2$" generated in this stoichiometric reaction was found to be catalytically active for the reactions of siliranes with alkynes. The mechanism of reduction of Pd(II) most likely follows a transmetalation reaction to generate an alkylpalladium chloride intermediate **20** with retention of configuration.[31] A subsequent β-silyl elimination[32−34] and reductive elimination of $Pd(PPh_3)_2$ would produce the observed products. The driving force for the reduction of Pd(II) is most likely due to the significant ring strain of siliranes (>40.5[35,36] kcal/mol) and the formation of two strong Si−Cl bonds (113[37] kcal/mol for Me_3SiCl).



The reactions of siliranes with electron-deficient alkynes also raise the question of whether palladium(IV) species might be involved.[38] Trost has studied the palladium-catalyzed reactions of enynes using tetracarbomethoxypalladacyclopentadiene (TCPC) catalyst **21** and has suggested that those reactions proceeded through palladium(IV) intermediates.[39] When we employed **21** as the catalyst in a reaction with *cis*-**1** and DMAD, a small amount of silole product **5** (<13%) was isolated along with extensive decomposition. Catalyst **21** also consumed the silirane at a slower rate than when $PdCl_2(PPh_3)_2$ was used as catalyst (18 h versus 20 min). The reaction of *trans*-**1** and phenylacetylene, unlike the reaction with DMAD, was catalyzed by **21**, producing silole **2** (81%) and silacyclopentene *trans*-**3** (2%, eq 12). It is possible that **21** decomposes under the reaction conditions to give a coordinatively unsaturated Pd(0) species, since this result is identical to that when $PdCl_2(PPh_3)_2$ was employed as a catalyst (eq 1).[11] These

(25) The following Pd(0) catalysts were employed: $Pd_2(DBA)_3$, $Pd(PPh_3)_4$, and $Pd[P(OEt_3)]_4$.

(26) The following Pd(II) catalysts were employed: $PdCl_2(PPh_3)_2$, $PdCl_2$(dppf), $Pd(OAc)_2$, $PdCl_2(P[o\text{-tol}]_3)_2$, $PdCl_2(PhCN)_2$, $Pd(CF_3CO_2)$, and $Pd(acac)_2$.

(27) Seyferth, D.; Goldman, E. W.; Escudié, J. *J. Organomet. Chem.* **1984**, *271*, 337−352.

(28) For examples of in-situ-generated $Pd(PPh_3)_2$, see: (a) Fitton, P.; McKeon, J. E. *J. Chem. Soc., Chem. Commun.* **1968**, 4−6. (b) Baba, S.; Negishi, E.-I. *J. Am. Chem. Soc.* **1976**, *98*, 6729−6731. (c) Amatore, C.; Azzabi, M.; Jutand, A. *J. Am. Chem. Soc.* **1991**, *113*, 8375−8384.

(29) Trost, B. M.; Caldwell, C. G.; Murayama, E.; Heissler, D. *J. Org. Chem.* **1983**, *48*, 3252−3265.

(30) Alternatively, a similar reaction was performed in which the crude reaction mixture was exposed to wet solvent and di-*tert*-butylsilanediol was isolated in 78% yield after purification by column chromatography.

(31) Franz, A. K.; Woerpel, K. A. *J. Am. Chem. Soc.* **1999**, *121*, 949−957.

(32) Randolph, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 3366−3374.

(33) Wakatsuki, Y.; Yamazuki, H.; Nakano, M.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 703−704.

(34) Marciniec, B.; Pietrazuk, C. *J. Chem. Soc., Chem. Commun.* **1995**, 2003−2004.

(35) Gordon, M. S.; Boatz, J. A.; Walsh, R. *J. Phys. Chem.* **1989**, *93*, 1584−1585.

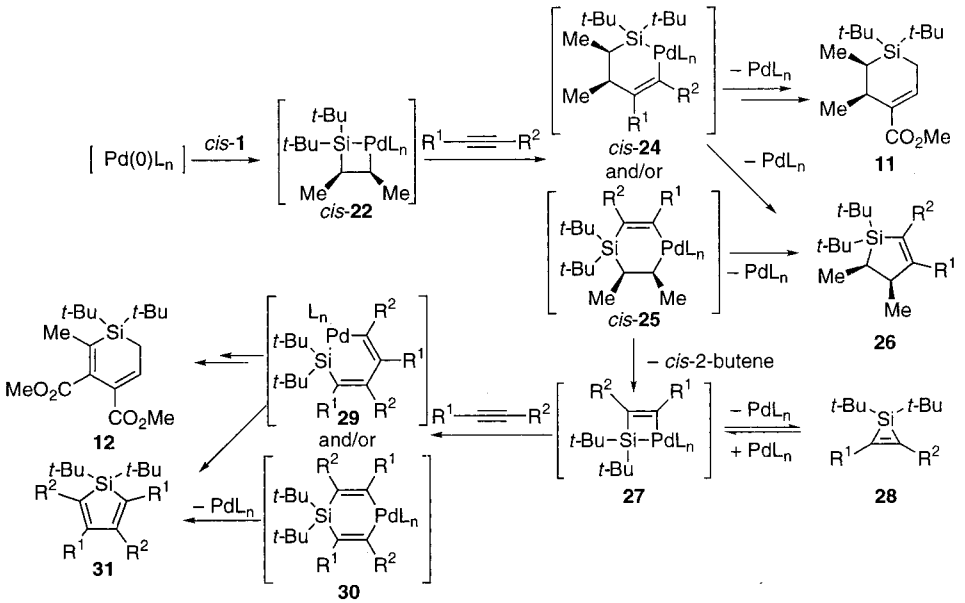
(36) Al-Rubaiey, N.; Carpenter, I. W.; Walsh, R.; Becerra, R.; Gordon, M. S. *J. Phys. Chem. A* **1998**, *102*, 8564−8572.

(37) *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; pp 371−391.

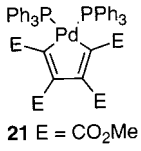
(38) The first silylpalladium(IV) complex has recently been reported, see: Shimada, S.; Tanaka, M.; Shiro, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1856−1858.

(39) Trost, B. M.; Tanoury, G. J. *J. Am. Chem. Soc.* **1987**, *109*, 4753−4755.

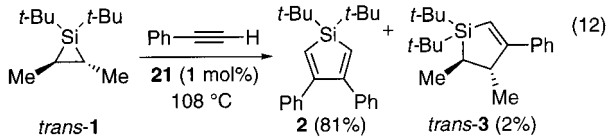
Scheme 1



results suggest that a Pd(IV) species such as **21** is not operating as a catalyst in the reaction of siliranes with alkynes.



21 E = CO_2Me



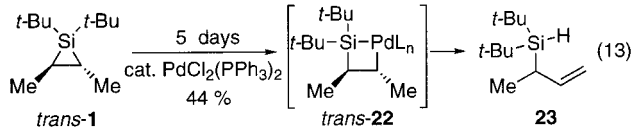
(12)

trans-**1** **2** (81%) *trans*-**3** (2%)

Reaction Mechanism. The isolation of diverse products in the palladium-catalyzed reactions of siliranes with alkynes suggests that several mechanistic pathways operate and that these pathways diverge depending on the nature of the alkyne. We previously suggested catalytic cycles to account for the production of siloles, silacyclopentenes,[11] and silirenes,[12] but the results with electron-deficient alkynes, most notably methyl 2-butynoate (eq 6), indicate that other intermediates are also involved. In this section, we propose a catalytic cycle and intermediates that are consistent with our experimental data (Scheme 1). For simplicity, the fate of silirane *cis*-**1** is shown, but the analysis also applies for *trans*-**1**.

The first step of the catalytic cycle involves oxidative addition of in-situ-generated Pd(0) into the Si−C bond of silirane *cis*-**1**. This process would occur with stereospecific retention of configuration at the carbon atom to give the intermediate palladasilacyclobutane *cis*-**22**. Similar stereospecificity must also pertain to *trans*-**1**.[11] A palladasilacyclobutane intermediate is consistent with our observation that silane **23** is the predominant product when no alkyne is present (eq 13).[11] This silane could be formed by a slow β-hydride elimination reaction of *trans*-**22**.

The palladacycle **22** can undergo insertion of an alkyne into either the Pd−C bond to give intermediate

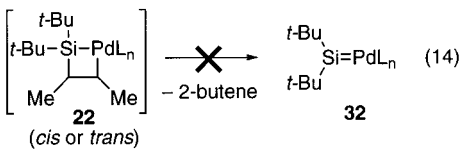


(13)

trans-**1** *trans*-**22** **23**

cis-**24** or the Pd−Si bond to give 1,4-palladasilacyclohexene *cis*-**25**. The selectivity between the reactivity of these bonds depends on both the stereochemistry of **22** and the electron density of the alkyne. It is important to note, however, that intermediate *cis*-**25** is on the pathway toward the production of most of the silacycles we have observed, but *cis*-**24** is an intermediate in the formation of only two minor products: silacyclopentenes **26** and silacyclohexene **11** obtained in the reaction of silirane *cis*-**1** with methyl 2-butynoate (eq 6, vide infra).

The second step of the catalytic cycle is unlikely to involve retro-cycloaddition to form palladium silylene complex **32** (eq 14). If this reaction were to occur, then both *cis*-**1** and *trans*-**1** would give a common intermediate upon dissociation of the alkene or complexation of an alkyne, and this common intermediate should provide the same product distribution for both diastereomers of the silirane. Because product distributions depend on the stereochemistry of the silirane, **32** cannot be an intermediate in both cases. Since both diastereomers of silirane give the same type of products only in different ratios, it is probable that both reactions proceed by diastereomeric intermediates that partition later in the catalytic cycle.



(14)

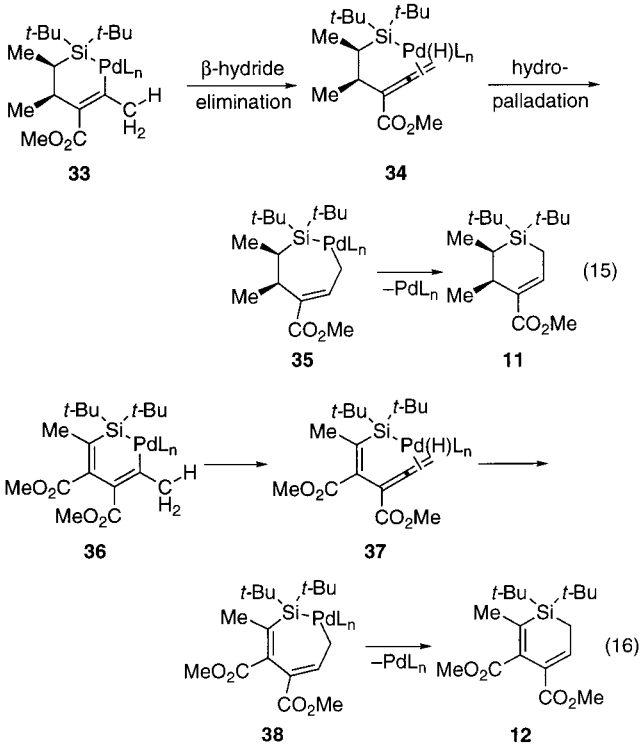
22 (*cis* or *trans*) **32**

The 1,4-palladasilacyclohexene *cis*-**25** accounts for the production of silacyclopentenes, silirenes, siloles, and silacycle **12**. Intermediate *cis*-**25** can undergo either a reductive elimination of Pd(0) to provide silacyclo-

pentenes **26** or a migratory deinsertion of *cis*-2-butene to form palladasilacyclobutene[23,40,41] intermediate **27**.

The fate of palladasilacyclobutene **27** depends on the nature of the alkyne. Because electron-rich internal alkynes favor silirenes **28**,[12] insertion of these alkynes into **27** must be slow. Silirenes **28** are the result of reductive elimination from **27**, a process that is reversible, since silirenes undergo further reactions with alkynes to produce siloles **31** (eqs 7 and 8). With either terminal alkynes or alkynes bearing ester groups, palladasilacyclobutene **27** inserts an alkyne either at the Pd−C bond or at the Pd−Si bond, yielding **29** or **30**, respectively. This choice is similar to that observed for intermediate *cis*-**22**. The formation of intermediate **29** would lead to either silole products **31** or to silacycle **12** in the reaction of methyl 2-butynoate (eq 6). Since both intermediates **29** and **30** could undergo a reductive elimination process to produce siloles **31**,[42] differentiating between these intermediates is impossible.

The reactions employing methyl 2-butynoate underscore the complexity of these palladium-catalyzed processes. The production of silacycles **11** and **12** from methyl 2-butynoate is thought to proceed by ring-enlargement of the palladacycles **33** (eq 15) and **36** (eq 16), respectively. For example, palladacycle **33** could undergo a β-hydride elimination to form the complexed allene **34**. A hydropalladation of the allene could form the seven-membered palladacycle **35**, and reductive elimination of Pd(0) would form the silacycle **11**.[43] The transformation of **36** to **12** could proceed by a similar pathway (eq 16). Oshima and Utimoto have reported a sequence of oxidative addition, insertion of an alkyne, and β-hydride elimination to explain palladium-catalyzed reactions of silacyclobutanes.[44]



Conclusion. Siliranes undergo palladium-catalyzed reactions with alkynes to give a variety of silacycles depending upon the alkyne. When terminal and electron-poor alkynes (DMAD and methyl 2-butynoate) are employed, siloles are the favored products. The formation of silirenes is the favored pathway when more electron-rich internal alkynes are involved. Competition experiments demonstrated that electronic effects influenced the regioselectivity of alkyne insertions more than steric effects did. A stereospecific reduction of Pd(II) to the active Pd(0) catalyst by an equivalent of silirane was demonstrated. Finally, a catalytic cycle that accounts for the production of all silacycles was proposed.

Experimental Section

General Procedures. General experimental details are provided as Supporting Information. Microanalyses were performed by Atlantic Microlab, Atlanta, GA, or by Microlytics, South Deerfield, MA. NMR tube experiments were carried out with 5 mm Wilmad J. Young tubes, using C_6D_6 (distilled from CaH_2) as solvent. Analytical gas−liquid chromatography (GLC) was performed on a Hewlett-Packard 5890 Level 4 chromatograph, equipped with split-mode capillary injection system and a flame ionization detector. Fused silica capillary columns (30 × 0.32 mm) wall coated with DB-1 (J & W Scientific) were used with helium as the carrier gas. All reactions were carried out under a stream of nitrogen in glassware that had been flame-dried. Solvents were dried and distilled prior to use. Siliranes *cis*-**1** and *trans*-**1** were prepared according to the method of Boudjouk.[10] Siliranes and silirenes were stored and handled in an Innovative Technologies nitrogen atmosphere drybox. The palladium catalyst, $PdCl_2(PPh_3)_2$, was dried in vacuo prior to use.

Synthesis of Silole 5 and Silacyclopentenes 6 (Eq 3). Method A. $PdCl_2(PPh_3)_2$ (12 mg, 1 mol %), *cis*-**1** (146 mg, 0.736 mmol), and DMAD (266 mg, 1.87 mmol) were dissolved in 7.0 mL of C_6H_6. The reaction mixture was stirred at ambient temperature for 2 days and concentrated in vacuo to give an orange liquid. Purification by column chromatography (30:70 EtOAc/hexanes) yielded **5** (45 mg, 14%) and *cis*-**6** (53 mg, 21%) as clear liquids.[42]

Method B. To a J. Young NMR tube was added $PdCl_2(PPh_3)_2$ (12 mg, 2 mol %), and the reaction mixture was dried in vacuo. Silirane *cis*-**1** (161 mg, 0.811 mmol), DMAD (142 mg, 0.999 mmol), and 0.7 mL of C_6D_6 were added. The NMR tube was heated in a 108 °C oil bath for 20 min. The reaction mixture quickly turned dark red and after 15 min was concentrated in vacuo. Purification by column chromatography (40:60 EtOAc/hexanes) yielded **5** (162 mg, 76% yield based on DMAD) as a liquid.

1,1-Di-*tert*-butyl-2,3,4,5-tetra(carboxymethyl)silacyclopentadiene (5): mp 85−86 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.81 (s, 6H), 3.80 (s, 6H), 1.15 (s, 18H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.5, 164.4, 149.1, 141.6, 52.5, 52.0, 28.0, 20.9; ^{29}Si NMR ($CDCl_3$, 99.3 MHz) δ 26.2; IR (KBr) 2958, 1719, 1240, 823 cm^{-1}; HRMS (CI/isobutane) calcd for $C_{20}H_{31}O_8Si$ $(M + H)^+$ 427.1788, found 427.1785. Anal. Calcd for $C_{20}H_{30}O_8Si$: C, 56.32; H, 7.09. Found: C, 56.06; H, 7.21. **1,1-Di-*tert*-butyl-2,3-dicarboxymethyl-4,5-*cis*-dimethylsilacyclopent-2-ene (*cis*-6).** ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.76 (s, 3H), 3.74

(40) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1977**, *99*, 3879−3880.

(41) A related nickelasilacyclobutene has been suggested in the nickel-catalyzed reactions of silirenes: Ohshita, J.; Isomura, Y.; Ishikawa, M. *Organometallics* **1989**, *8*, 2050−2054.

(42) A related 1,4-platinasilacyclohexadiene has been isolated and a thermally induced reductive elimination of Pt(0) formed the dimethylsilyl analogue of silole **2** (ref 7).

(43) A related metal-catalyzed intramolecular hydrosilation process employing allyl alcohols and allylamines has been reported: Tamao, K.; Nakagawa, Y.; Ito, Y. *Organometallics* **1993**, *12*, 2297−2308, and references therein.

(44) Takeyama, Y.; Nozaki, K.; Matsumoto, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1461−1466.

(s, 3H), 3.27 (m, 1H), 1.70 (m, 1H), 1.20 (d, J = 7.9, 3H), 1.12 (s, 9H), 1.11 (d,[45] J = 8.4, 3H), 1.06 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.7, 166.3, 158.9, 141.0, 52.0, 51.5, 43.1, 29.3, 28.8, 20.7, 20.2, 19.5, 15.9, 12.4; ^{29}Si NMR ($CDCl_3$, 99.3 MHz) δ 28.6; IR (thin film) 2948, 1732, 1242, 821 cm^{-1}; HRMS (CI) m/z calcd for $C_{18}H_{32}O_4Si$ (M^+) 340.2070, found 340.2061; Anal. Calcd for $C_{18}H_{32}O_4Si$: C, 63.49; H, 9.47. Found: C, 63.41; H, 9.41. **1,1-Di-*tert*-butyl-2,3-di(carboxymethyl)-4,5-*trans*-dimethylsilacyclopent-2-ene (*trans*-6).** This material was prepared in a similar manner as *cis*-**6** using silirane *trans*-**1**. The product trans-**6** was isolated as a yellow liquid: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.79 (s, 3H), 3.72 (s, 3H), 2.63 (m, 1H), 1.29 (d, J = 7.7, 3H), 1.14 (d, J = 6.6, 3H), 1.10 (s, 9H), 1.04 (s, 9H), 0.94 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 169.0, 168.2, 163.0, 136.0, 51.9, 51.5, 47.3, 28.4, 28.3, 25.6, 21.8, 19.8, 18.0, 13.5; IR (thin film) 1716, 1238, 821 cm^{-1}; HRMS (CI/isobutane) calcd for $C_{18}H_{32}O_4Si$ (M^+) 340.2070, found 340.2074; Anal. Calcd for $C_{18}H_{32}O_4Si$: C, 63.49; H, 9.47. Found: C, 63.52; H, 9.62.

Synthesis of (*Z*)-Vinylsilanol 8 from *trans*-1 and DMAD (Eq 4). Silirane *trans*-**1** (103 mg, 0.519 mmol), $PdCl_2(PPh_3)_2$ (12 mg, 3 mol %), and DMAD (143 mg, 1.01 mmol) were dissolved in 5.0 mL of C_6H_6. After 10 min, 2 drops of water were added and the mixture was stirred for an additional 22 h. The reaction mixture was concentrated in vacuo, and purification by column chromatography (20:80 EtOAc/hexanes) yielded **8** (84 mg, 54%) and **5** (10 mg, 5%) as yellow liquids.

(*Z*)-Di-*tert*-butyl(2-dimethylmaleic)silanol (8): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.34 (s, 1H), 3.81 (s, 3H), 3.75 (s, 3H), 2.18 (br s, 1H), 1.08 (s, 18H); ^{13}C NMR (C_6D_6, 125 MHz) δ 171.3, 164.3, 152.4, 132.3, 51.7, 51.4, 27.7, 20.9; IR (thin film) 3533, 2951, 1732, 1435, 1243, 1201, 824 cm^{-1}; HRMS (EI) calcd for $C_{10}H_{17}O_5Si$ ($M - C_4H_9$)$^+$ 245.0845, found 245.0833. Anal. Calcd for $C_{14}H_{26}O_5Si$: C, 55.60; H, 8.66. Found: C, 55.47; H, 8.75.

Synthesis of Siloles 9 and 10 from *trans*-1 (Eq 5). Compounds **9** and **10** were prepared in a similar manner as above using *trans*-**1** at 117 °C for 18 h. Purification by column chromatography (15:85 EtOAc/hexanes) afforded **9** (98 mg, 50%) and **10** (24 mg, 12%) as yellow liquids.

1,1-Di-*tert*-butyl-2,4-dicarboxymethyl-3,5-dimethylsilacyclopentadiene (9): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.83 (s, 3H), 3.72 (s, 3H), 2.29 (s, 3H), 2.07 (s, 3H), 1.07 (s, 18H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 168.6, 167.6, 163.8, 149.3, 148.4, 125.4, 51.4, 50.6, 28.5, 19.8, 18.0, 17.8; ^{29}Si NMR (C_6D_6, 99.3 MHz) δ 19.5; IR (thin film) 2950, 1732, 1213, 1036, 822 cm^{-1}; HRMS (CI/isobutane) m/z calcd for $C_{18}H_{30}O_4Si$ (M^+) 338.1913, found 338.1918. Anal. Calcd for $C_{18}H_{30}O_4Si$: C, 63.87; H, 8.93. Found: C, 63.97; H, 8.98. **1,1-Di-*tert*-butyl-3,4-dicarboxymethyl-2,5-dimethylsilacyclopentadiene (10).** ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.75 (s, 6H), 2.14 (s, 6H), 1.08 (s, 18H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.1, 145.9, 142.8, 51.3, 28.3, 19.5, 17.3; ^{29}Si NMR (C_6D_6, 99.3 MHz) δ 19.2; IR (thin film) 2949, 1731, 1199, 822 cm^{-1}; HRMS (CI/isobutane) m/z calcd for $C_{18}H_{30}O_4Si$ (M^+) 338.1913, found 338.1908; Anal. Calcd for $C_{18}H_{30}O_4Si$: C, 63.87; H, 8.93. Found: C, 63.69; H, 9.02.

Synthesis of Silacycles 9, 11, and 12 from *cis*-1 (Eq 6). To a J. Young NMR tube were added $PdCl_2(PPh_3)_2$ (15 mg, 3 mol %), *cis*-**1** (134 mg, 0.675 mmol), methyl 2-butynoate (302 mg, 3.08 mmol), and 0.7 mL of C_6D_6. The NMR tube was sealed and placed in a 114 °C oil bath for 6 h. The reaction mixture was concentrated in vacuo, and successive purification by column chromatography (5−10:95−90 EtOAc/hexanes) yielded silacycles **9** (24 mg, 11%), **11** (48 mg, 24%), and **12** (41 mg, 18%), as liquids.

1,1-Di-*tert*-butyl-*cis*-2,3-dimethyl-4-carboxymethylsilacyclohex-4-ene (11): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.65 (m, 1H), 3.68 (s, 3H), 2.66 (m, 1H), 2.53 (d, J = 15.9, 1H), 2.05 (dd, J = 15.8, 2.1, 1H), 1.49 (m, 1H), 1.10 (d, J = 8.0, 3H), 1.08 (s, 9H), 1.03 (d, J = 7.2, 3H), 0.99 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 172.1, 167.8, 110.4, 50.6, 48.1, 29.4, 28.5, 21.3, 20.3, 20.2, 15.5, 14.6, 12.0; ^{29}Si NMR ($CDCl_3$, 99.3 MHz) δ 19.5; IR (thin film) 2935, 1716, 1640, 1471, 1216, 1148, 821 cm^{-1}; HRMS (CI/isobutane) m/z calcd for $C_{17}H_{32}O_2Si$ (M^+) 296.2171, found 296.2175. Anal. Calcd for $C_{17}H_{32}O_2Si$: C, 68.86; H, 10.88. Found: C, 68.63; H, 10.84.

1,1-Di-*tert*-butyl-3,4-dicarboxymethyl-2-methylsilacyclohexa-2,4-diene (12): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.79 (br s, 1H), 3.84 (s, 3H), 3.71 (s, 3H), 2.17 (d, J = 2.0, 2H), 2.10 (s, 3H), 1.04 (s, 18H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.85, 167.76, 158.8, 156.6, 150.9, 113.2, 51.8, 50.9, 28.5, 19.8, 18.4, 12.9; ^{29}Si NMR (C_6D_6, 99.3 MHz) δ 26.1; IR (thin film) 2950, 1732, 1606, 1470, 1212, 1170, 822 cm^{-1}; HRMS (CI/isobutane) m/z calcd for $C_{18}H_{30}O_4Si$ (M^+) 338.1913, found 338.1910. Anal. Calcd for $C_{18}H_{30}O_4Si$: C, 63.87; H, 8.93. Found: C, 64.09; H, 8.99.

Synthesis of Silole 9 from Silirene 13[12] (Eq 8). To a J. Young NMR tube were added $PdCl_2(PPh_3)_2$ (5 mg, 0.8 mol %), silirene **13** (198 mg, 0.882 mmol), methyl 2-butynoate (135 mg, 1.38 mmol), and 0.9 mL of C_6D_6. The NMR tube was sealed and placed in a 110 °C oil bath for 9 h. The reaction mixture was concentrated in vacuo. Purification by column chromatography (10:90 EtOAc/hexanes) yielded silole **9** (225 mg, 75%) as a clear liquid.

Synthesis of Siloles 16[11] and 17 and Silacyclopentene *trans*-18 from *trans*-1 (Eq 9). Silirane *trans*-**1** (138 mg, 0.695 mmol), 1-hexyne (238 mg, 2.90 mmol), ethyl propiolate (267 mg, 2.72 mmol), and $PdCl_2(PPh_3)_2$ (12 mg, 3 mol %) were dissolved in 4.0 mL of C_6H_6. The reaction mixture was stirred at ambient temperature under an inert atmosphere for 18 h. The reaction mixture was concentrated in vacuo, and purification by column chromatography (10:90 EtOAc/hexanes) yielded silole **16** (183 mg, 78%) as a yellow liquid and an inseparable mixture of silole **17** (4%) and silacyclopentene *trans*-**18** (3%) as a yellow liquid (15 mg, their relative compositions determined by ^{1}H NMR spectroscopy).

1,1-Di-*tert*-butyl-3-carboxyethyl-4-(1-butyl)silacyclopentadiene (17): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.89 (d, J = 1.6, 1H), 5.68 (d, J = 1.3, 1H), 4.23 (m, 2H), 2.54 (m, 2H), 1.43 (m, 2H), 1.35 (m, 2H), 1.33 (t, J = 7.3, 3H), 1.04 (s, 18H), 0.91 (t, J = 7.2, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.2, 160.1, 152.1, 140.9, 124.0, 60.4, 34.4, 31.1, 28.8, 25.6, 22.5, 19.2, 14.1; HRMS (CI) m/z calcd for $C_{19}H_{35}O_2Si$ ($M + H$)$^+$ 323.2406, found 323.2409. **1,1-Di-*tert*-butyl-3-carboethoxy-*trans*-dimethylsilacyclopent-2-ene (*trans*-18)**. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.84 (d, J = 2.0, 1H), 4.20 (m, 3H), 2.56 (m, 1H), 1.32 (t, J = 7.2, 3H), 1.28 (d, J = 7.7, 3H), 1.20 (d, J = 6.8, 3H), 1.03 (s, 9H), 1.01 (s, 9H); HRMS (CI) m/z calcd for $C_{17}H_{33}O_2Si$ ($M + H$)$^+$ 297.2250, found 297.2253.

Synthesis of Siloles 5 and 19 from *trans*-1 (Eq 10). Silirane *trans*-**1** (130 mg, 0.66 mmol), $PdCl_2(PPh_3)_2$ (12 mg, 3 mol %), phenylacetylene (105 mg, 1.03 mmol), and DMAD (151 mg, 1.06 mmol) were dissolved in 5.5 mL of C_6H_6. The reaction mixture was stirred at ambient temperature for 1 day. The reaction mixture was concentrated in vacuo. Purification by column chromatography (30:70 EtOAc/hexanes) yielded silole **5** (114 mg, 40%) and silole **19** (62 mg, 24%) as yellow liquids. Silole **19** was further purified by column chromatography (30:70 EtOAc/hexanes) to give a yellow viscous oil, which solidified upon standing (54 mg, 21%).

1,1-Di-*tert*-butyl-2,3-dicarboxymethyl-4-phenylsilacyclopentadiene (19): mp = 80−83 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.31 (m, 5H), 6.32 (s, $^2J_{Si-H}$ = 11.0, 1H), 3.77 (s, 3H), 3.65 (s, 3H), 1.15 (s, 18H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.9, 166.9, 158.8, 157.6, 139.0, 134.9, 134.5, 128.2, 128.0, 126.7, 52.0, 51.7, 28.7, 20.1; IR (KBr) 3058, 2952, 1737, 1706, 1268, 1232, 1115, 824, 783 cm^{-1}; HRMS (CI/isobutane) calcd for $C_{22}H_{30}O_4Si$ (M^+) 386.1913, found 386.1905. Anal. Calcd for $C_{22}H_{30}O_4Si$: C, 68.36; H, 7.82. Found: C, 68.13; H, 7.94.

(45) One of the doublet peaks overlaps with the *tert*-butyl singlet at 1.12 ppm.

Stoichiometric Reduction of $PdCl_2(PPh_3)_2$ with *trans*-1 (Eq 11). To a flask were added $PdCl_2(PPh_3)_2$ (446 mg, 0.635 mmol), C_6H_6 (8.0 mL), and *trans*-**1** (131 mg, 0.660 mmol). The reaction mixture quickly turned black upon stirring. After 20 h, the solution was concentrated in vacuo. Purification by bulb-to-bulb distillation (95 °C/ 0.05 Torr) afforded di-*tert*-butyldichlorosilane[29] (65 mg, 48%) as a clear liquid. The generation of *trans*-2-butene was observed (^1H and ^{13}C NMR spectroscopy) by running a similar reaction in a bomb employing C_6D_6 as solvent.

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Supporting Information Available: Spectra (^1H and ^{13}C NMR) for compounds **17** and *trans*-**18**. This material is available free of charge via the Internet at http://pubs.acs.org.

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