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Catalytic Transition-Metal-Mediated Tetraene Carbocyclizations: A New Carbocyclization via Hydrosilylation?[1]

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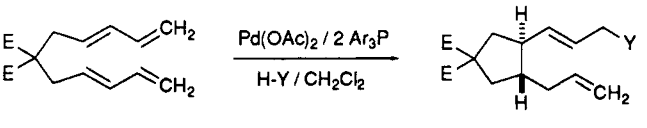
Summary: The palladium- or nickel-catalyzed carbocyclization of a tetraene substrate proceeds with incorporation of a hydrosilane to yield functionalized ring systems possessing trans-vicinal divinyl substituents on the newly formed ring, one of which is generated as an allylsilane. In one example, tributylstannane is shown to participate in the analogous cyclization reaction. Studies utilizing isotopic labeling, crossover experiments, and competition experiments provide evidence against a mechanism involving the initial hydrosilylation of one of the 1,3-diene subunits.

We recently reported investigations into a facile new palladium-catalyzed carbocyclization of tetraene substrates (e.g., 1, E = CO_2Et), a novel palladium-catalyzed cyclization that proceeds with incorporation of a protic H–Y trapping reagent[2] (Y = OR, NR_2, SO_2Ar, CH_2NO_2, $CH(CO_2R)_2$, $R(R_2N)C{=}C(H)R$) to afford functionalized cyclopentanes and *N*-acylpyrrolidines.[3]

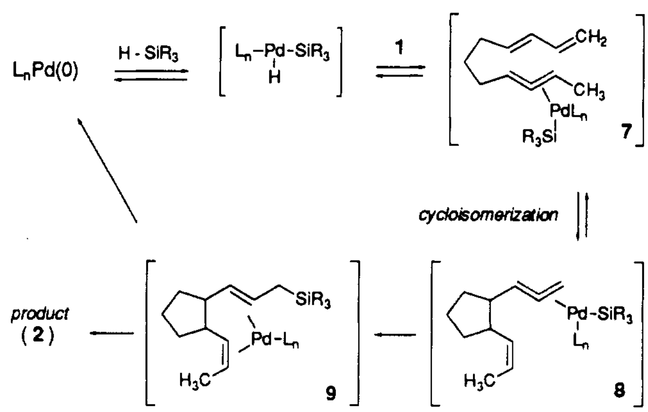


1 (E = CO_2Et)

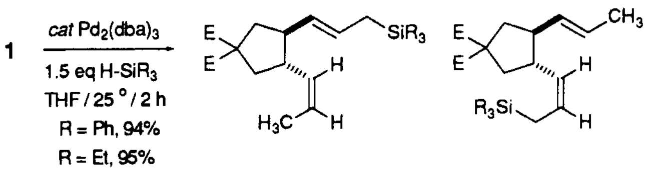
This methodology defines an intramolecular variant of the telomerization of 1,3-butadiene,[4] a widely explored process that yields 1-substituted octadienes from the coupling of two molecules of butadiene with one molecule of an H–Y trapping reagent.

Several catalytic transition-metal-mediated reductive carbocyclizations involving hydrosilanes have recently been reported.[5] The nickel-catalyzed cyclization-via-hydrosilylation of 1,7-diynes[5a] provides a novel strategy for the introduction of a vinylsilane moiety concomitant with the cyclization. We reasoned that cyclization of tetraene substrate 1 with incorporation of a hydrosilane could potentially provide a convenient method for the preparation of ring systems bearing a pendent allylsilane moiety. The use of hydrosilanes as trapping reagents for the palladium-catalyzed telomerization of butadiene was first reported in the late 1960s by the groups of Hagihara and Tsuji.[6] In contrast to the telomerizations of butadiene with protic H–Y trapping reagents, which yield 1-substituted 2,7-octadiene products, telomerizations with certain hydrosilane trapping reagents give 1-silyl-2,6-octadienes. A series of reports published in the mid-1970s described the analogous nickel-catalyzed telomerization.[7] Whether the reaction is nickel- or palladium-catalyzed, simple hydrosilylation of butadiene generally competes with the telomerization pathway. Moreover, substituted 1,3-dienes (e.g., isoprene, piperylene) give predominantly to exclusively simple hydrosilylation products rather than telomerization products.[6,7]

Scheme I. Potential Carbocyclization-via-Hydrosilylation Mechanism for the Formation of 2 and 3 from the Palladium-Catalyzed Cyclization of Tetraene 1 with a Hydrosilane



In spite of the poor reactivity of substituted 1,3-dienes in the intermolecular telomerization, treatment of tetraene 1 with 1.5 equiv of triphenylsilane in the presence of 3 mol % of the (dibenzylideneacetone)palladium(0) complex (3 mol % $Pd_2(dba)_3$/THF/1–2 h/25 °C) effects rapid carbocyclization of the tetraene.



2a (R = Ph)
b (R = Et)

3a (R = Ph)
b (R = Et)

A 6:1 mixture of two diastereomeric cyclopentanes, **2a** and

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[1] A preliminary account of this work was presented: Takacs, J. M.; Chandramouli, S.; Zhu, J. 199th National Meeting of the American Chemical Society, Boston, MA, April 1990; ORGN 12.

[2] The term "protic trapping reagent" is used to differentiate from H–Y reagents (e.g., hydrosilanes, hydrostannanes) that would more likely serve as a hydride source than a proton source.

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[5] (a) Tamao, K.; Kobayashi, K.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 1286–8. (b) Trost, B. M.; Lee, D. C. *J. Am. Chem. Soc.* **1988**, *110*, 7255–8. (c) Trost, B. M.; Rise, F. *J. Am. Chem. Soc.* **1987**, *109*, 3161–3.

[6] (a) Takahashi, S.; Shibano, T.; Hagihara, N. *J. Chem. Soc., Chem. Commun.* **1969**, 161. (b) Takahashi, S.; Shibano, T.; Kojima, H.; Hagihara, N. *Organomet. Chem. Synth.* **1970**, *1*, 193. (c) Hara, M.; Ohno, K.; Tsuji, J. *J. Chem. Soc., Chem. Commun.* **1971**, 247. (d) Tsuji, J.; Hara, M.; Ohno, K. *Tetrahedron* **1974**, *30*, 2143–6. (e) Langova, J.; Hetflejs, J. *Collect. Czech. Chem. Commun.* **1975**, *40*, 420–31. (f) Kaneda, K.; Kurosaki, H.; Terasawa, M.; Imanaka, T.; Teranishi, S. *J. Org. Chem.* **1981**, *46*, 2356–62.

[7] (a) Capka, M.; Hetflejs, J. *Coll. Czech. Chem. Commun.* **1975**, *40*, 3186–9. (b) Capka, M.; Hetflejs, J. *Collect. Czech. Chem. Commun.* **1975**, *40*, 3020–9. (c) Capka, M.; Hetflejs, J. *Collect. Czech. Chem. Commun.* **1975**, *40*, 2073–82. (d) Yurev, V. P.; Salimgareeva, I. M.; Zhebarov, O. Z.; Tolstikov, G. A. *J. Gen. Chem. USSR (Engl. Transl.)* **1975**, *45*, 368–70. (e) Yurev, V. P.; Salimgareeva, I. M.; Zhebarov, O. Z.; Tolstikov, G. A.; Rafikov, S. R. *Dokl. Chem. (Engl. Transl.)* **1975**, *224*, 609–12. (f) Yurev, V. P.; Salimgareeva, I. M.; Zhebarov, O. Z.; Tolstikov, G. A. *Bull. Acad. Sci. USSR (Engl. Transl.)* **1975**, 1772–3. (g) Yurev, V. P.; Salimgareeva, I. M.; Zhebarov, O. Z.; Tolstikov, G. A. *Bull. Acad. Sci. USSR (Engl. Transl.)* **1975**, 2027. (h) Vaisarova, V.; Schraml, J.; Hetflejs, J. *Collect. Czech. Chem. Commun.* **1978**, *43*, 265–77.

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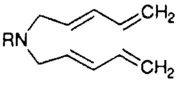
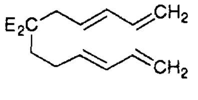
3a, is obtained in excellent yield Similar products are obtained when dimethylphenylsilane (95%) or triethylsilane (95%) is employed. In the latter case, capillary gas chromatographic analysis of the crude product mixture reveals an 80:14 mixture of **2b** and **3b**. A small amount (6%) of another close running compound is also detected by GC; however, its structure has not yet been determined. Treatment of tetraene **1** with 3 equiv of triethylsilane in the presence of a nickel catalyst (5 mol % $Ni(acac)_2$/11 mol % DIBAL-H/10 mol % Ph_3P/THF/65 °C/10 h) yields a 2:3 mixture of **2b** and **3b** in 85% yield.[11a]

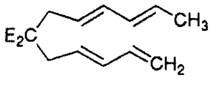
The reactions of three related tetraene substrates have been investigated. The *N*-acylpyrrolidine precursor **4** (Ph_3SiH 82%), the six-membered ring precursor **5** (Ph_3SiH 80%),[11b] and the methyl-substituted tetraene **6** (Ph_3SiH 57% yield) also undergo palladium-catalyzed cyclization. About 65% of the products obtained in the cyclization of **6** derive from addition of the silyl group to the less substituted diene subunit.[12]



4 (R = PhC(O))



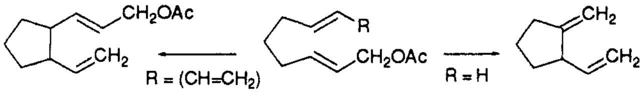
5 (E = CO_2Et)



6 (E = CO_2Et)

The structures of diastereoisomers **2** and **3** are related in an unusual way. Six contiguous stereochemical centers are formed as a consequence of the carbocyclization. Yet, out of the multitude of possible stereoisomeric products, the stereochemistry of the carbon skeleton is identical in both diastereomeric products. Structures **2** and **3** differ only with respect to which of the termini in the newly formed carbon skeleton the triphenylsilyl group and the hydrogen respectively become attached. In essence, while **2** and **3** are formally stereoisomers, they result from regioisomeric modes of H–Si addition. The palladium-catalyzed carbocyclization to assemble the carbon skeleton of the product apparently proceeds with very high levels of simple diastereoselectivity[13] and alkene stereoselectivity. This curious relationship between **2** and **3** must somehow relate to the role of the metal in the catalytic mechanism for the cyclization.

It has long been a puzzle as to why butadiene/hydrosilane telomerizations give 2,6-octadienes while other H–Y trapping reagents give 2,7-octadienes. To explain the formation of 1-silyl-2,6-octadiene, it is generally postulated that the reaction proceeds via the initial partial hydrosilylation[14] of one butadiene molecule followed by capture of the intermediate (π-allyl)palladium complex (i.e., $[\pi\text{-}(CH_2CHCHCH_3)]Pd(SiR_3)L_n$) by insertion of another butadiene unit.[4,6,7] This mechanism is in contrast to the one postulated for the reaction with protic trapping reagents, for which initial oxidative coupling of two molecules of butadiene has been proposed.[3,4,15] A hydrosilylation pathway can be imagined that would account for the formation of **2** and **3** (Scheme I). The viability of the key cycloisomerization step (**7** to **8**) is amply supported by examples of other palladium-, nickel-, and platinum-catalyzed carbocyclizations for which the cycloisomerization of a (π-allyl)metal intermediate has been implicated.[16–19] For example, Trost[16] recently reported palladium-catalyzed cyclizations of the type **10** (R = $CH{=}CH_2$) to **11**. Similarly, Oppolzer[17] and Negishi[18] reported cyclizations of the type **10** (R = H) to **12**.



11 **10** **12**

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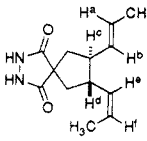
(8) All new compounds isolated were characterized spectroscopically, and the elemental composition was determined by combustion analysis and/or high-resolution mass spectrometry.

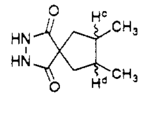
(9) The structural assignments of **2** and **3** are consistent with the following analysis and spectroscopic data. Treatment of the mixture (**2a** and **3a**) with excess hydrazine hydrate (EtOH, 65 °C) gives a mixture of products from which the major diazine derivative i can be crystallized.



structure i

With appropriate decoupling experiments, the vicinal coupling constant $J_{c,d}$ = 10.8 Hz is measured for the vicinal ring methine hydrogens in i. Due to the structural constraints of the relatively rigid spirocyclic ring system,[10] the trans relative stereochemistry is assigned to i and by inference to **2**. The trans double bond in the allylsilane side chain and the *cis*-propenyl side chain assigned to **2** are consistent with the vicinal coupling constants ($J_{a,b}$ = 14.5 Hz, $J_{e,f}$ = 10.2 Hz) and with the ^{13}C chemical shifts for the appropriate methyl (13.1 ppm) and (triphenylsilyl)methyl (19.3 ppm) groups. The minor component from the cyclization, diastereomer **3**, must also possesses the trans relative stereochemistry. Hydrogenation (5% rhodium on alumina, 1 atm of H_2, EtOH, 25 °C) of the individual diastereomers **2b** and **3b** yields the same saturated cyclopentane. The appropriate ^{13}C chemical shifts (methyl, 17.9; (triphenylsilyl)methyl, 15.2 ppm) and vicinal coupling constants (*trans*-propenyl, J = 15.3 Hz; *cis*-(triphenylsilyl)propenyl, J = 10.8 Hz) in **3a** are consistent with the stereochemical assignments shown for the two double bonds.

(10) All possible isomeric cis/trans spirocycles ii were modeled with use of PCModel (v 2.0) and MMX85. The most stable trans-disubstituted conformer (corresponding to i) is estimated to have a vicinal coupling constant $J_{c,d}$ = 11.8 Hz; the most stable conformer of the corresponding cis diastereomer is estimated at 5.4 Hz.



model structure ii

(11) (a) A small amount (10%) of a [4 + 4]-cycloaddition product is formed when fewer equivalents of the hydrosilane are employed. See: Wender, P. A.; Ihle, N. C. *J. Am. Chem. Soc.* **1986**, *108*, 4678–9. (b) This yield is based upon recovered starting material.

(12) The low regioselectivity observed in the cyclization of **6** is surprising in light of the aforementioned fact that substituted dienes such as piperylene are poor substrates for telomerization reactions with hydrosilanes.[6,7] If a carbocyclization-via-hydrosilylation mechanism were operating (vide infra), much higher discrimination favoring the regioselective hydrosilylation of the monosubstituted over the disubstituted 1,3-diene subunit within tetraene **6** would be expected. See: Cornish, A. J.; Lappert, M. F.; Nile, T. A. *J. Organomet. Chem.* **1977**, *132*, 133–48.

(13) Heathcock, C. H. In *Asymmetric Synthesis: Stereodifferentiating Addition Reactions*; Morrison, J. D., Ed.; Academic Press: New York, 1983; ISBN 0-12-507703-3, Vol. 3, Part B, pp 110–212.

(14) For a general review including the hydrosilylation of 1,3-dienes, see: Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoprt, Z., Eds.; John Wiley & Sons Ltd: New York, 1989; Vol. 2, pp 1479–1526 and references therein. For a recent discussion of the alkene hydrosilylation mechanism, see: Seitz, F.; Wrighton, M. S. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 289–91 and references therein.

(15) (a) Jolly, P. W.; Mynott, R.; Raspel, B.; Schick, K. P. *Organometallics* **1986**, *5*, 473–81. (b) For an alternative mechanistic proposal, see: Behr, A.; Ilsemann, G. V.; Keim, W.; Krueger, C.; Tsay, Y. H. *Organometallics* **1986**, *5*, 514–18.

(16) Trost, B. M.; Luengo, J. I. *J. Am. Chem. Soc.* **1988**, *110*, 8239–41.

(17) (a) Oppolzer, W.; Gaudin, J. M. *Helv. Chim. Acta* **1987**, *70*, 1477–81. (b) Oppolzer, W.; Gaudin, J. M.; Birkinshaw, T. N. *Tetrahedron Lett.* **1988**, *29*, 4705–8.

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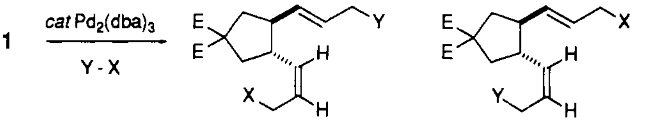
(19) (a) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 38–52. (b) Oppolzer, W.; Keller, T. H.; Bedoya-Zurita, M.; Stone, C. *Tetrahedron Lett.* **1989**, *30*, 5883–6. (c) Grigg, R.; Sridharan, V.; Sukanthini, S.; Worakun, T. *Tetrahedron Lett.* **1989**, *30*, 1139–42. (d) Trost, B. M.; Tour, J. M. *J. Am. Chem. Soc.* **1988**, *110*, 5231–3.

Nonetheless, the experimental evidence described below raises doubts about the likelihood of the carbocyclization-via-hydrosilylation mechanism.

The palladium-catalyzed reaction of tetraene **1** with triphenylsilane-*d* gives the regiospecifically monodeuterated products corresponding to **2** and **3** [i.e., **13a** (X = D, Y = $SiPh_3$) and **14a** (X = D, Y = $SiPh_3$)].[20]

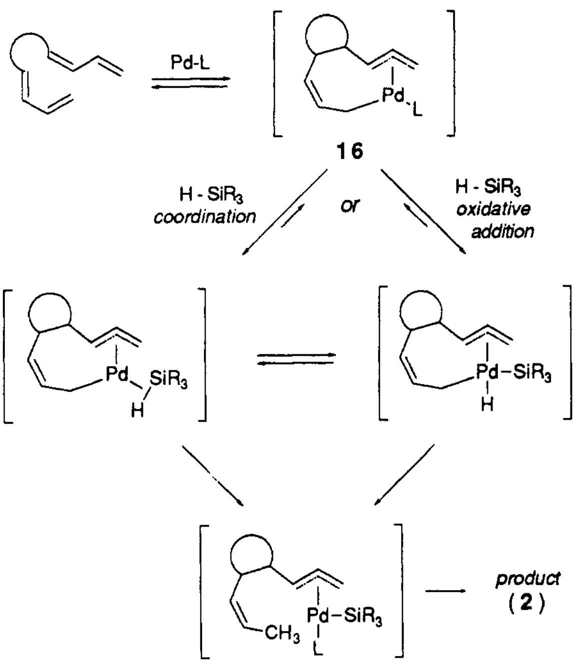


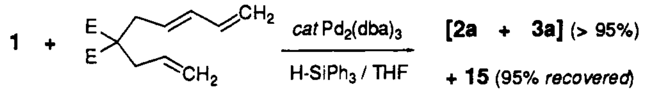
13a (X = D, Y = $SiPh_3$) **14a** (X = D, Y = $SiPh_3$)
b (X = H, Y = $SiMe_2Ph$) **b** (X = H, Y = $SiMe_2Ph$)

When admixed in the absence of tetraene **1**, $Pd_2(dba)_3$ catalyzes the rapid H/D-exchange and competitive dehydrogenative coupling[21] of a mixture of deuteriosilane and hydrosilane (0.03 mmol of $Pd_2(dba)_3$/0.75 mmol of Ph_3SiD/0.75 mmol of Me_2PhSiH/5 mL of THF/25 °C/0.5 h). Nonetheless, a competition experiment in which a limiting amount of tetraene **1** is reacted under otherwise standard conditions with a mixture of triphenylsilane-*d* and dimethylphenylsilane yields only four cyclized products (0.03 mmol $Pd_2(dba)_3$/1.0 mmol of **1**/0.75 mmol of Ph_3SiD/0.75 mmol of Me_2PhSiH/5 mL of THF/25 °C/3 h/98% combined yield of products).[22] Triphenylsilyl-containing products are separated from dimethylphenylsilyl-containing products by chromatography on silica. Analysis of the product mixture containing the triphenylsilyl moiety shows that this material also has stoichiometric deuterium incorporation; a mixture of **13a** (X = D, Y = $SiPh_3$) and **14a** (X = D, Y = $SiPh_3$) is isolated (46%). Products containing the dimethylphenylsilyl moiety show no deuterium incorporation. That is, **13b** (X = H, Y = $SiMe_2Ph$) and **14b** (X = H, Y = $SiMe_2Ph$) are isolated (52%). We find no evidence for any crossover products and estimate an upper limit of 5% undetected crossover under our reaction conditions.

A second competition experiment also yields interesting results. If diene hydrosilylation is an important step in the catalytic conversion of **1** to the mixture of **2** and **3**, consider the implications for a triene such as **15**. If diene hydrosilylation is an important step, then **15** should also yield silylated products. The products derived from **15** might be silylated and cyclized products, cyclizing in analogy to the conversion of **10** to **12**, or silylated acyclic products resulting from simple hydrosilylation of the 1,3-diene subunit within **15**, but nonetheless some silyl-containing products resulting from **15** are expected.[6,7,14] In a competition experiment (0.03 mmol of $Pd_2(dba)_3$/0.5 mmol of **1**/0.5 mmol of **15**/1.5 mmol of Ph_3SiH/5 mL of THF/25 °C/12 h), a 1:1 mixture of **1** and **15** gives essentially quantitative conversion of **1** to **2a** and **3a**, whereas 95% **15** is recovered unchanged.

Scheme II. An Alternative Mechanistic Postulate. Capture of the Tetraene-Derived Metallacycle 16 by Addition of the Hydrosilane





15 (E = CO_2Et)

When treated separately, **15** (1.5 eq of Ph_3SiD/0.03 mmol of $Pd_2(dba)_3$/THF/25 °C) is recovered unchanged even after 12 h.

These experimental results (crossover experiments, **1** vs **15** competition experiments, and the nonselective reaction of **6**) argue against the carbocyclization-via-hydrosilylation mechanism. An alternative mechanistic possibility, which is consistent with all of the data collected to date and which adequately accounts for the stereoselective formation of only diastereomers **2** and **3**, involves addition of the hydrosilane[23] to an initially formed palladacycle such as **16**. The latter species is analogous to a catalytically relevant intermediate proposed in the telomerization of butadiene with protic trapping reagents.[15,24] Ligand coupling and/or reductive elimination would complete the catalytic cycle and generate the observed products (Scheme II).

This novel catalytic metal-mediated tetraene carbocyclization methodology provides a chemically efficient, stereoselective route to the preparation of ring systems bearing an allylsilane side chain. The facility of the carbocyclization suggests that it will be possible to extend the method to other trapping reagents. The palladium-catalyzed reaction of tetraene **1**, using tributylstannane in place of the hydrosilane, provides one example demonstrating this potential. The mixture of allylstannanes **13c** (X = H, Y = $SnBu_3$) and **14c** (X = H, Y = $SnBu_3$) is obtained in

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[20] Similar results were reported for the palladium-catalyzed reaction of butadiene with trimethylsilane-*d*: Langova, J.; Hetflejs, J. *Collect. Czech. Chem. Commun.* **1975**, *40*, 432–41.

[21] Brown-Wensley, K. A. *Organometallics* **1987**, *6*, 1590–2.

[22] The hydrosilanes, triphenylsilane and (dimethylphenyl)silane, react with tetraene 1 at comparable rates. Teatment of a limiting amount of 1 with a 1:1 mixture of triphenylsilane and dimethylphenylsilane (0.03 mmol of $Pd_2(dba)_3$/1.0 mmol of 1/(0.75 mmol of Ph_3SiH/0.75 mmol of Me_2PhSiH/5 mL of THF/25 °C/3 h/95% combined yield of products) affords a mixture of **2a** and **3a** (combined 50% yield) and a mixture of **13b** (X = H, Y = $SiMe_2Ph$) and **14b** (X = H, Y = $SiMe_2Ph$) (combined 45% yield) after chromatographic separation. Taken in conjunction with the results of the competition between triphenylsilane-*d* and dimethylphenylsilane, we must conclude that the palladium-catalyzed cyclization reaction has only a modest deuterium isotope effect. This is confirmed by the results of a competition between triphenylsilane-*d* and triphenylsilane, the details of which will be published elsewhere.

[23] (a) Luo, X.-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 2527–35. (b) Lichtenberger, D. L.; Rai-Chaudhuri, A. *J. Am. Chem. Soc.* **1990**, *112*, 2492–7.

[24] (a) Benn, R.; Jolly, P. W.; Joswig, T.; Mynott, R.; Schick, K. P. *Z. Naturforsch.* **1986**, *41b*, 680–91. (b) Barnett, B.; Bussemeier, B.; Heimbach, P.; Jolly, P. W.; Kruger, C.; Tkatchenko, I.; Wilke, G. *Tetrahedron Lett.* **1972**, 1457–60.

excellent yield (96%). Further studies in tetraene carbocyclizations are in progress.

Acknowledgment. Financial support for these investigations from the University of Nebraska and the National Institutes of Health (GM34927) is greatefully acknowledged. High-resolution mass spectral analyses were performed by the Midwest Center for Mass Spectrometry, an NSF Regional Instrumentation Facility (Grant 8620177). We thank our colleague, Professor Robert Hembre (University of Nebraska—Lincoln), for a helpful discussion.

Reductive-Elimination Reactions from Platinum Dimers Bridged by (Diphenylphosphino)cyclopentadienyl Ligands

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Summary: [$Pt_2Me_2(CO)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2$] (**2**), obtained by reaction of [$Pt_2Me_2(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)_2$] (**1**) with CO, has been characterized by X-ray crystallography as a face-to-face dimer, in which the cyclopentadienyl ring is 1,2-substituted. Thermolysis of **2** at 55 °C yields acetone and the platinum(I) dimer [$Pt_2(CO)_2(\mu\text{-}C_5H_4PPh_2)_2$] (**3**), and the crystal structure of the latter reveals that the platinum atoms have migrated to the ipso carbons of the cyclopentadienyl rings. The analogous [$Pt_2\{P(CH_2CH_2CN)_3\}_2(\mu\text{-}C_5H_4PPh_2)_2$] is produced, along with ethane, when **1** is treated with $P(CH_2CH_2CN)_3$.

Ligands that display variable hapticity are useful in the design of catalyst precursors, since changes in hapticity provide low-energy pathways between coordinatively saturated and unsaturated species.[1] The cyclopentadienyl group is one such ligand, and we have made an extensive study of the factors that affect its mode of binding to palladium and platinum.[2] The (diphenylphosphino)cyclopentadienyl (dppc) group has been used to construct homo- and heterobimetallic complexes,[3-7] and it also has the potential to adopt differing bonding modes. We have shown recently that platinum dimers bridged by η^5-dppc ligands may be converted to 16-electron η^1 species under suitable conditions.[8] We report here the structures of two different η^1-bonded dppc complexes and the reductive elimination of acetone or ethane from methylplatinum species bridged by dppc ligands.

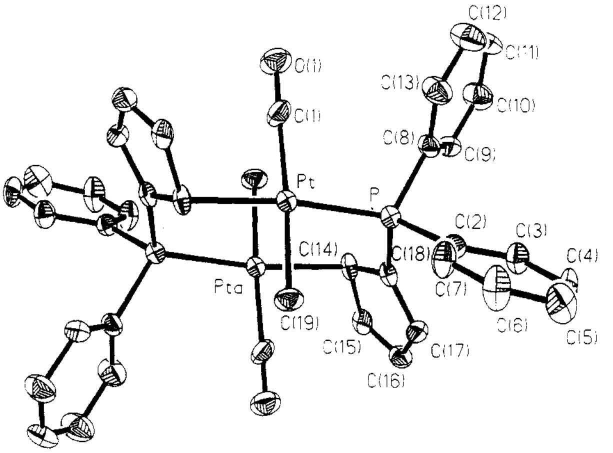

Figure 1. Projection drawing of [$Pt_2Me_2(CO)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2$], showing the atom-labeling scheme. The molecule contains a crystallographic $\bar{1}$ symmetry element. Selected bond distances (Å) and angles (deg) include the following: Pt–P = 2.298 (3), Pt–C1 = 1.897 (12), Pt–C19 = 2.088 (11), Pt–C14A = 2.160 (11), Pt···PtA = 3.157 (1), P–C2 = 1.835 (11), P–C8 = 1.834 (11), P–C18 = 1.796 (12), C18–C14 = 1.508 (14), C14–C15 = 1.479 (18), C15–C16 = 1.358 (16), C16–C17 = 1.400 (20), C17–C18 = 1.378 (16); P–Pt–C1 = 97.2 (4), P–Pt–C19 = 87.8 (4), P–Pt–C14A = 171.6 (3), C1–Pt–C19 = 173.6 (6).

Treatment of [$Pt_2Me_2(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)_2$] (**1**)[8] with carbon monoxide (1 atm) in dichloromethane or benzene solution affords, within a few minutes, [$Pt_2Me_2(CO)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2$] (**2**) as a yellow solid in 90% yield. The structure of **2** has been determined by single-crystal X-ray crystallography (Figure 1).[9] The dimer has a face-to-face, square-planar structure, with a nonbonded Pt···Pt distance of 3.157 Å. The cyclopentadienyl groups of the bridging

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[9] Crystal data for [$Pt_2Me_2(CO)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2$]·$Et_2O$: $C_{42}H_{44}O_3P_2Pt_2$; space group *C*2/c (selected over *Cc* on the basis of behavior toward refinement); cell dimensions a = 14.989 (3) Å, b = 16.031 (4) Å, c = 16.469 (4) Å, β = 104.31 (2)°; Z = 4; V = 3834.5 (15) Å^3; d(calcd) = 1.817 Mg/m^3. The 3534 measured reflections were collected with use of the 2θ–θ scanning technique and graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) on a Siemens R3 diffractometer. The structure was solved by Patterson methods with use of the SHELXTL PLUS program. Hydrogen atoms were incuded in their calculated positions and were held fixed. Refinement of the 1764 unique observed reflections with $F > 6.0\sigma(F)$ converged at R = 0.0288 and R_w = 0.0348.

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