trans-Bis(5-alkoxy- and 5-hydroxy-1-3-η^3-cyclohexenyl)palladium Complexes by Palladium(II)-Promoted Addition of Alcohols and Water to 1,2-Dialkyl-1,4-cyclohexadienes[1]

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Aliphatic alcohols and water add to 1,2-dialkyl-1,4-cyclohexadienes in the presence of bis(acetonitrile)palladium dichloride to form *trans*-bis(5-alkoxy- and 5-hydroxy-1,2-dialkyl-1-3-η^3-cyclohexenyl)palladium chloride complexes, respectively. In the alcohol series, the reaction is sensitive to the steric bulk of the alcohol nucleophile. To demonstrate synthetic utility, the derived palladium complexes in the water series were regioselectively and stereoselectively converted by subsequent methoxycarbonylation to the corresponding methyl *trans*-5-hydroxy-2,3-dialkyl-2-cyclohexene-1-carboxylates.

Since discovery 30 years ago,[2] (η^3-allyl)palladium complexes have become important intermediates in organic synthesis.[3] Standard preparation procedures include insertion of palladium(0) into the carbon–heteroatom bond of allylic systems,[4] direct substitution of the allylic hydrogen of alkenes by palladium(II),[5] and palladium(II)-promoted addition of nucleophiles and palladium across 1,3-dienes.[6] Both Larock's group with acyclic nonconjugated dienes[7] and this group with 1,4-cyclohexadienes[1,8] demonstrated that nonconjugated dienes afford (η^3-allyl)palladium complexes via the initial addition of palladium(II) and a nucleophile across the less hindered double bond. Subsequent migration of the metal toward the remaining double bond generates the (η^3-allyl)palladium system.

In earlier studies, this group showed that *trans*-bis(5-methoxy-1-3-η^3-cyclohexenyl)palladium chloride complexes can be stereoselectively and, depending on the reaction conditions, regioselectively formed by palladium(II)-promoted addition of methanol and palladium to a large variety of substituted 1,4-cyclohexadienes.[1,8] A selection of the derived (η^3-cyclohexenyl)palladium compounds was subsequently regioselectively and stereoselectively methoxycarbonylated to illustrate the synthetic efficacy of the reaction sequence. Herein are described the palladium(II)-promoted addition of a series of aliphatic alcohols and water to 1,2-dialkyl-1,4-cyclohexadienes[9] to prepare the corresponding *trans*-bis(5-alkoxy- and 5-hydroxy-1,2-dialkyl-1-3-η^3-cyclohexenyl)palladium complexes. To demonstrate the synthetic utility of the reactions, as well as to corroborate the relative stereochemistry of the palladium complexes, a selection of the *trans*-bis(5-hydroxy-1,2-dialkyl-1-3-η^3-cyclohexenyl)palladium complexes was further selectively functionalized with carbon monoxide and methanol and with dimethyl malonate anion.

Addition of Alcohols. The previous study was designed to determine the scope and limitations of the palladium(II)-promoted addition of methanol to the 1,4-cyclohexadiene as a function of the alkyl substituents and alkyl-substituent patterns on the cyclohexadiene system.[1,8] In order to examine the effect of alcohol structure in this reaction,[10] a series of aliphatic alcohols was added to 1,2-dimethyl-1,4-cyclohexadiene in the presence of an equimolar amount of bis(acetonitrile)palladium dichloride. The corresponding *trans*-bis(5-alkoxy-1,2-dimethyl-1-3-η^3-cyclohexenyl)palladium chloride complexes **1–5** were isolated in respectable yields after flash chromatography. As the progression was made from methanol (**1**, 88%), ethanol (**2**, 79%), isopropyl alcohol (**3**, 73%), isobutyl alcohol (**4**, 66%), to *tert*-butyl alcohol (**5**, 53%), the reactions became more sluggish and the isolated yields degenerated moderately. These effects probably reflect the increasing steric bulk of the alcohol nucleophile, which must undergo

(1) (a) 1,4-Diene-Derived (η^3-Allyl)palladium Complexes. 4. Part 3: Söderberg, B. C.; Åkermark, B.; Hall, S. S. *J. Org. Chem.* **1988**, *53*, 2925–2937. (b) Taken from the Ph.D. (Teknisk Doktor) Dissertation of B.C.S., Royal Institute of Technology, Dec 1987. (c) Initially disclosed at the 3rd Chemical Congress of North America and the 195th National Meeting of the American Chemical Society, Toronto, Ontario, June 1988, paper ORGN 250, and at the 22th Middle Atlantic Regional Meeting of the American Chemical Society, Millersville, PA, May 1988, paper INOR 197.

(2) (a) Slade, P. E., Jr.; Jonassen, H. B. *J. Am. Chem. Soc.* **1957**, *79*, 1277–1279. (b) Jonassen, H. B.; Kirsch, W. B. *Ibid.* **1957**, *79*, 1279–1281.

(3) (a) Trost, B. M. *Tetrahedron* **1977**, *33*, 2615–2649. (b) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer Verlag: New York, 1980; pp 37–42. (c) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: London, 1985; pp 7–14.

(4) (a) Smidt, J.; Hafner, W. *Angew. Chem.* **1959**, *71*, 284. (b) Dent, W. T.; Long, R.; Wilkinson, A. J. *J. Chem. Soc.* **1964**, 1585–1588. (c) Maitlis, P. M.; Espinet, P.; Russell, M. J. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 6, pp 386–404. (d) Åkermark, B.; Hansson, S.; Krakenberger, B.; Vitagliano, A.; Zetterberg, K. *Organometallics* **1984**, *3*, 679–682. (e) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 175–182.

(5) (a) Hüttel, R.; Dietl, H.; Christ, H. *Chem. Ber.* **1964**, *97*, 2037–2045. (b) Trost, B. M.; Strege, P. E.; Weber, L.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3407–3415. (c) Hartley, F. R. *The Chemistry of Palladium and Platinum*; Applied Science: London, 1973; pp 420–421.

(6) (a) Maitlis, P. M. *The Organic Chemistry of Palladium*; Academic: New York, 1971; Vol. I, Chapter V. (b) Reference 5c, pp 421–422. (c) Henry, P. M. *Palladium Catalyzed Oxidation of Hydrocarbons*; Reidel: Dordrecht, Holland, 1980; Vol. 2, pp 243–267. (d) Bäckval, J.-E. *Acc. Chem. Res.* **1983**, *16*, 335–342.

(7) (a) Larock, R. C.; Takagi, K. *J. Org. Chem.* **1984**, *49*, 2701–2705. (b) Larock, R. C.; Takagi, K. *Tetrahedron Lett.* **1983**, *24*, 3457–3460.

(8) Hall, S. S.; Åkermark, B. *Organometallics* **1984**, *3*, 1745–1748.

(9) (a) Birch, A. J. *Q. Rev.* **1950**, *4*, 69–93. (b) Birch, A. J.; Smith, H. *Ibid.* **1958**, *12*, 17–33. (c) Smith, H. *Organic Reactions in Liquid Ammonia*; Wiley-Interscience: New York, 1963; Vol. 1, Part 2, p 262. (d) Smith, M. In *Reduction*; Augustine, R. L., Ed.; Marcel Dekker: New York, 1968; pp 121–125. (e) Birch, A. J.; Subba Rao, G. In *Advances in Organic Chemistry-Methods and Results*; Taylor, E. C., Ed.; Wiley-Interscience: New York, 1972; Vol. 8, pp 1–66.

(10) 2-Chloroethanol and 2-methoxyethanol afforded intractable reaction mixtures, which were accompanied by the formation of palladium(0). Perhaps these alcohols chelate preferentially at the metal to yield alkoxypalladium complexes after deprotonation, which subsequently decompose with the formation of palladium(0). (See Choudary, B. M.; Reddy, N. P.; Kantam, M. L.; Jamil, Z. *Tetrahedron Lett.* **1985**, *26*, 6257–6258.) Surprisingly, neither phenol nor benzyl alcohol reacted, and in these cases the 1,2-dimethyl-1,4-cyclohexadiene was recovered.

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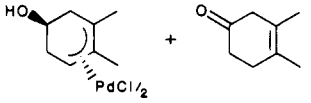
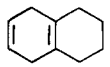
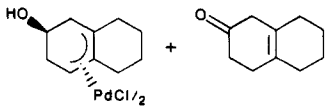
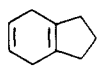
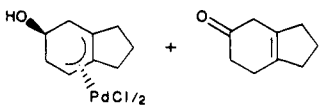
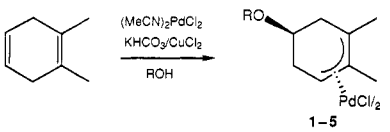
Table I. Palladium(II)-Promoted Addition of Water[a]

1,4-cyclohexadiene	products (% yield)[b]	
		
	6 (77%)	(18%)
		
	7 (67%)	(25%)[c]
		
	8 (57%)	(20%)[d]

[a] Details are in the Experimental Section. [b] Isolated yields after flash chromatography. [c] Tetralin was also isolated (8%). [d] Indan was also isolated (12%).

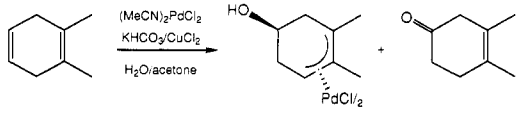
an initial distal addition with the palladium(II) across the double bond.



1-5

^{1}H NMR studies clearly secure the stereochemistry assignments for the *trans*-bis(5-alkoxy-1,2-dimethyl-1-3-η^3-cyclohexenyl)palladium chloride complexes **1–5**, whose spectra were extremely similar. The preferred conformation of *trans*-bis(5-methoxy-1,2-dimethyl-1-3-η^3-cyclohexenyl)palladium complex (**1**) has been previously established to be pseudochair, where the vicinal coupling constants between the C-5 and the C-4 and C-6 protons are $J_{5a,4a} = J_{5a,6a} = 7.6$ Hz.[8] For the *trans*-bis(5-alkoxy-1,2-dimethyl-1-3-η^3-cyclohexenyl)palladium complex series **1–5**, where the alkoxy groups are progressively more bulky, these coupling constants increase from $J_{5a,4a} = J_{5a,6a} = 7.6$ to 9.4 Hz, suggesting that the preferred conformation is also progressing from pseudochair to chair as the bulkier alkoxy groups demand an equitorial position, rather than a pseudoequitorial position.

Addition of Water. 1,2-Dimethyl-1,4-cyclohexadiene and bis(acetonitrile)palladium dichloride in aqueous acetone, in the presence of potassium bicarbonate and cupric chloride, afforded *trans*-bis(5-hydroxy-1,2-dimethyl-1-3-η^3-cyclohexenyl)palladium chloride (**6**, 77%), as well as the Wacker oxidation product 3,4-dimethyl-3-cyclohexen-1-one (18%).[11] Both 1,2,3,4,5,8-hexahydronaphthalene and 4,7-dihydroindan yielded the corresponding *trans*-bis(5-hydroxy-1,2-dialkyl-1-3-η^3-cyclohexenyl)palladium chloride complex **7** (67%) and **8** (57%) with these conditions, as well as 1,2,3,4,5,6,7,8-octahydronaphthalen-2-one (25%) and 2,3,4,5,6,7-hexahydro-1*H*-inden-5-one (20%), respectively (Table I). In addition, the corresponding rearomatized products tetralin (8%) and indan (12%) were also isolated in the latter two reactions.[12]



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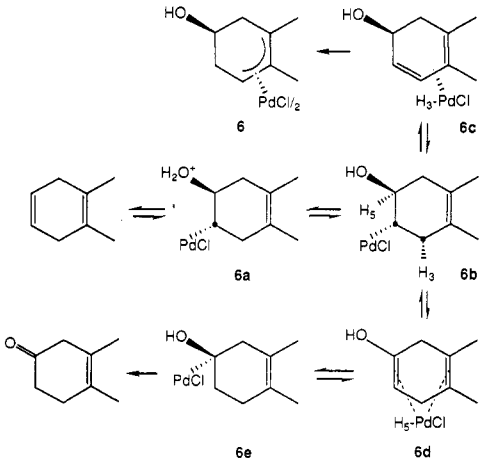
(11) Åkermark, B.; Söderberg, B. C.; Hall, S. S. *Organometallics* **1987**, *6*, 2608–2610.

Scheme I



The effect of excluding either the weak base ($KHCO_3$, 1 equiv) or the oxidant ($CuCl_2$, ca. 20%) was dramatic. Without base 1,2-dimethyl-1,4-cyclohexadiene afforded a meager yield of **6** (6%) by using the same reaction conditions and without oxidant 1,2,3,4,5,8-hexahydronaphthalene produced only tetralin (68%).

Both products from the reaction of 1,2-dimethyl-1,4-cyclohexadiene with bis(acetonitrile)palladium dichloride and water are presumably derived from the same palladium intermediates **6a** and **6b** (Scheme I). Distal addition of water and palladium(II) to the less substituted double bond of the 1,2-dimethyl-1,4-cyclohexadiene, followed by deprotonation by base, affords the σ-cyclohexenylpalladium complex **6b**. β-Elimination of hydride (H_3) from the allylic carbon of **6b** forms the 1,3-cyclohexadienylpalladium complex **6c**, followed by readdition of palladium hydride from the same face,[13] and produces *trans*-bis(5-hydroxy-1,2-dimethyl-1-3-η^3-cyclohexenyl)palladium complex (**6**). Competing β-elimination of hydride (H_5) from the carbinol carbon of **6b** forms the 1,4-cyclohexadienylpalladium complex **6d**, followed by readdition of palladium hydride from the same face, and generates the σ-cyclohexenylpalladium complex **6e**. Finally, β-elimination of hydride from the carbinol oxygen of **6e** yields 3,4-dimethyl-3-cyclohexen-1-one.[14] The derived palladium hydride eliminated in the ketone-forming process can decompose to palladium(0), which no doubt serves as a very active catalyst to rearomatize the 1,4-cyclohexadiene starting material. Cupric chloride probably minimizes this competing side reaction by selectively reoxidizing the palladium(0).[15]

Extensive ^{1}H NMR studies clearly secure the structure and relative stereochemistry of the *trans*-bis(5-hydroxy-1,2-dialkyl-1-3-η^3-cyclohexenyl)palladium chloride complexes **6–8**. All of these complexes appear to prefer a chair

(12) *o*-Xylene was probably formed in this reaction with 1,2-dimethyl-1,4-cyclohexadiene as well but lost during isolation due to its volatility.

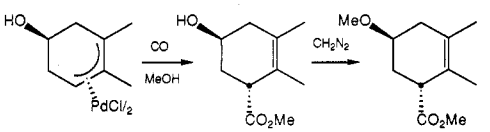
(13) (a) Parra-Hake, M.; Rettig, M. F.; Wing, R. M. *Organometallics* **1983**, *2*, 1013–1017. (b) Albelo, G.; Wiger, G.; Rettig, M. F. *J. Am. Chem. Soc.* **1975**, *97*, 4510–4518. (c) Larock, R. C.; Mitchell, M. A. *Ibid.* **1978**, *100*, 180–188. (d) Larock, R. C.; Takagi, K.; Hershberger, S. S.; Mitchell, M. A. *Tetrahedron Lett.* **1981**, 5231–5234.

(14) In support of this mechanism, when this experiment was performed in D_2O/acetone, no deuterium was incorporated into the products. It has also been suggested by a referee that α-elimination of hydride (H_4) in **6b**, followed by transfer of a β hydride, accomplishes the same chemistry and might explain the observed regioselectivity.

(15) (a) Smidt, J.; Hafner, W.; Jira, R.; Sedlmeier, J.; Sieber, R.; Ruttinger, R.; Kojer, H. *Angew. Chem.* **1959**, *71*, 176–182. (b) Smidt, J.; Hafner, W.; Sieber, R.; Sedlmeier, J.; Sable, A.; Jira, R. *Ibid.* **1962**, *74*, 93–102.

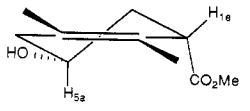
or pseudochair conformation. For example, for *trans*-bis(5-hydroxy-1,2-dimethyl-1-3-η^3-cyclohexenyl)palladium chloride (**6**), the vicinal coupling constants between the C-5 and the C-4 and C-6 protons are $J_{5a,4a}$ = 7.8 Hz, $J_{5a,6a}$ = 8.1 Hz, and $J_{5a,4e} = J_{5a,6e}$ = 5.7 Hz. For complex **7** the corresponding vicinal couplings are $J_{3a,2a}$ = 8.2 Hz, $J_{3a,4a}$ = 8.0 Hz, $J_{3a,2e}$ = 6.4 Hz, and $J_{3a,4e}$ = 5.6 Hz. For complex **8**, although the axial–axial couplings could not be accurately determined, the corresponding axial–equitorial couplings are $J_{6a,5e}$ = 5.6 Hz and $J_{6a,7e}$ = 5.9 Hz. Another diagnostic feature that was noted in the *trans*-bis(5-methoxy-1-3-η^3-cyclohexenyl)palladium complex series is that the geminal coupling values are $J_{4a,4e} = J_{6a,6e}$ = ca. 16 Hz for chair conformers and ca. 18.5 Hz for boat conformers.[1,8] In this series, the geminal coupling constants for complex **6** are $J_{4a,4e}$ = 15.7 Hz and $J_{6a,6e}$ = 15.9 Hz. The corresponding couplings for complex **7** are $J_{2a,2e}$ = 15.2 Hz and $J_{4a,4e}$ = 15.0 Hz and for complex **8** are $J_{5a,5e}$ = 15.7 Hz and $J_{7a,7e}$ = 16.2 Hz, clearly indicating chair conformations.

In addition, the structure and stereochemistry of the *trans*-bis(5-hydroxy-1,2-dimethyl-1-3-η^3-cyclohexenyl)-palladium chloride (**6**) was confirmed by a two-step transformation to methyl *trans*-5-methoxy-2,3-dimethyl-2-cyclohexene-1-carboxylate (**12**). The first step employed methoxycarbonylation using the improved procedure of Milstein[16] to afford **9**, followed by diazomethane treatment for the second.[11]



6 9 (89%) 12 (63%)

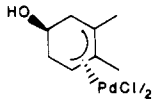
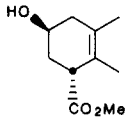
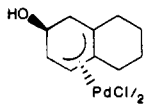
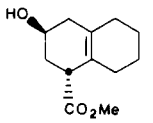
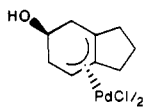
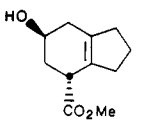
trans-5-Methoxy-2,3-dimethyl-2-cyclohexene-1-carboxylate (**12**) was previously prepared by palladium(II)-promoted addition of methanol to 1,2-dimethyl-1,4-cyclohexadiene, followed by methoxycarbonylation.[1,8] As previously noted by Milstein in acyclic (η^3-allyl)palladium complexes,[16] the methoxycarbonylation reaction is highly regioselective. With the (η^3-cyclohexenyl)palladium complexes insertion occurs exclusively at the less substituted terminus of the η^3-allyl system.[1] Since insertion of carbon monoxide into palladium–carbon bonds proceeds with complete retention of configuration,[17] the methoxycarbonyl group is trans to the C-5 hydroxy group. Since the C-5 hydroxy group prefers the equitorial position ($J_{5a,6a}$ = 9.7 Hz, $J_{5a,4a}$ = 7.4 Hz, $J_{5a,6e}$ = 4.5 Hz, and $J_{5a,4e}$ = 2.7 Hz) and the C-1 methyl carboxylate group prefers the pseudoaxial position ($J_{1e,6a}$ = 6.4 Hz and $J_{1e,6e}$ = 3.3 Hz), the preferred conformation for **9** is shown.



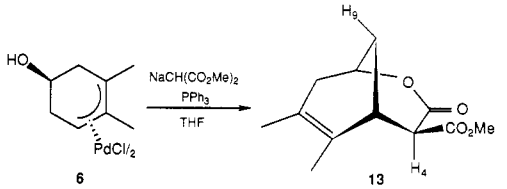
9

The relative stereochemistry of complex **6** was also corroborated by its conversion with dimethyl malonate anion to an intermediate hydroxy malonate derivative, which spontaneously cyclized to lactone **13** (53%) under the conditions of reaction. Dimethyl malonate anion alkylations occur directly at carbon on the face of the η^3-allyl unit distal to the palladium.[18] In addition, the relative stereochemistry of the exo 4-carbomethoxy group of lactone **13** was determined by the long-range coupling between the endo H-4 proton and the anti H-9 proton (J = ca. 1.6 Hz, homonuclear decoupling study).

Table II. Methoxycarbonylation of *trans*-Bis(5-hydroxy-1-3-η^3-cyclohexenyl)palladium Chloride Complexes[a]

palladium complex	product (% yield)[b]
	
6	9 (89%)
	
7	10 (77%)
	
8	11 (91%)

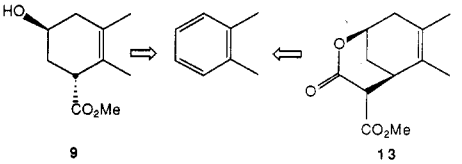
[a] Details are in the Experimental Section. [b] Isolated yields after flash chromatography.



6 13

To demonstrate the general synthetic value of these *trans*-bis(5-hydroxy-1,2-dialkyl-1-3-η^3-cyclohexenyl)palladium complexes and this methodology, the entire derived series **6**–**8** was regioselectively and stereoselectively methoxycarbonylated by the general method of Milstein.[16] Table II compiles the results from this mild and efficient procedure. The isolated yields of the corresponding methyl *trans*-5-hydroxy-2,3-dialkyl-2-cyclohexene-1-carboxylates **9**–**11**, after flash chromatography, were gratifying (77–91%).

It is noteworthy that by starting with 1,2-dialkyl-1,4-cyclohexadienes derived from the corresponding aromatic compounds,[9] one can in three simple manipulations—reduction, alkoxy- or hydroxypalladation, and methoxycarbonylation or alkylation with dimethyl malonate anion—efficiently and selectively elaborate intricate structures of predictable stereochemistry, regiochemistry, and functionality.



9 13

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Experimental Section[19]

All reactions to generate (η^3-cyclohexenyl)palladium complexes were performed under a static N_2 atmosphere in oven-dried, 25-mL or 50-mL, two-neck, round-bottomed flasks equipped with magnetic stir bars. Palladium dichloride was from Engelhard and Johnson Matthey, Inc. Bis(acetonitrile)palladium dichloride was prepared by the general method of Kharasch et al.[20] The preparations of the 1,2-dialkyl-1,4-cyclohexadienes have been described.[1,8] Flash chromatography was performed on silica gel 60 (230–400 mesh, E. Merck).[21] Apparently the (η^3-cyclohexenyl)palladium complexes decompose in the presence of Pd(0), consequently cupric chloride (ca. 20%) was used during their formation to minimize this reaction. It is recommended that the entire reaction sequence to generate the (η^3-cyclohexenyl)palladium complexes and the subsequent flash chromatography be performed without interruption to remove the product complex as quickly as possible from the impurities. Once pure, these (η^3-cyclohexenyl)palladium complexes are relatively stable and are not air-sensitive, but as a precaution they were usually stored neat as oils or as crystals at −18 °C under N_2. The preparation and characterization of complex 1 has been described.[8] Methoxycarbonylations were performed in a 19 × 3 (i.d.) cm Fischer and Porter pressure vessel equipped with a Nalgene star-head magnetic stir bar and executed by the general procedure of Milstein.[16] The *trans*-bis(5-hydroxy-1,2-dialkyl-1–3-η^3-cyclohexenyl)palladium chloride complexes 6–8, which were oils that slowly solidified after flash chromatography, did not give entirely satisfactory elemental analyses (C, H); however, the derived methyl *trans*-5-hydroxy-2,3-dialkyl-2-cyclohexene-1-carboxylates 9–11 did after distillation. See ref 1 for other general experimental comments.

Di-μ-chlorobis[(1,2,3-η)-5-ethoxy-1,2-dimethyl-2-cyclohexen-1-yl]dipalladium (2). To a stirred yellow slurry of 325 mg (1.25 mmol) of bis(acetonitrile)palladium dichloride, 120 mg (1.20 mmol) of $KHCO_3$, and 34 mg (0.20 mmol) of cupric chloride (dihydrate) in 10 mL of absolute EtOH at 20 °C was added (dropwise, 5 min) a solution of 105 mg (0.97 mmol) of 1,2-dimethyl-1,4-cyclohexadiene in 6 mL of EtOH. Within seconds the yellow slurry turned yellow-brown, and after a few minutes a yellow flocculent precipitate began to appear. After 25 h the yellow supernatant with a yellow flocculent precipitate was filtered (Celite pad), and the filter was rinsed with 50 mL of EtOAc. The yellow filtrate was concentrated in vacuo (water aspirator pressure) on a rotary evaporator to afford a yellow-brown oil, which was immediately flash chromatographed (2.5 × 15-cm column packed and eluted with EtOAc–petroleum ether, 1:3). Removal of solvent at reduced pressure (water aspirator) afforded 226 mg (0.39 mmol, 79%) of 2 as a yellow oil, which solidified to yellow crystals in a freezer (−18 °C): mp 75 °C (with decomposition to black particles); IR (film) 2975, 2930, 2890, 2870, 1480, 1455, 1435, 1410, 1370, 1355, 1230, 1150, 1130, 1090, 1060, 1040, 1005, 930, 900, 885, 670 cm^{-1}; ^1H NMR (200 MHz, chair conformation) δ 4.49 (1 H, H-3, t, $J_{3,4a} = J_{3,4e} = 3.5$ Hz), 4.40 (1 H, H-5a, tt, $J_{5a,4a} = J_{5a,6a} = 8.2$ Hz, $J_{5a,4e} = J_{5a,6e} = 5.9$ Hz), 3.45 (2 H, q, $J = 7.0$ Hz), 2.45 (1 H, H-6e, dd, $J_{6e,6a} = 15.6$ Hz, $J_{6e,5a} = 5.8$ Hz), 2.32 (1 H, H-4e, ddd, $J_{4e,4a} = 15.6$ Hz, $J_{4e,5a} = 5.8$ Hz, $J_{4e,3} = 3.9$ Hz), 2.06 (3 H, MeC-2, s), 1.38 (3 H, MeC-1, s), 1.30 (1 H, H-6a, dd, $J_{6a,6e} = 15.8$ Hz, $J_{6a,5a} = 8.1$ Hz), 1.13 (3 H, t, $J = 7.0$ Hz) superimposed on 1.23–1.10 (1 H, H-4a, m); homonuclear decoupling, irradiation at δ 4.49 collapsed the signal at δ 2.32 to a dd and simplified the m at δ 1.23–1.10, irradiation at δ 4.40 collapsed the signals at δ 2.45 and 1.30 to d and at δ 2.32 to a dd and affected the signal at δ 1.23-1.10, irradiation at δ 3.45 collapsed the signal at δ 1.13 to a s, irradiation at δ 2.45 collapsed the signal at δ 4.40 to an apparent td and at δ 1.30 to a d, irradiation at δ 2.32 collapsed the signals at δ 4.49 to a d and at δ 4.40 to a td and affected the signal at δ 1.23–1.10, irradiation at δ 1.30 collapsed the signal at δ 4.40 to a dt and at δ 2.45 to a d, irradiated at ca. δ 1.1 collapsed the signals at δ 4.49 to a d and at δ 2.32 to a dd and simplified the signal at δ 4.40, and collapsed the signal at δ 3.45 to a s; ^{13}C NMR (50 MHz) 112.42 (s), 87.45 (s), 72.06 (2 C, d), 63.32 (t), 41.45 (dd), 34.49 (dd), 21.82 (q), 18.98 (q), 15.50 (q) ppm. Anal. Calcd for $(C_{10}H_{17}OPdCl)_2$: C, 40.70; H, 5.81. Found: C, 40.50; H, 5.80.

Di-μ-chlorobis[(1,2,3-η)-5-(1-methylethoxy)-1,2-dimethyl-2-cyclohexen-1-yl]dipalladium (3). Similar treatment of 105 mg (0.97 mmol) of 1,2-dimethyl-1,4-cyclohexadiene, as described for 2 except that isopropyl alcohol was the solvent, after flash chromatography (EtOAc–petroleum ether, 2:3) afforded 217 mg (0.35 mmol, 73%) of 3 as a yellow oil, which solidified to yellow crystals in a freezer (−18 °C): mp 62–64 °C (with decomposition to black particles); IR (film) 2965, 2930, 2890, 2830, 1455, 1380, 1370, 1345, 1235, 1170, 1145, 1125, 1065, 1040, 1010, 975, 920 cm^{-1}; ^1H NMR (200 MHz, chair conformation) δ 4.49 (1 H, H-3, t, $J_{3,4a} = J_{3,4e} = 3.3$ Hz), 4.44 (1 H, H-5a, tt, $J_{5a,4a} = J_{5a,6a} = 8.0$ Hz, $J_{5a,4e} = J_{5a,6e} = 5.8$ Hz), 3.62 (1 H, septet, $J = 6.1$ Hz), 2.40 (1 H, H-6e, dd, $J_{6e,6a} = 15.6$ Hz, $J_{6e,5a} = 5.7$ Hz), 2.27 (1 H, H-4e, ddd, $J_{4e,4a} = 15.5$ Hz, $J_{4e,5a} = 5.7$ Hz, $J_{4e,3} = 3.6$ Hz), 2.05 (3 H, MeC-2, s), 1.37 (3 H, MeC-1, s), 1.29 (1 H, H-6a, dd, $J_{6a,6e} = 15.1$ Hz, $J_{6a,5a} = 8.9$ Hz) partially superimposed on 1.17 (1 H, H-4a, ddd, $J_{4a,4e} = 15.5$ Hz, $J_{4a,5a} = 7.7$ Hz, $J_{4a,3} = 2.6$ Hz), 1.11 (6 H, d, $J = 6.1$ Hz); homonuclear decoupling, irradiation at δ 4.49 collapsed the signals at δ 2.27 and 1.17 to dd, irradiation at δ 4.44 collapsed the signals at δ 2.40 and 1.29 to d and at δ 2.27 and 1.17 to dd, irradiation at δ 3.62 collapsed the signal at δ 1.11 to a s, irradiation at δ 2.40 collapsed the signals at δ 4.44 to an apparent td and at δ 1.29 to a d, irradiation at δ 2.27 collapsed the signals at δ 4.49 to a d and at δ 4.44 to an apparent td and at δ 1.17 to a dd, irradiation at ca. δ 1.3 affected the signals at δ 4.44 and 2.40, irradiation at δ 1.17 collapsed the signals at δ 4.49 to a d and at δ 2.27 to a dd and simplified the signal at δ 4.44, irradiation at δ 1.11 collapsed the signal at δ 3.62 to a s; ^{13}C NMR (50 MHz) 112.43 (s), 87.53 (s), 72.09 (d), 69.80 (d), 68.72 (d), 42.04 (dd), 35.19 (dd), 22.80 (q), 22.74 (q), 21.86 (q), 18.94 (q) ppm. Anal. Calcd for $(C_{11}H_{19}OPdCl)_2$: C, 42.74; H, 6.20. Found: C, 42.90; H, 6.40.

Di-μ-chlorobis[(1,2,3-η)-5-(2-methylpropoxy)-1,2-dimethyl-2-cyclohexen-1-yl]dipalladium (4). Similar treatment of 104 mg (0.96 mmol) of 1,2-dimethyl-1,4-cyclohexadiene, as described for 2 except that the reaction was performed for 96 h in isobutyl alcohol, after flash chromatography (EtOAc–petroleum ether, 1:3) afforded 205 mg (0.32 mmol, 66%) of 4 as a yellow oil, which solidified to yellow crystals in a freezer (−18 °C): mp 88–92 °C (with decomposition to black particles); IR (film) 2955, 2925, 2900, 2870, 1465, 1435, 1380, 1365, 1230, 1180, 1130, 1090, 1060, 1040, 1005, 925 cm^{-1}; ^1H NMR (200 MHz, chair conformation) δ 4.49 (1 H, H-3, t, $J_{3,4a} = J_{3,4e} = 3.5$ Hz), 4.27 (1 H, H-5a, tt, $J_{5a,4a} = J_{5a,6a} = 7.5$ Hz, $J_{5a,4e} = J_{5a,6e} = 5.6$ Hz), ca. 3.14 (1 H, dd, $J =$ ca. 10 and 6.7 Hz) superimposed on ca. 3.11 (1 H, dd, $J =$ ca. 10 and 6.7 Hz), 2.44 (1 H, H-6e, dd, $J_{6e,6a} = 16.1$ Hz, $J_{6e,5a} = 5.6$ Hz), 2.28 (1 H, H-4e, ddd, $J_{4e,4a} = 15.8$ Hz, $J_{4e,5a} = 5.8$ Hz, $J_{4e,3} = 3.4$ Hz), 2.05 (3 H, MeC-2, s), 1.73 (1 H, 9-line pattern, $J = 6.7$ Hz), 1.38 (3 H, MeC-1, s) superimposed on 1.37 (1 H, H-6a, dd, $J_{6a,6e} = 15.6$ Hz, $J_{6a,5a} = 7.6$ Hz), which is partially superimposed on 1.24 (1 H, H-4a, ddd, $J_{4a,4e} = 16$ Hz, $J_{4a,5a} = 7.9$ Hz, $J_{4a,3} = 3.5$ Hz), 0.85 (6 H, d, $J = 6.7$ Hz); homonuclear decoupling, irradiation at δ 4.49 collapsed the signals at δ 2.28 and 1.24 to dd, irradiation at δ 4.27 collapsed the signals at δ 2.44 and 1.37 to d and at δ 2.28 and 1.24 to dd, irradiation at δ 2.44 affected the signals at δ 4.27 and 1.37, irradiation at δ 2.28 collapsed the signals at δ 4.49 to a d and at δ 1.24 to a dd and simplified the signal at δ 4.27 to an apparent q, irradiation at δ 1.73 collapsed the overlapping signals at δ 3.14 and 3.11 to d and at δ 0.85 to a s, irradiation at ca. δ 1.3 affected the signals at δ 4.49, 4.27, 2.44, and 2.28, irradiation at

(19) Melting points (uncorrected) were determined with a Büchi Model 510 apparatus. The IR spectra were determined with a Perkin-Elmer Model 257 grating infrared spectrophotometer. All NMR spectra were determined in $CDCl_3$, and the chemicals shifts are express in δ values (ppm) relative to a Me_4Si internal standard. The ^1H NMR spectra were determined at 200 MHz with a Bruker Model WP 200 and at 400 MHz with a Bruker Model AM 400 Fourier transform spectrometer. The ^{13}C NMR spectra were determined at 50 and 100 MHz and broad-band proton-decoupled and off-resonance proton-decoupled spectra were collected for all new products. Mass spectra were determined on a Finnigan Model 4000 spectrometer (70 eV) with Finnigan Model 9610 GLC and Data General Model Nova 3 data system attachments. After flash chromatography, the methoxycarbonylation products 9–11 were further purified for elemental analysis by bulb-to-bulb distillation on a Büchi Model GKR-50 Kugelrohr apparatus, and the boiling point temperature cited was the oven temperature. Microanalyses were performed by Mikro Kemi AB, Uppsala, Sweden.

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δ 0.85 collapsed the signal at δ 1.73 to a t; ^{13}C NMR (50 MHz) 113.32 (s), 87.66 (s), 75.44 (t), 72.47 (d), 72.15 (d), 41.80 (dd), 34.78 (dd), 28.82 (d), 22.05 (q), 19.36 (2 C, q), 18.99 (q) ppm. Anal. Calcd for $(C_{12}H_{21}OPdCl)_2$: C, 44.60; H, 6.55. Found: C, 44.30; H, 6.70.

Di-μ-chlorobis[(1,2,3-η)-5-(1,1-dimethylethoxy)-1,2-dimethyl-2-cyclohexen-1-yl]dipalladium (5). Similar treatment of 108 mg (1.00 mmol) of 1,2-dimethyl-1,4-cyclohexadiene, as described for **2** except that the reaction was performed at 40 °C for 72 h in *tert*-butyl alcohol, after flash chromatography (EtOAc–petroleum ether, 1:3) afforded 172 mg (0.27 mmol, 53%) of **5** as a yellow oil, which solidified to yellow crystals on cooling (−78 °C) for several hours: mp 30–35 °C (with decomposition to black particles); IR (film) 2970, 2930, 2900, 2835, 1455, 1435, 1390, 1365, 1230, 1180, 1130, 1060, 1025, 1005, 970, 900, 885 cm^{-1}; ^{1}H NMR (200 MHz, chair conformation) δ 4.79 (1 H, H-5a, tt, $J_{5a,4a} = J_{5a,6a}$ = 9.4 Hz, $J_{5a,4e} = J_{5a,6e}$ = 6.2 Hz), 4.49 (1 H, H-3, dd, $J_{3,4e}$ = 4.2 Hz, $J_{3,4a}$ = 2.6 Hz), 2.29 (1 H, H-6e, dd, $J_{6e,6a}$ = 15.0 Hz, $J_{6e,5a}$ = 6.2 Hz), which was partially superimposed on 2.20 (1 H, H-4e, ddd, $J_{4e,4a}$ = 15.4 Hz, $J_{4e,5a}$ = 6.5 Hz, $J_{4e,3}$ = 4.4 Hz), 2.03 (3 H, MeC-2, s), 1.34 (3 H, MeC-1, s), 1.19 (9 H, s), 1.14 (1 H, H-6a, dd with further fine splitting, $J_{6a,6e}$ = 15.3 Hz, $J_{6a,5a}$ = 9.8 Hz), 0.99 (1 H, H-4a, ddd with further fine splitting, $J_{4a,4e}$ = 15.2 Hz, $J_{4a,5a}$ = 9.5 Hz, $J_{4a,3}$ = 2.4 Hz); homonuclear decoupling, irradiation at δ 4.79 collapsed the signals at δ 2.29 and 1.14 to d and at δ 2.20 to a dd and at δ 0.99 to a br d, irradiation at δ 4.49 collapsed the signals at δ 2.20 and 0.99 to dd, irradiation at ca. δ 2.3 collapsed the signals at δ 4.79 to a br t and at δ 1.14 to a d and affected the signals at δ 4.49 and 0.99, irradiation at ca. δ 2.2 collapsed the signals at δ 4.79 to a br t and at δ 4.49 to a d and affected the signal at δ 0.99, irradiation at ca. δ 1.1 affected the signals at δ 4.79 and 2.29, irradiation at ca. δ 1.0 affected the signal at δ 4.79 and collapsed the signals at δ 4.49 to a d and at δ 2.20 to a dd; ^{13}C NMR (50 MHz) 111.80 (s), 89.31 (s), 73.59 (d), 73.24 (s), 66.04 (d), 43.84 (dd), 36.95 (dd), 28.27 (3 C, q), 21.73 (q), 19.02 (q) ppm. Anal. Calcd for $(C_{12}H_{21}OPdCl)_2$: C, 44.60; H, 6.55. Found: C, 44.30; H, 6.60.

Di-μ-chlorobis[(1,2,3-η)-5-hydroxy-1,2-dimethyl-2-cyclohexen-1-yl]dipalladium (6) and 3,4-Dimethyl-3-cyclohexen-1-one.[11] To a yellow slurry of 1.30 g (5.00 mmol) of bis(acetonitrile)palladium dichloride, 480 mg (4.80 mmol) of $KHCO_3$, and 136 mg (0.80 mmol) of cupric chloride (dihydrate) in 30 mL of acetone at 20 °C was added a solution of 432 mg (4.00 mmol) of 1,2-dimethyl-1,4-cyclohexadiene in 3.6 mL (200 mmol) of water and 10 mL of acetone. Within seconds an orange-black solution formed, and after a few minutes a yellow flocculent precipitate began to appear. After 24 h the yellow supernatant with a yellow-black flocculent precipitate was filtered (Celite pad), and the filter was rinsed with 150 mL of EtOAc. The yellow filtrate—a green-black precipitate remained on the filter—was concentrated in vacuo (water aspirator pressure) on a rotary evaporator to afford 1.05 g of a yellow oil–solid, which was immediately dissolved in 3–4 mL of EtOAc–EtOH (95:5) and flash chromatographed (3.5 × 23-cm column packed and eluted with EtOAc–EtOH, 95:5). Removal of solvent at reduced pressure (water aspirator) afforded 90 mg (0.72 mmol, 18%) of the cyclohexenone as a pale yellow oil, followed by 817 mg (1.53 mmol, 77%) of **6** as a yellow oil, which slowly formed yellow crystals. 3,4-Dimethyl-3-cyclohexen-1-one:[22] ^{1}NMR (200 MHz) δ 2.78 (2 H, br s, $W_{1/2}$ = 7 Hz), 2.53–2.31 (4 H, m), 1.72 (3 H, t, J = 0.8 Hz), 1.66 (3 H, apparent d, J = 0.8 Hz); mass spectrum, m/z (relative intensity) 124 (M$^+$, 57), 82 (72), 81 (24), 67 (100), 54 (12), 41 (21), 39 (27). (η^3-Cyclohexenyl)palladium complex **6**:[11] mp 67–70 °C (with decomposition to black particles); IR (KBr) 3390 (br), 2970, 2890, 2820, 1430, 1125, 1040, 995, 925, 780, 730 cm^{-1}; ^{1}H NMR (200 MHz, chair conformation) δ 4.78 (1 H, H-5a, apparent quintet, J = ca. 7 Hz), 4.52 (1 H, H-3, t, $J_{3,4a} = J_{3,4e}$ = 3.3 Hz), 3.24 (1 H, OH, br s, $W_{1/2}$ = 8.4 Hz, exchangeable with D_2O), 2.43 (1 H, H-6e, dd, $J_{6e,6a}$ = 15.9 Hz, $J_{6e,5a}$ = 5.7 Hz), 2.29 (1 H, H-4e, ddd, $J_{4e,4a}$ = 15.7 Hz, $J_{4e,5a}$ = 5.7 Hz, $J_{4e,3}$ = 3.7 Hz), 2.07 (3 H, MeC-2, s), 1.39 (3 H, MeC-1, s) superimposed on 1.34 (1 H, H-6a, dd, $J_{6a,6e}$ = 15.7 Hz, $J_{6a,5a}$ = 8.1 Hz) and 1.24 (1 H, H-4a, ddd, $J_{4a,4e}$ = 15.1 Hz, $J_{4a,5a}$ = 7.8 Hz, $J_{4a,3}$ = 3.0 Hz); homonuclear decoupling, irradiation at δ 4.78 collapsed the signals at δ 2.43 and 1.34 to d and at δ 2.29 and 1.24 to dd, irradiation at δ 4.52 collapsed the signals at δ 2.29 and 1.24 to dd, irradiation at ca. δ 2.4 affected the signals at δ 4.78 and 1.34, irradiation at ca. δ 2.3 affected the signals at δ 4.78 and 1.24 and collapsed the signal at δ 4.52 to a d, irradiation at δ 1.30 affected the signals at δ 4.78, 2.43, and 2.29 and collapsed the signal at δ 4.52 to a d; ^{13}C NMR (50 MHz) 113.19 (s), 87.91 (s), 72.26 (d), 65.21 (d), 44.33 (dd), 37.39 (dd), 22.04 (q), 19.08 (q) ppm. Anal. Calcd for $(C_8H_{13}OPdCl)_2$: C, 35.98; H, 4.91. Found: C, 37.00; H, 5.10.

Di-μ-chlorobis[(1,4a,8a-η)-1,2,3,4,5,6,7,8-octahydro-3-hydroxy-1-naphthalenyl]dipalladium (7) and 1,2,3,4,5,6,7,8-Octahydronaphthalen-2-one. Similar treatment of 530 mg (4.00 mmol) of 1,2,3,4,5,8-hexahydronaphthalene, as described for **6**, after flash chromatography (EtOAc–EtOH, 95:5) afforded a pale yellow oil, which was a mixture of 38 mg (0.29 mmol, 8%) of tetralin and 134 mg (0.89 mmol, 25%) of 1,2,3,4,5,6,7,8-octahydronaphthalen-2-one, followed by 707 mg (1.21 mmol, 67%) of **7** as a yellow oil, which slowly formed yellow crystals. 1,2,3,4,5,6,7,8-Octahydronaphthalen-2-one:[23] ^{1}H NMR (200 MHz, from the mixture) δ 2.73 (2 H, br s, $W_{1/2}$ = 7 Hz), 2.54–2.25 (4 H, complex m), 2.03–1.72 (4 H, complex m), 1.68–1.52 (4 H, complex m); mass spectrum, m/z (relative intensity) 150 (M$^+$, 66), 109 (8), 108 (100), 107 (10), 94 (13), 93 (80), 91 (28), 80 (21), 79 (59), 77 (24), 67 (11), 65 (10), 53 (10), 41 (18). (η^3-Naphthalenyl)palladium complex **7**: mp 82–85 °C (with decomposition to black particles); IR (film) 3420 (br), 2990, 2930, 2850, 2830, 1430, 1410, 1075, 1035, 920, 790, 750 cm^{-1}; ^{1}H NMR (200 MHz, chair conformation) δ 4.92 (1 H, H-3a, apparent quintet, J = ca. 6 Hz), 4.43 (1 H, H-1, t, $J_{1,2a} = J_{1,2e}$ = 3.2 Hz), 3.39 (1 H, OH, br s, $W_{1/2}$ = 28 Hz, exchangeable with D_2O), 2.51 (2 H, H-5e and H-8e, m) partially superimposed on 2.45 (1 H, H-4e, dd, $J_{4e,4a}$ = 15.0 Hz, $J_{4e,3a}$ = 5.6 Hz), 2.31 (1 H, H-2e, ddd, $J_{2e,2a}$ = 15.2 Hz, $J_{2e,3a}$ = 6.4 Hz, $J_{2e,1}$ = 3.7 Hz), 2.05–1.43 (5 H, H-6, H-7, and H-8a, m), 1.34 (1 H, H-4a, dd, $J_{4a,4e}$ = 15.8 Hz, $J_{4a,3a}$ = 8.0 Hz) superimposed on 1.43–1.22 (1 H, H-5a, m), 1.13 (1 H, H-2a, ddd, $J_{2a,2e}$ = 15.2 Hz, $J_{2a,3a}$ = 8.2 Hz, $J_{2a,1}$ = ca. 2 Hz); homonuclear decoupling, irradiation at δ 4.92 collapsed the signals at δ 2.31 and 1.13 to dd and at δ 2.45 and 1.34 to d, irradiation at δ 4.43 collapsed the signals at δ 2.31 and 1.31 to dd, irradiation at ca. δ 2.5 collapsed the signal at δ 1.34 to a d and affected the signals at δ 4.92 and 4.43, irradiation at ca. δ 2.3 collapsed the signal at δ 4.43 to a d and at δ 1.13 to a dd, irradiation at ca. δ 1.3 collapsed the signal at δ 2.45 to a d and affected the signal at δ 4.92, irradiation at δ 1.13 collapsed the signals at δ 4.43 to a d and at δ 2.31 to a dd and affected the signal at δ 4.92; ^{13}C NMR (50 MHz) 114.12 (s), 93.76 (s), 68.76 (d), 65.76 (d), 43.37 (dd), 36.99 (dd), 32.64 (dd), 28.82 (t), 22.07 (t), 21.80 (t) ppm. Anal. Calcd for $(C_{10}H_{15}OPdCl)_2$: C, 40.98; H, 5.16. Found: C, 41.90; H, 5.40.

Di-μ-chlorobis[(3a,4,7a-η)-2,3,4,5,6,7-hexahydro-6-hydroxy-1*H*-inden-4-yl]dipalladium (8) and 2,3,4,5,6,7-Hexahydro-1*H*-inden-5-one. Similar treatment of 480 mg (4.00 mmol) of 4,7-dihydroindan, as described for **6**, after flash chromatography (EtOAc–EtOH, 95:5) afforded a pale yellow oil, which was a mixture of 57 mg (0.48 mmol, 12%) of indan and 107 mg (0.79 mmol, 20%) of 2,3,4,5,6,7-hexahydro-1*H*-inden-5-one, followed by 636 mg (1.14 mmol, 57%) of **8** as a yellow oil, which slowly formed yellow crystals. 2,3,4,5,6,7-Hexahydro-1*H*-inden-5-one:[24] ^{1}H NMR (200 MHz, from the mixture) δ 2.90 (2 H, H-6, t, $J_{6,7}$ = 7.4 Hz), 2.64 (2 H, H-4, s), 2.26 (4 H, H-1 and H-3, t, $J_{1,2} = J_{3,2}$ = 7.2 Hz), 2.05 (2 H, H-7, t, $J_{7,6}$ = 7.3 Hz), 1.83 (2 H, H-2, apparent quintet, J = ca. 7 Hz); homonuclear decoupling, irradiation at δ 2.90 collapsed the signal at δ 2.05 to a s, irradiation at δ 2.26 collapsed the signal at δ 1.83 to a s, irradiation at δ 2.05 collapsed the signal at δ 2.90 to a s, irradiation at δ 1.83 collapsed the signal at δ 2.26 to a s; mass spectrum, m/z (relative intensity) 136 (M$^+$, 45), 94 (94), 93 (23), 91 (20), 79 (100), 77 (30), 53 (10), 51 (14), 41 (12), 40 (11). (η^3-Indenyl)palladium complex **8**: mp 44–57 °C (with subsequent decomposition to black particles at

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84–85 °C); IR (film) 3420 (br), 3000, 2950, 2900, 2870, 2840, 1455, 1425, 1360, 1295, 1220, 1190, 1150, 1090, 1055, 1030, 910, 760 cm^{-1}; ^1H NMR (200 MHz, chair conformation) δ 4.92 (1 H, H-6a, apparent quintet, J = ca. 6 Hz), 4.72 (1 H, H-4, t, $J_{4,5a} = J_{4,5e}$ = 3.3 Hz), 2.57 (1 H, H-7e, dd, $J_{7e,7a}$ = 16.2 Hz, $J_{7e,6a}$ = 5.9 Hz), 2.52–2.40 (2 H, H-1e and H-3e, m), 2.34 (1 H, H-5e, ddd, $J_{5e,5a}$ = 15.7 Hz, $J_{5e,6a}$ = 5.6 Hz, $J_{5e,4}$ = 3.7 Hz), 2.13–1.86 (3 H, H-2 and H-3a, complex overlapping m), 1.69 (1 H, OH, br s, $W_{1/2}$ = 10 Hz, exchangeable with D_2O), 1.38–1.13 (3 H, H-1a, H-5a, and H-7a, complex overlapping m); homonuclear decoupling, irradiation at δ 4.92 collapsed the signals at δ 2.57 to a d and at δ 2.34 to a dd and simplified the signal at δ 1.38–1.13, irradiation at δ 4.72 collapsed the signal at δ 2.34 to a dd and affected the signal at δ 1.38–1.13, irradiation at δ 2.57 collapsed the signal at δ 4.92 to an apparent q and affected the signal at δ 1.38–1.13, irradiation at δ 2.34 collapsed the signal at δ 4.92 to an apparent q and affected the signal at δ 1.38–1.13, irradiation at ca. δ 1.3 collapsed the signals at δ 4.92 to an apparent t and at δ 4.72 to a d and affected the signals at δ 2.57 and 2.34; ^{13}C NMR (50 MHz) 121.56 (s), 97.94 (s), 66.00 (d), 65.33 (d), 39.73 (dd), 37.21 (t), 36.54 (t), 32.64 (t), 23.74 (t) ppm. Anal. Calcd for $(C_9H_{13}OPdCl)_2$: C, 38.74; H, 6.23. Found: C, 39.70; H, 4.90.

Methyl *trans*-5-Hydroxy-2,3-dimethyl-2-cyclohexene-1-carboxylate (9). Upon pressurizing a sealed 90-mL Fischer and Porter pressure tube containing a stirred yellow solution of 534 mg (1.00 mmol) of (η^3-cyclohexenyl)palladium complex **6** and 960 mg (10.0 mmol) of sodium propionate in 35 mL of MeOH to 3.8 atm with carbon monoxide, the mixture immediately turned black as a flocculent black precipitate formed.[16] After 4.5 h the black slurry was filtered (Celite pad), and the filter was rinsed with 100 mL of EtOAc to reveal a colorless filtrate, which clouded as the EtOAc was introduced. Removal of the solvent at reduced pressure (water aspirator) on a rotary evaporator yielded a white-gray crystalline residue, which was triturated with 20 mL of pentane, the slurry was refiltered (Celite pad), and the filter was rinsed with 50 mL of pentane. Removal of the pentane from the filtrate at reduced pressure afforded 371 mg of a colorless oil, which after flash chromatography (2.5 × 14-cm column packed and eluted with EtOAc–petroleum ether, 2:3) afforded 320 mg (1.78 mmol, 89%) of **9** as a colorless oil: bp 100 °C (0.05 Torr); IR (film) 3390 (br), 2990, 2950, 2920, 2860, 2840, 1735, 1720, 1440, 1165, 1150, 1135, 1070, 1055, 1040 cm^{-1}; ^1H NMR (200 MHz) δ 4.11 (1 H, H-5a, dddd, $J_{5a,6a}$ = 9.7 Hz, $J_{5a,4a}$ = 7.4 Hz, $J_{5a,6e}$ = 4.5 Hz, $J_{5a,4e}$ = 2.7 Hz), 3.86 (1 H, OH, br s, $W_{1/2}$ = 42 Hz, exchangeable with D_2O), 3.69 (3 H, s), 3.17 (1 H, H-1e, m, $W_{1/2}$ = 12 Hz), 2.34 (1 H, H-4e, dd with further fine splitting, $J_{4e,4a}$ = ca. 17 Hz, $J_{4e,5a}$ = ca. 4 Hz), 2.07 (1 H, H-6e, dddd, $J_{6e,6a}$ = 12.8 Hz, $J_{6e,5a}$ = 4.6 Hz, $J_{6e,1e}$ = 3.3 Hz, $J_{6e,4e}$ = 1.3 Hz) partially superimposed on 1.96 (1 H, H-4a, dd with further fine splitting, $J_{4a,4e}$ = ca. 17 Hz, $J_{4a,5a}$ = ca. 8 Hz), 1.78 (1 H, H-6a, ddd, $J_{6a,6e}$ = 12.7 Hz, $J_{6a,5a}$ = 9.8 Hz, $J_{6a,1e}$ = 6.4 Hz), and two overlapping Me multiplets with signals at δ 1.67, 1.67, 1.66, 1.66, 1.65, 1.64, 1.64, 1.64 (6 H, MeC-2 and MeC-3); homonuclear decoupling, irradiation at δ 4.11 collapsed the signals at δ 2.34 and 1.96 to d and at δ 2.07 to a ddd and at δ 1.78 to a dd, irradiation at δ 3.17 collapsed the signals at δ 2.07 to a ddd and at δ 1.78 to a dd, irradiation at δ 2.34 collapsed the signals at δ 4.11 to a ddd and at δ 1.96 to a d, irradiation at ca. δ 2.0 collapsed the signals at δ 4.11 and 1.78 to apparent dd and at δ 3.17 to a d, irradiation at ca. δ 1.9 affected the signal at δ 4.11 and collapsed the signal at δ 2.34 to a br s, irradiation at δ 1.78 collapsed the signals at δ 4.11 to an apparent ddd and at δ 3.17 to a d and affected the signal at δ 2.07, irradiation at δ 1.65 sharpened the signals at δ 3.17 to an apparent t and at δ 2.34 and 1.96 to dd; ^{13}C NMR (50 MHz) 175.43 (s), 127.49 (s), 122.20 (s), 64.73 (d), 51.76 (q), 46.56 (d), 40.56 (t), 34.72 (t), 19.56 (q), 17.55 (q) ppm; mass spectrum, m/z (relative intensity) 184 (M^+, 8), 152 (16), 125 (20), 109 (14), 107 (100), 106 (13), 91 (21), 79 (19), 55 (28), 43 (22), 41 (20), 39 (12). Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 64.80; H, 8.90.

Methyl *trans*-1,2,3,4,5,6,7,8-Octahydro-3-hydroxy-1-naphthalenecarboxylate (10). Similar treatment of 538 mg (0.92 mmol) of (η^3-cyclohexenyl)palladium complex **7**, as described for **9** except the reaction was performed for only 1.5 h, afforded 390 mg of a colorless oil, which was flash chromatographed (EtOAc–petroleum ether, 2:3) to yield 297 mg (1.41 mmol, 77%) of **10** as a colorless oil: bp 150 °C (0.08 Torr); IR (film) 3390 (br), 2930, 2890, 2860, 2835, 1735, 1720, 1440, 1180, 1160, 1130, 1085, 1050 cm^{-1}; ^1H NMR (200 MHz) δ 4.14 (1 H, H-3a, 12-line m, $J_{3a,2a}$ = 9.5 Hz, $J_{3a,4a}$ = 7.5 Hz, $J_{3a,2e}$ = 5.4 Hz, $J_{3a,4e}$ = 3.5 Hz), 3.68 (3 H, s), 3.11 (1 H, H-1e, m, $W_{1/2}$ = 13 Hz), 2.57 (1 H, OH, br s, $W_{1/2}$ = 9 Hz, exchangeable with D_2O), 2.28 (1 H, H-4e, dd with further fine splitting, $J_{4e,4a}$ = 16.6 Hz, $J_{4e,3a}$ = 3.9 Hz), 2.07 (1 H, H-2e, dddd, $J_{2e,2a}$ = 12.8 Hz, $J_{2e,3a}$ = 4.7 Hz, $J_{2e,1e}$ = 3.4 Hz, $J_{2e,4e}$ = 1.3 Hz), 1.94 (4 H, H-5 and H-8, m, $W_{1/2}$ = 14 Hz) superimposed on 1.90–1.82 (1 H, H-4a, m), 1.79 (1 H, H-2a, ddd, $J_{2a,2e}$ = 12.8 Hz, $J_{2a,3a}$ = 9.5 Hz, $J_{2a,1e}$ = 6.4 Hz), 1.60 (4 H, H-6 and H-7, m, $W_{1/2}$ = 12 Hz); homonuclear decoupling, irradiation at δ 4.14 collapsed the signals at δ 2.28 and 1.90–1.82 to d and at δ 2.07 and 1.79 to a dd, irradiation at δ 3.11 collapsed the signals at δ 2.07 to a ddd and at δ 1.79 to a dd, irradiation at δ 2.28 affected the signals at δ 4.14 and 3.11 and 2.07 and 1.90–1.82, irradiation at δ 2.07 collapsed the signals at δ 4.14 to an apparent q and at δ 3.11 to a d and at δ 1.79 to a dd, irradiation at ca. δ 1.8 collapsed the signals at δ 4.14 to an apparent quintet and at δ 2.07 to an apparent dd; ^{13}C NMR (50 MHz) 175.42 (s), 129.40 (s), 124.68 (s), 64.72 (d), 51.73 (q), 45.57 (d), 39.38 (t), 34.59 (t), 30.73 (t), 28.60 (t), 23.07 (t), 22.63 (t) ppm; mass spectrum, m/z (relative intensity) 210 (M^+, 17), 192 (11), 178 (36), 160 (22), 151 (20), 150 (16), 133 (93), 132 (10), 107 (16), 105 (29), 91 (100), 79 (33), 77 (19), 67 (22), 55 (19), 41 (26), 39 (16). Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63. Found: C, 68.20; H, 8.80.

Methyl *trans*-2,3,4,5,6,7-Hexahydro-6-hydroxy-1*H*-indene-4-carboxylate (11). Similar treatment of 584 mg (1.05 mmol) of (η^3-cyclohexenyl)palladium complex **8**, as described for **9** except the reaction was performed at 3.5 atm of carbon monoxide pressure for 25 h, after flash chromatography (EtOAc–petroleum ether, 2:3) afforded 373 mg (1.90 mmol, 91%) of **11** as a colorless oil: bp 150 °C (0.08 Torr); IR (film) 3280 (br), 2950, 2920, 2840, 1730, 1435, 1180, 1095, 1050, 1025, 960, 935, 915, 840, 730 cm^{-1}; ^1H NMR (200 MHz) δ 4.32–4.18 (1 H, H-6a, m), 3.70 (3 H, s), 3.32–3.19 (1 H, H-4e, m, $W_{1/2}$ = 16 Hz), 2.47–2.17 (5 H, H-1, H-3, and H-7e, overlapping m), 2.11 (1 H, H-5e, dddd, $J_{5e,5a}$ = 13.0 Hz, $J_{5e,4e}$ = 5.5 Hz, $J_{5e,6a}$ = 3.1 Hz, $J_{5e,7e}$ = 0.8 Hz), 2.04–1.77 (5 H, H-2, H-5a, H-7a, and OH, overlapping m); homonuclear decoupling, irradiation at δ 4.25 collapsed the signal at δ 2.11 to a dd and simplified the signals at δ 2.47–2.17 and 2.04–1.77, irradiation at δ 3.25 collapsed the signal at δ 2.11 to a dd and simplified the signals at δ 2.04–1.77, irradiation at δ 2.35 collapsed the signal at δ 4.32–4.18 to an apparent td and affected the signals at δ 2.04–1.77, irradiation at δ 2.11 simplified the signals at δ 4.32–4.18 and 3.32–3.19 and affected the signals at δ 2.04–1.77; ^{13}C NMR (50 MHz) 174.49 (s), 135.78 (s), 130.36 (s), 65.67 (d), 51.63 (q), 40.88 (d), 36.06 (t), 34.91 (t), 34.37 (t), 34.27 (t), 22.14 (t) ppm; mass spectrum, m/z (relative intensity) 196 (M^+, 19), 178 (15), 177 (13), 164 (27), 146 (11), 137 (20), 119 (100), 118 (15), 93 (30), 91 (62), 79 (21), 77 (19), 67 (12), 55 (12), 41 (23), 39 (17). Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.50; H, 8.30.

Methyl *trans*-5-Methoxy-2,3-dimethyl-2-cyclohexene-1-carboxylate (12). After adding 20 mL of a yellow solution of diazomethane (10 mmol, 0.5 M, Et_2O)[25] to a stirred solution of 253 mg (1.38 mmol) of methyl *trans*-5-hydroxy-2,3-dimethyl-2-cyclohexene-1-carboxylate (**9**) and ca. 0.5 mL of tetrafluoroboric acid etherate (HFB_4·Et_2O, 50–52% in Et_2O, Alfa Products) in 20 mL of methylene chloride at 20 °C, the resulting solution immediately turned colorless and evolved gas.[26] After the evolution of gas ceased (ca. 30 min), the solution was partitioned with 50 mL of water, and the organic phase was dried ($MgSO_4$), filtered, and concentrated in vacuo (water aspirator pressure) on a rotary evaporator to afford a pale brown oil. Flash chromatography (2.5 × 15-cm column packed with EtOAc–petroleum ether, 1:9) by first eluting with a 250-mL portion of the same solvent mixture, followed by a 250-mL portion of EtOAc–petroleum ether (2:3) afforded 144 mg (0.73 mmol, 63%) of **12**,[1,11] followed by the recovery of 40 mg (0.22 mmol) of **9**.

4-*exo*-Carbomethoxy-6,7-dimethyl-2-oxabicyclo[3.3.1]-

(25) The diazomethane was prepared by the procedure of de Boer, T. J.; Backer, H. J. *Organic Syntheses*; Wiley: New York, 1963; Vol. IV, pp 250–253.

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non-6-en-3-one (13). To a stirred, yellow solution of 534 mg (1.00 mmol) of (η^3-cyclohexenyl)palladium complex **6** and 2.10 g (8.01 mmol) of triphenylphosphine in 40 mL of anhydrous THF (freshly distilled from sodium-benzophenone ketyl radical) under a N_2 atmosphere was added a solution containing 4.0 mmol of sodium dimethyl malonate in 30 mL of anhydrous THF.[18] After 40 h at 21 °C, the resulting yellow-green slurry was diluted with 200 mL of water and extracted twice with 200-mL portions of Et_2O. The combined organic phase was washed with 200 mL of water and dried ($MgSO_4$), and the solvent was removed at reduced pressure (water aspirator) on a rotary evaporator to afford a red-black oil, which was flash chromatographed (2.5 × 15-cm column packed and eluted with EtOAc-hexane, 3:7). Removal of solvent at reduced pressure (water aspirator) afforded 236 mg (1.05 mmol, 53%) of **13** as a pale yellow oil: IR (film) 2950, 2910, 2860, 1730, 1440, 1385, 1235, 1220, 1065, 1020, 960 cm^{-1}; ^{1}NMR (400 MHz) δ 4.92 (1 H, H-1, 10-line m, J = ca. 1.5 Hz), 3.78 (3 H, s), 3.51 (1 H, H-4_{endo}, t, J = ca. 1.6 Hz), 2.64-2.60 (1 H, H-5, m), 2.36-2.34 (1 H, H-8_{endo}, m with fine splitting, J = 0.9 Hz), 2.28 [1 H, H-9_{syn} (lactone), ddd with further fine splitting, J = 13.6, 4.7, 2.3 Hz], 1.81 [1 H, H-9_{anti} (lactone), ddt, J = 13.6, 4.1, 1.4 Hz], 1.74-1.72 (1 H, H-8_{exo}, m with fine splitting, J = 0.9 Hz), 1.62 (3 H, br s with fine splitting, J = 0.9 Hz), 1.54 (3 H, s); homonuclear decoupling, irradiation at δ 4.92 affected the signal at δ 2.36-2.34 and collapsed the signals at δ 2.28 to a dd and at δ 1.81 to a ddd, irradiation at δ 3.51 affected the signal at δ 2.64-2.60 and collapsed the signal at δ 1.81 to a ddd, irradiation at δ 2.62 collapsed the signals at δ 3.51 to a d and at δ 2.28 to a dd and at δ 1.81 to a dt, irradiation at δ 2.35 simplified the signal at δ 4.92 and sharpened the signal at δ 1.74-1.72, irradiation at δ 2.28 simplified the signal at δ 4.92 and sharpened the signal at δ 2.64-2.60 and collapsed the signal at δ 1.81 to a dt, irradiation at δ 1.81 affected the signals at δ 4.92 and 2.64-2.60 and collapsed the signals at δ 3.51 to a d and at δ 2.28 to a dd, irradiation at δ 1.73 sharpened the signal at δ 2.36-2.34 to a d with further fine splitting and affected the signal at δ 1.62, irradiation at δ 1.62 affected the signal at δ 2.36-2.34 and collapsed the signal at δ 1.74-1.72 to a t; ^{13}C NMR (100 MHz) 168.90 (s), 165.95 (s), 126.53 (s), 124.15 (s), 75.24 (d), 52.50 (q), 50.75 (d), 38.26 (t), 35.73 (d), 24.48 (t), 18.02 (q), 17.13 (q); mass spectrum, m/z (relative intensity) 224 (M^+, 9), 180 (6), 165 (6), 149 (7), 121 (14), 119 (16), 118 (15), 108 (9), 107 (99), 106 (100), 105 (21), 95 (22), 93 (17), 91 (54), 79 (20), 77 (18), 67 (15), 55 (15), 53 (13), 43 (11), 41 (29), 39 (21). Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.28; H, 7.19. Found: C, 64.20; H, 7.10.

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Solid-Supported Sodium Azide Reagents: Their Preparation and Reactions with Epoxides

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Sodium azide is supported on three types of porous solid acids (zeolite, alumina, and silica gel) and applied to several reactions with epoxides. A systematic investigation reveals that the reactivities of the supported reagents are greatly influenced by loading amounts of NaN_3, amounts of adsorbed water in the reagents, acidic properties of the solid acids, and reaction solvents. For demonstrating the utility of supported NaN_3 reagents in selective organic syntheses, nucleophilic ring-opening reactions of 2,3-epoxy alcohols with the supported reagents are examined. Among the supported reagents, only the Ca^{2+}-exchanged zeolite-supported reagent induces a C-3 ring opening in a highly regioselective manner (>90%). It is deduced that the role of calcium ions in the zeolite is to increase the acid strength of the zeolite facilitating the ring cleavage of epoxides and to fix the conformation of epoxy alcohols through forming chelate complexes with calcium ions.

The elaborate design of supported reagents for liquid-phase organic reactions is now an intriguing area of current research in organic synthesis since the impregnation of inorganic reagents, which are insoluble in organic solvents, on porous solid supports is as efficient to activate the reagents as the use of phase-transfer catalysts such as onium salts and crown compounds.[1] Effectiveness of these supported reagents is ascribed to a combination of several factors. (1) An increase in the effective surface area of the reagent owing to high dispersion on the support. (2) An activation of the reagent by the interaction between the support surface and the reagent. (3) A decrease in activation entropy of reactions due to preadsorption of substrates in close proximity. (4) Synergistic effect of acid and base sites of the support on substrates.

The present paper describes the characteristics of a supported sodium azide reagent in regioselective ring-opening reactions of unsymmetrical epoxides.[2]

Azides are important precursors of nitrenes or amino compounds and also belong to a large family of 1,3-dipoles, which undergo cycloaddition to alkenes.[3] Nucleophilic

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