in a nitrogen atmosphere. BF_3·OEt_2 was distilled over CaH_2[21] and stored in a nitrogen atmosphere.

Acetals and Orthoesters 1a–t. Compounds **1a,b,f,g,n,r,s,t** are commercially available. The acetals **1c–e** were prepared from the corresponding aldehydes and methanol in presence of $CaCl_2$,[22] and compounds **1g–m** and **1o–q** were obtained by treating the corresponding aldehydes with methyl orthoformate in the presence of catalytic amounts of NH_4NO_3.[23]

BF_3·OEt_2-Catalyzed Reactions of 1a–t with Methyl Vinyl Ether 2′. Method A. BF_3·OEt_2 (0.75 mL, 6.0 mmol) was added to a solution of **1** (30.0 mmol) in 30 mL of CH_2Cl_2 at −78 °C. A solution of **2′** (1.74 g, 30.0 mmol) in 20 mL of CH_2Cl_2 was added within 30 min. After the mixture was stirred at −78 °C for some time (see Table I), 20 mL of concentrated aqueous ammonia were added, and the aqueous layer was extracted with two 20-mL portions of ether. The combined organic layers were dried with $CaCl_2$ and distilled.

Method B. A solution of **1** (30.0 mmol) and **2′** (1.74 g, 30.0 mmol) in 40 mL of CH_2Cl_2 was added dropwise within 1 h to a precooled (−78 °C) solution of BF_2·OEt_2 in 10 mL of CH_2Cl_2. The mixture was worked up as in method A. Results are given in Table I and physical and spectral data of the adducts **3** and **4** in Table II and 1S–3S.

Competition Experiments. Two of the compounds **1b–r** or **3b** were placed into a 100-mL flask in a nitrogen atmosphere. In order to obtain mixtures suited for GC analysis, the more reactive compound (≈0.4 mmol) was combined with an excess of the less reactive compound so that the ratio of adducts was between 1 and 10. After the addition of 0.05 mmol of the standard (5 mL of a 0.01 M solution of ethylbenzene or hexamethylbenzene in CH_2Cl_2), 45 mL of CH_2Cl_2 was added, and the mixture was cooled at −78 °C. With a gas-tight Hamilton syringe, ~4.5 mL (0.20 mmol) of **2′** was added and the reaction was initiated by adding BF_3·OEt_2 (0.2 equiv based on the total amount of acetals). After 1 h the reaction was terminated by adding concentrated aqueous ammonia. The organic layer was dried with $CaCl_2$, and the bulk of solvent was carefully evaporated in vacuo to give a residue, which was analyzed by GC (20% GE-SE-30; carrier N_2, 50 mL/min). Details of the GC separations are given in Table 4S, and the competition experiments (quantities of reactants and products) are listed in Table 5S.

Acknowledgment. We thank the Deutsche Forschungsgesellschaft and the Fonds der Chemischen Industrie for financial support, Dynamit Nobel and Degussa for gifts of chemicals, and Dr. E. Bäuml for discussions.

Registry No. **1a**, 109-87-5; **1b**, 534-15-6; **1c**, 4744-10-9; **1d**, 4461-87-4; **1e**, 41632-89-7; **1f**, 77-76-9; **1g**, 1125-88-8; **1h**, 881-67-4; **1i**, 24856-58-4; **1j**, 3395-81-1; **1k**, 32691-93-3; **1l**, 3395-83-3; **1m**, 2186-92-7; **1n**, 6044-68-4; **1o**, 21962-24-3; **1p**, 77731-51-2; **1q**, 4364-06-1; **1r**, 149-73-5; **1s**, 1445-45-0; **1t**, 707-07-3; **2′**, 107-25-5; $(2')_x$, 9003-09-2; **3b**, 10138-89-3; **3c**, 32377-24-5; **3d**, 6281-05-6; **3e**, 114533-81-2; **3f**, 73452-12-7; **3g**, 26278-70-6; **3i**, 114533-82-3; **3j**, 114533-83-4; **3k**, 114533-84-5; **3l**, 114533-85-6; **3m**, 114533-86-7; **3n**, 114533-87-8; **3o**, 114533-88-9; **3p**, 114533-89-0; **3q**, 114533-90-3; **3r**, 102-52-3; **4b**, 25724-11-2; **4c**, 114533-91-4; **4d**, 86218-77-1; **4e**, 114533-92-5; **4f**, 114533-93-6; **4g**, 114533-94-7; **4h**, 114533-95-8; **4r**, 55546-58-2.

Supplementary Material Available: Tables with ^1H NMR, IR, mass spectroscopic, and analytical data of compounds **3** and **4**, ^{13}C NMR data of compounds **4**, and experimental details of the competition experiments (14 pages). Ordering information is given on any current masthead page.

(21) Zweifel, G.; Brown, H. C. *Org. React.* **1963**, *13*, 28.
(22) Effenberger, F.; Prossel, G.; Fischer, P. *Chem. Ber.* **1971**, *104*, 2002.
(23) Organikum, *Organisch-Chemisches Grundpraktikum*, 15th Ed. VEB Deutscher Verlag der Wissenschaften, Berlin, 1977; p 488.

trans-Bis(5-methoxy-1-3-η^3-cyclohexenyl)palladium Complexes by Palladium(II)-Promoted Addition of Methanol to 1,4-Cyclohexadienes. Synthesis of Methyl *trans*-5-Methoxy-2-cyclohexene-1-carboxylates by Subsequent Methoxycarbonylation[1]

Björn C. Söderberg, Björn Åkermark,* and Stan S. Hall*,[2]

Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden, and Department of Chemistry, Rutgers University, Newark, New Jersey 07102

Received December 11, 1987

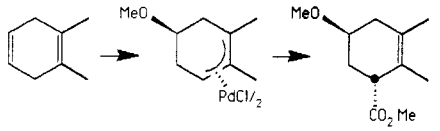
1,4-Cyclohexadienes in the presence of bis(acetonitrile)palladium dichloride in methanol are stereoselectively converted to *trans*-bis(5-methoxy-1-3-η^3-cyclohexenyl)palladium chloride complexes. A series of substituted 1,4-cyclohexadienes was studied to determine the effects of substituents. Subsequent methoxycarbonylation regioselectively and stereoselectively afforded the corresponding methyl *trans*-5-methoxy-2-cyclohexene-1-carboxylates. The two-reaction sequence can be coupled in a tandem reaction procedure.

Applications of (η^3-allyl)palladium complexes in organic synthesis engenders keen interest today.[3] Standard procedures to form (η^3-allyl)palladium complexes include palladium(II)-initiated addition of nucleophiles across 1,3-diene systems.[4] Larock recently demonstrated that

(1) (a) 1,4-Diene-Derived (η^3-Allyl)palladium Complexes. 3. Part 1: Hall, S. S.; Åkermark, B. *Organometallics* **1984**, *3*, 1745–1748. (b) Part 2: Åkermark, B.; Söderberg, B. C.; Hall, S. S. *Ibid.* **1987**, *6*, 2608–2610. (c) Initially disclosed at the 194th National Meeting of the Americal Chemical Society, New Orleans, LA, Aug 1987, paper ORGN 213, and at the XIIth International IUPAC Conference on Organometallic Chemistry, Vienna, Austria, Sept 1985. (d) Taken from the Ph.D. (Teknisk Doktor) Dissertation of B.C.S., Royal Institute of Technology, Dec 1987.
(2) Visiting professor and Rutgers University Faculty Academic Study Participant at the Royal Institute of Technology, July 1982–Aug 1983, July–Aug 1984, July–Aug 1985.
(3) (a) Trost, B. M. *Tetrahedron* **1977**, *33*, 2615–2649. (b) Chiusoli, G. P.; Cassar, L. In *Organic Synthesis Via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Part II, p 297. (c) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385–393. (d) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer Verlag: New York, 1980. (e) Trost, B. M.; Verhoeven, T. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G. Ed.; Pergamon: Oxford, 1982; Vol. 8, p 799.
(4) (a) Robinson, S. D.; Shaw, B. L. *J. Chem. Soc.* **1964**, 5002–5008. (b) Heck, R. F. *J. Am. Chem. Soc.* **1968**, *90*, 5542–5546. (c) Staken, F. G.; Heck, R. F. *J. Org. Chem.* **1980**, *45*, 3584–3593. (d) Bäckvall, J.-E. *Acc. Chem. Res.* **1983**, *16*, 335–342.

0022-3263/88/1953-2925$01.50/0

(η^3-allyl)palladium complexes could be regioselectively generated from acyclic 1,4-dienes with alkyl- and phenylmercuric chloride and Li_2PdCl_4, as well.[5] Initial organopalladium addition to the less hindered double bond of the diene, followed by palladium hydride elimination–readdition, explains the formation of the (η^3-allyl)palladium complex. In an exploratory study, this group recently demonstrated that *trans*-bis(5-methoxy-1–3-η^3-cyclohexenyl)palladium chloride complexes could be stereoselectively and, depending on the reaction conditions, regioselectively formed by palladium(II)-promoted addition of methanol to a series of dimethyl-1,4-cyclohexadienes.[1a] Since rather complex 1,4-cyclohexadienes can be prepared by tandem alkylation–reduction procedures,[6] as well as by Birch metal–ammonia reduction of aromatic compounds,[7] and since (η^3-allyl)palladium complexes can be stereoselectively functionalized, intricate structures of defined stereochemistry with important synthetic utility might be quickly elaborated from benzene derivatives by using this rather simple reaction sequence. Herein are described the results of palladium(II)-initiated addition of methanol to a large selection of substituted 1,4-cyclohexadienes, prepared by Birch reduction of the corresponding aromatics, to prepare (η^3-allyl)palladium complexes. The study was designed to determine the scope and limitations of the reaction. A selection of the derived (η^3-allyl)palladium compounds was subsequently regioselectively and stereoselectively methoxycarbonylated to demonstrate the potential and synthetic utility of the entire reaction sequence, which can be performed as a tandem procedure.



1 24

***trans*-Bis(5-methoxy-1–3-η^3-cyclohexenyl)palladium Chloride Complexes.** Table I lists the 1,4-cyclohexadienes that were treated with an equimolar amount of bis(acetonitrile)palladium dichloride in methanol. Table entries 1–5 have been previously discussed.[1a] Reaction of 1-isopropyl-4-methyl-1,4-cyclohexadiene (entry 6) with the Pd(II) reagent in the presence of 1 equiv of $KHCO_3$ at ambient temperature afforded primarily **9** (63%), the product of kinetic control of addition, along with a mixture of **8**, the product of thermodynamic control of addition, and its isomerization product **7**. When the same reaction was performed at −74 °C and allowed to warm slowly to 15 °C (entry 8), the kinetic-control addition product **9** was formed exclusively (53%). In contrast, the same conditions without base formed only the thermodynamic-control addition product **8** (entry 7), albeit in lower yield (12%). With 1,4-diisopropyl-1,4-cyclohexadiene, in the absence of base (entry 9), no reaction occurred even after 60 h, indicating that the interaction and subsequent reaction of bis(acetonitrile)palladium dichloride with a substituted 1,4-cyclohexadiene is sensitive to steric congestion.

Reaction of the Pd(II) reagent with 1,2,3,4,5,8-hexahydronaphthalene (entry 10) and 4,7-dihydroindan (entry 11) in the presence of 1 equiv of base afforded the corresponding (1–3-η^3-cyclohexenyl)palladium complexes **10** (87%) and **11** (83%), respectively, in superior isolated yields. From the 3,6-dihydrobenzocyclobutane no stable complex could be isolated (entry 12).

These reaction conditions did not affect 1,2,4,5-tetramethyl-1,4-cyclohexadiene (entry 13), emphasizing the deactivating and steric effects of the four methyl double-bond substituents. On the other hand, reaction of 1,2,4-trimethyl-1,4-cyclohexadiene with Pd(II) in the presence of base at ambient temperature afforded predominantly the kinetic-control addition product **14** in serviceable yield (70%), plus a mixture of thermodynamic-control addition product **12** and its isomerization product **13** (entry 14). Without base and at low temperature (−78 to 20 °C), only the thermodynamic-control addition product **12** was isolated (29%, entry 15). In contrast, 1,3,5-trimethyl-1,4-cyclohexadiene reacted very sluggishly. At ambient temperature in the presence of base the expected (5-methoxy-1–3-η^3-cyclohexenyl)palladium complex **16** was formed in low yield, plus the (1–3-η^3-cyclohexenyl)palladium complex **15** (entry 16). At low temperature (−76 to 17 °C) only the hydride–addition complex **15** was isolated (entry 17).

In the monosubstituted series, 3-phenyl-1,4-cyclohexadiene afforded only the rearomatized material (biphenyl, 97%, entry 18).[8] 1-*tert*-Butyl-1,4-cyclohexadiene, in the presence of base at ambient temperature, afforded the two palladium complexes **17** and **18** in a ratio of 1:9 (entry 19). In contrast, the 1:2 ratio of the related products **19** and **20** from 1-methyl-1,4-cyclohexadiene indicates the influencial directing effect of a bulky double-bond substituent on the reaction (entry 20).

For unsubstituted 1,4-cyclohexadiene itself (entry 21), only after an extended reaction period (117 h) at low temperature (−78 to −18 °C) were *trans*- and *cis*-(5-methoxy-1–3-η^3-cyclohexenyl)palladium complex (**22** and **23**, 21%) formed, along with the hydride addition product **21**. *cis*-**23** was probably derived from *trans*-**22** by palladium exchange.[9]

These results characterize the scope and limitations of the palladium(II)-promoted addition of methanol to substituted 1,4-cyclohexadienes. The influence of a substituent appears to be at least threefold in that initially the substituent both moderates and directs the addition and then stabilizes the (1–3-η^3-cyclohexenyl)palladium complexes once formed. This effect is illustrated in the 1,2-dimethyl-1,4-cyclohexadiene, 1-methyl-1,4-cyclohexadiene, and 1,4-cyclohexadiene series (entries 1, 20, and 21), where the isolated yields of bis(5-methoxy-1–3-η^3-cyclohexenyl)palladium chloride complexes range from 88% to 71% to 21%, respectively.

The importance of steric hindrance is dramatically demonstrated where both double bonds are either fully

(5) (a) Larock, R. C.; Takagi, K. *Tetrahedron Lett.* **1983**, *24*, 3457–3460. (b) It has now also been demonstrated that a variety of organomercurials with Li_2PdCl_4 react regioselectively with acyclic 1,4-, 1,5-, 1,6-, and 1,7-dienes to yield (η^3-allyl)palladium complexes by remote palladium migration. Larock, R. C.; Takagi, K. *J. Org. Chem.* **1984**, *49*, 2701–2705.

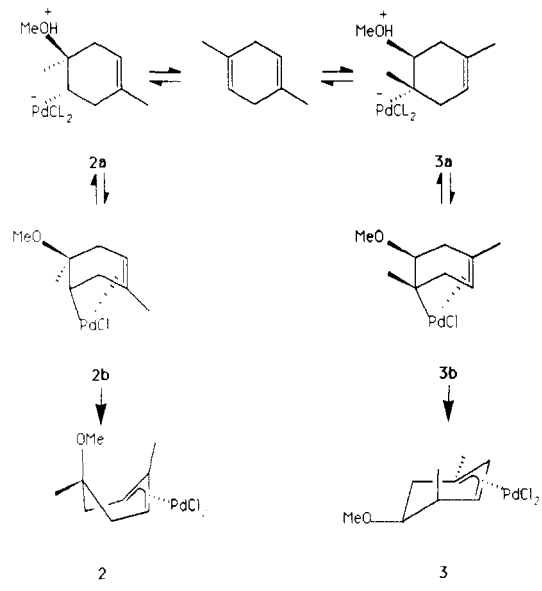
(6) (a) Ryan Zilenovski, J. S.; Hall, S. S. *J. Org. Chem.* **1981**, *46*, 4139–4142. (B) Flisak, J. R., Ph.D. Thesis, Rutgers Unversity, Oct 1985.

(7) (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.

(8) The only other dienes that rearomatized with these conditions were 4-alkyl-3,6-dihydroanisoles and perhaps 1,4-cyclohexadiene.

(9) The result would also be obtained by both proximal and distal addition of methanol. However, this seems unlikely since only distal addition is observed for the other 1,4-cyclohexadienes and methanol usually adds distal. See: (a) Stille, J. K.; Morgan, R. A. *J. Am. Chem. Soc.* **1966**, *88*, 5135–5141. (b) Stille, J. K.; James, D. E. *Ibid.* **1973**, *95*, 5062–5064. (c) Majima, T.; Kurosawa, H. *J. Chem. Soc., Chem. Commun.* **1977**, 610–611. (d) Kursawa, H.; Majima, T.; Asada, N. *J. Am. Chem. Soc.* **1980**, *102*, 6996–7003.

Scheme I



substituted, as with 1,2,4,5-tetramethyl-1,4-cyclohexadiene (entry 13), or 1,4-disubstituted with bulky groups, as with 1,4-diisopropyl-1,4-cyclohexadiene (entry 9). In these situations no addition occurred. The influence of steric factors can also be subtle. For example, 1,2,4-trimethyl-1,4-cyclohexadiene afforded the best isolated yield (96%) of addition products of all the cyclohexadienes (entry 14), while 1,3,5-trimethyl-1,4-cyclohexadiene was one of the worst (16%, entry 16). In the latter case, it seems plausible that the C-3 methyl group tempers the addition by forcing the methanol to add both distal to the C-3 methyl group and the metal to sluggishly afford the (1-3-η^3-cyclohexenyl)palladium complex **16**. This, in turn, allows time for the hydride addition reaction to compete favorably to form **15**.[10]

The substituent directing effect is exemplified throughout Table I. Addition always occurred at the less substituted double bond or the less sterically hindered double bond. The stabilizing effect of the double bond substituents on the (1-3-η^3-cyclohexenyl)palladium complexes is demonstrated by the excellent isolated yields from the 1,2-disubstituted 1,4-cyclohexadienes (entries 1, 10, and 11).

Scheme I outlines the proposed mechanism for the palladium(II)-promoted addition of methanol to 1,4-cyclohexadienes using 1,4-dimethyl-1,4-cyclohexadiene as the example (entries 2 and 3, Table I). Since the addition of methoxide, or a combination of methanol and sodium carbonate, retards the formation of complex **2**, the nucleophile is probably methanol.[1b] In addition the η^3-allyl complex **3** is formed even in the absence of external base (entry 3). Optimal yields of **2** were obtained by addition of a weak base such as potassium bicarbonate, which can either deprotonate the η^1-intermediate **2a** or scavenge the liberated HCl. In accordance with earlier studies of palladium-promoted addition of methanol to olefins, the addition of methanol should occur in a distal manner[9] to form intermediates **2a** and **3a**. After deprotonation, ensuing β-elimination–readdition of palladium hydride with retention of configuration[11] affords the observed products **2** or **3**, depending on the reaction conditions.

When the reaction is performed in the presence of a weak base product **2** forms exclusively by addition of methanol to the more substituted position of the double bond. Similar results were observed for palladium(II)-promoted amination.[12] However, as long as protons preside, intermediates **2a** and **2b** apparently equilibrate with the starting 1,4-cyclohexadiene and intermediates **3a** and **3b**. Since the latter are more thermodynamically stable, complex **3** becomes the exclusive (or dominant) product when no base is present.

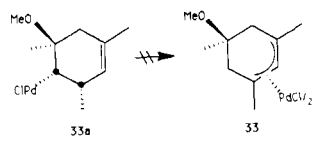
A delicate balance exists between methanol addition to the more or less substituted terminus of the double bond and for many 1,4-cyclohexadienes fair amounts of complex from methanol addition to the less substituted terminus was observed even in the presence of weak base. For example, 1,5-dimethyl-1,4-cyclohexadiene afforded complex **5** (entry 4) as well from methanol addition to the less substituted teminus. Both 1-isopropyl-4-methyl-1,4-cyclohexadiene (entry 6) and 1,2,4-trimethyl-1,4-cyclohexadiene (entry 14) gave similar results.

Under basic conditions, isomerization of (1-alkyl-1-3-η^3-cyclohexenyl)palladium complexes to (2-alkyl-1-3-η^3-cyclohexenyl)palladium complexes also occurred. Examples of this ratchet reaction include the isomerization of **4** to **6**, **8** to **7**, and **12** to **13**. This observation suggests that the alkyl substituent prefers to be at the C-2 position rather than the C-1 position of the (1-3-η^3-cyclohexenyl)palladium complex.

The extensive NMR data for the *trans*-bis(5-methoxy-1-3-η^3-cyclohexenyl)palladium chloride complexes (as well as the methoxycarbonylation reaction products discussed in the following section) reconcile with the reaction stereoselectivity outlined in Scheme I. X-ray studies of related (1-3-η^3-cyclohexenyl)palladium systems,[13] in contrast to (1-3-η^3-cyclohexenyl)molybdenum complexes, which have also been analyzed by both X-ray crystallographic and NMR techniques,[14] show rather planar (1-3-η^3-cyclohexenyl)palladium complexes. While the (1-3-η^3-cyclohexenyl)molybdenum complexes preferred a chair conformation, it is clear that both pseudochair and pseudoboat conformations are observed for the (1-3-η^3-cyclohexenyl)palladium complexes.[1a] The *trans*-**22** and *cis*-**23** complexes illustrate this.

For the palladium complexes **22** and **23**, the vicinal coupling constants between the C-5 and the C-4 and C-6 protons are $J_{5,4a} = J_{5,6a} = 6.8$ Hz for **22** and 8.8 Hz for **23** and $J_{5,4e} = J_{5,6e} = 5.6$ Hz for **22** and 5.4 Hz for **23**. One complex must be in a boat conformation and the other in a chair, rather than both in chair conformations (**22** and **23a**). Complex **22** is the chair structure since the vicinal

(10) In the formation of **15** both hydride and palladium have added from the face of the double bond opposite the C-3 methyl group, as would be expected for steric reasons. This result suggests that if both double bonds are coordinating, which cannot be completely excluded, this bidentate behavior does not interfere with proximal addition. Interestingly, the kinetic-control addition adduct **33** was not observed in this reaction. Presumably the requisite intermediate **33a**, if formed, can not undergo cis β-elimination.

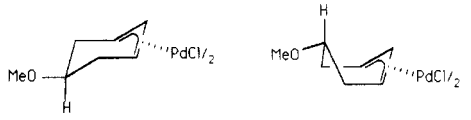


(11) Parra-Hake, M.; Rettig, M. F.; Wing, R. M. *Organometallics* **1983**, *2*, 1013–1017.

(12) Åkermark, B.; Bäckvall, J.-E.; Hegedus, L. S.; Zetterberg, K.; Siirala-Hansén, K.; Sjöberg, K. *J. Organomet. Chem.* **1974**, *72*, 127–138.

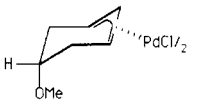
(13) (a) Churchill, M. R. *Inorg. Chem.* **1966**, 1608–1612. (b) Kilbourn, B. T.; Mais, R. H. B.; Owston, P. G. *J. Chem. Soc., Chem. Commun.* **1968**, 1438–1440.

(14) Faller, J. W.; Murray, H. H.; White, D. L.; Chao, K. H. *Organometallics* **1983**, *2*, 400–409.



22

23



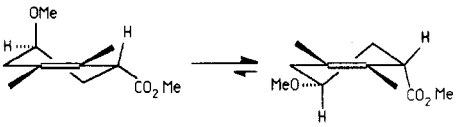
23a

couplings between the terminal η^3-allyl protons at C-1 and C-3 and the C-4 and C-6 protons are $J_{1,6a} = J_{3,4a} = J_{1,6e} = J_{3,4e}$ = ca. 3.5 Hz. These couplings are very similar to those for complexes **1**, **3**, and **5**, which have been previously assigned pseudochair conformations.[1a] In contrast, the corresponding couplings for complex **23** are $J_{1,6a} = J_{3,4a}$ = 0 Hz and $J_{1,6e} = J_{3,4e}$ = 6.0 Hz, which are similar to the values for the pseudoboat complexes **2** and **4**.[1a] Examination of molecular models shows that these couplings reconcile with the expected dihedral angles. The boat conformation should have vicinal dihedral angles of ca. 90° for the H-1 and H-6 protons and 15° for the H-1 and H-6e protons. For the chair conformation, the vicinal dihedral angles are ca. 60° for these protons. An additional indication of the boat conformation for complex **23** is the shielding of the axial C-5 proton, which resonates at δ 3.03. The corresponding H-5a signal in the complex **22** (chair conformation) is at δ 4.13. Apparently the boat conformation relieves the serious interaction between the endo-face C-5 methoxy group and the metal and thereby positions the exo-face C-5 proton directly over the shielding region of the η^3-cyclohexenyl system. The effect is even more dramatic for complex **15** (boat conformation), which has no C-5 methoxy group, where the H-5a proton resonates at δ 0.04. Another diagnostic feature that has also been noted previously,[1a] the geminal couplings values of $J_{4a,4e}$ and $J_{6a,6e}$ = ca. 16 Hz for chair conformers and ca. 18.5 Hz for boat conformers, was also observed here. For the chair complex **22** the $J_{4a,4e}$ and $J_{6a,6e}$ = ca. 16.6 Hz, and for the boat complex **23** the $J_{4a,4e} = J_{6a,6e}$ = ca. 18.3 Hz.

For the *trans*-bis(5-methoxy-1-3-η^3-cyclohexenyl)palladium complexes, the most revealing NMR feature that is useful to quickly establish the conformation is the position of the resonance (both ^{1}H and ^{13}C) of the C-5 methoxy group. For the boat conformers, because of the shielding of the C-5 methoxy group by the η^3-cyclohexenyl system, the methoxy protons resonate upfield at ca. δ 3.0 and the methoxy carbon at ca. δ 49. The corresponding C-5 methoxy signals in the chair conformers resonate at ca. δ 3.3 (^{1}H) and 56 (^{13}C). The boat conformation avoids the serious interaction between the endo-face C-5 methyl group and the palladium in complexes **2**, **4**, **9**, and **14**, thereby positioning the exo-face C-5 methoxy group directly over the shielding region of the η^3-cyclohexenyl system.

Methyl *trans*-5-Methoxy-2-cyclohexene-1-carboxylates. In order to demonstrate the synthetic utility of these (η^3-cyclohexenyl)palladium complexes, a selection of the derived complexes were regioselectively and stereoselectively methoxycarbonylated according to the improved procedure of Milstein.[15] Table II compiles the (η^3-cyclohexenyl)palladium complexes subjected to this mild and efficient procedure. The isolated yields (first percent in brackets) of the corresponding methyl *trans*-5-methoxy-2-cyclohexene-1-carboxylates, after flash chromatography, were gratifying (63–95%).

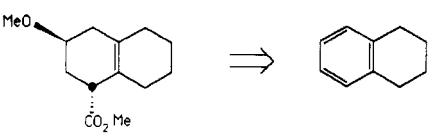
As previously noted by Milstein in acyclic (η^3-allyl)palladium complexes,[15] the methoxycarbonylation reaction was highly regioselective. With the (η^3-cyclohexenyl)palladium complexes insertion occurred exclusively at the less substituted terminus of the η^3-allyl system. Since insertion of carbon monoxide into palladium–carbon bonds is known to proceed with complete retention of configuration,[16] the methoxycarbonyl group will be trans to the C-5 methoxy group. Table III lists the vicinal coupling constants for methyl *trans*-5-methoxy-2,3-dimethyl-2-cyclohexene-1-carboxylate (**24**), which was derived from complex **1**. Since the C-5 methoxy group prefers the equatorial position ($J_{4a,5}$ = ca. 8 Hz, $J_{6a,5}$ = 9.3 Hz) and the C-1 carboxylate group prefers the axial position ($J_{6a,1}$ = 6.1 Hz, $J_{6e,1}$ = 3.2 Hz), the preferred conformation is **24b**.



24a **24b**

The methoxycarbonylation reaction was also selected to demonstrate the general utility of the palladium(II)-promoted addition of methanol to 1,4-cyclohexadienes reaction because the reaction conditions for both sequences were compatible. Thus performance of the reactions in tandem in the same reaction vessel without isolation of the intermediate (1–3-η^3-cyclohexenyl)palladium complex was feasible and the entire sequence was executed in a Fischer and Porter pressure vessel. After the palladium complex had been formed, sodium propionate was added and the vessel sealed and pressurized to ca. 5 atm with carbon monoxide, which afforded the corresponding methyl *trans*-5-methoxy-2-cyclohexene-1-carboxylate. The isolated yields (second percent in brackets) are listed in Table II and are based on the starting 1,4-cyclohexadienes. The advantages of the tandem sequence was that the intermediate complexes did not have to be isolated and purified, and the overall isolated yields (35–87%) of the corresponding carboxylates were higher in more cases than when the two steps were discharged independently.

This study demonstrates that substituted 1,4-cyclohexadienes can be selectively difunctionalized by using palladium(II)-promoted addition of methanol to form *trans*-bis(5-methoxy-1-3-η^3-cyclohexenyl)palladium chloride complexes, which can be subsequently methoxycarbonylated. It is remarkable that starting with 1,4-cyclohexadienes derived from aromatic compounds, one can in three simple manipulations—reduction, methoxypalladation, and methoxycarbonylation—selectively elaborate intricate molecules with well defined functionality and relative stereochemistry.



30

(15) Milstein, D. *Organometallics* **1982**, *1*, 888–890.

(16) (a) Stille, J. K.; Hines, L. F. *J. Am. Chem. Soc.* **1970**, *92*, 1798–1799; (b) **1972**, *94*, 485–490. (c) James, D. E.; Stille, J. K. *Ibid.* **1976**, *98*, 1810–1823. (d) Stille, J. K.; Divakaruni, R. *J. Org. Chem.* **1979**, *44*, 3474–3482.

Experimental Section[17]

All reactions to generate (η^3-allyl)palladium complexes were performed in oven-dried, 25-mL or 50-mL, two-neck, round-bottomed flasks equipped with magnetic stir bars under a static N_2 atmosphere. Palladium dichloride was from Engelhard. Bis(acetonitrile)palladium dichloride was prepared by the general method of Kharasch et al.[18] Cupric chloride (dihydrate) and methanol (0.1% H_2O) were from E. Merck (Darmstadt, W. Germany). 1,4-Cyclohexadiene was from Aldrich Chemical Co. The preparation of 1,2-dimethyl-1,4-cyclohexadiene, 1,4-dimethyl-1,4-cyclohexadiene, and 1,5-dimethyl-1,4-cyclohexadiene has been described.[1a] The Celite was Johns Manville Hyflo Super-cel. Flash chromatography[19] was performed on silica gel 60 (230–400 mesh, E. Merck). Analytical thin-layer chromatography (TLC) was conducted on E. Merck aluminum plates precoated with 0.2 mm of silica gel 60 F_{254}. Thin-layer chromatograms were visualized with UV light and with 5% phosphomolybdic acid reagent (Aldrich Chemical Co.) in 95% ethanol. Apparently the (η^3-allyl)palladium complexes decompose in the presence of Pd(0); consequently cupric chloride (ca. 10%) is used during their formation to minimize this reaction. It is recommended that the entire reaction sequence to generate the (η^3-allyl)palladium complexes and the subsequent flash chromatography be performed without interruption to remove the product complex as quickly as possible from impurities. Once pure, these (η^3-cyclohexenyl)palladium complexes are relatively stable and are not air sensitive, but as a precaution they were always stored neat as oils or in crystalline form at −26 °C under N_2. The preparation and characterization of the (η^3-cyclohexenyl)palladium complexes **1–6** have been described.[1a] Methoxycarbonylations were performed in a 19 × 3 (i.d.) cm Fischer and Porter pressure vessel equipped with a Nalgene star-head magnetic stir bar. Sodium propionate was from Riedel-de Haën (Hannover, W. Germany). Carbon monoxide was from AGA Special Gas (Lidingö, Sweden). The progress of the methoxycarbonylations were periodically monitored by TLC using EtOAc–petroleum ether (2:3) as eluant. The low-pressure methoxycarbonylations were executed by using the general procedure of Milstein.[15]

Di-μ-chlorobis[(1,2,3-η)-4-methoxy-2-isopropyl-5-methyl-2-cyclohexen-1-yl]dipalladium (7), Di-μ-chlorobis[(1,2,3-η)-5-methoxy-1-isopropyl-4-methyl-2-cyclohexen-1-yl]dipalladium (8), and Di-μ-chlorobis[(1,2,3-η)-5-methoxy-2-isopropyl-5-methyl-2-cyclohexen-1-yl]dipalladium (9). To a stirred yellow slurry of 810 mg (3.12 mmol) of bis(acetonitrile)-palladium dichloride, 284 mg (2.84 mmol) of $KHCO_3$, and 75 mg (0.44 mmol) of cupric chloride in 15 mL of MeOH at 20 °C was added (dropwise, 5 min) a solution of 340 mg (2.50 mmol) of 1-isopropyl-4-methyl-1,4-cyclohexadiene in 10 mL of MeOH. Within seconds the yellow slurry turned red-brown, and after a few minutes a yellow flocculent precipitate began to appear. After 24 h the yellow supernatant with a yellow flocculent precipitate was filtered through a 5-mm pad of Celite (dry packed), and the filter was rinsed first with 25 mL of MeOH and then with 100 mL of EtOAc. The yellow filtrate—a pale yellow-green precipitate remained on the filter—was concentrated in vacuo at water aspirator pressure on a rotary evaporator to afford a yellow-brown oil that was immediately diluted in 2–3 mL of EtOAc and flash chromatographed through a 2 × 15 cm SiO_2 column packed with EtOAc–petroleum ether (2:3) and eluted with this solvent mixture. Removal of the solvent at reduced pressure (water aspirator) afforded first 123 mg (0.20 mmol, 16%) of a 57:43 mixture of **7** and **8** as a yellow oil followed by 487 mg (0.79 mmol, 63%) of **9** as yellow crystals. Separation of **7** and **8** was achieved by HPLC (EtOAc–petroleum ether, 5:95), which afforded **7** followed by **8**, both as yellow crystals. (η^3-Cyclohexenyl)palladium complex **7**: ^{1}H NMR (200 MHz, $CDCl_3$, chair conformation) δ 4.85 (1 H, H-1, superficial t, J = 3.7 Hz), 4.80 (1 H, H-3, dd, $J_{3,4e}$ = 3.7 Hz, $J_{3,1}$ = 1.3 Hz), 3.60 (1 H, H-4e, superficial t, $J_{4e,3} = J_{4e,5a}$ = 4.1 Hz), 3.40 (3 H, MeO, s), ca. 2.86 (1 H, H-5, complex m, $w_{1/2}$ = 20 Hz), 2.42 (1 H, septet, J = 6.8 Hz), 1.99 (1 H, H-6e, ddd, $J_{6e,6a}$ = 16.1 Hz, $J_{6e,5a}$ = 6.1 Hz, $J_{6e,1}$ = 4.1 Hz), 1.21 (3 H, d, J = 6.8 Hz), 1.20 (3 H, d, J = 6.8 Hz), 0.96 (1 H, H-6a, ddd, $J_{6a,6e}$ = 16.1 Hz, $J_{6a,5a}$ = 9.7 Hz, $J_{6a,1}$ = 2.8 Hz), 0.86 (3 H, MeC-5, d, J = 6.8 Hz); homonuclear decoupling, irradiation at δ 4.85 sharpened the signal at δ 3.60 to a dd and collapsed the signals at δ 1.99 to a dd and at δ 0.96 to a dd, irradiation at δ 3.60 collapsed the signals at δ 4.80 to a s and at δ 2.86 to a d of quintets, irradiation at δ 2.86 collapsed the signals at δ 3.60 to a d, at δ 1.99 to a dd, at δ 0.96 to an apparent dd, and at δ 0.86 to a s, irradiation at δ 2.42 collapsed the signals at δ 1.21 and 1.20 to s, irradiation at δ 1.99 collapsed the signals at δ 4.85 to a br s and at δ 0.96 to an apparent dd, and simplified the m at δ 2.86, irradiation at δ 0.96 collapsed the signals at δ 4.85 to an apparent d, at δ 2.86 to a m ($w_{1/2}$ = 14 Hz), and at δ 1.99 to a superficial t, and irradiation at δ 0.86 collapsed the signal at δ 2.86 to an apparent dt.

Di-μ-chlorobis[(1,2,3-η)-5-methoxy-1-isopropyl-4-methyl-2-cyclohexen-1-yl]dipalladium (8). To a cold (−78 °C, dry ice–acetone in a Dilvac Dewar bath), stirred yellow slurry of 650 mg (2.50 mmol) of bis(acetonitrile)palladium dichloride and 64 mg (0.38 mmol) of cupric chloride in 15 mL of MeOH was added (dropwise, 5 min) a solution of 272 mg (2.00 mmol) of 1-isopropyl-4-methyl-1,4-cyclohexadiene in 10 mL of MeOH. After 26 h—the temperature of the reaction mixture had slowly risen to 15 °C—the red solution with some black particles was filtered through a 5-mm pad of Celite (dry packed) and the filter rinsed first with 25 mL of MeOH and then with 100 mL of EtOAc. The red filtrate was concentrated in vacuo at water aspirator pressure on a rotary evaporator to afford a dark red-brown oil–solid with some black particles that was immediately slurried in 2–3 mL of EtOAc and flash chromatographed through a 2 × 15 cm SiO_2 column packed with EtOAc–petroleum ether (2:3) and eluted with the same solvent mixture. Removal of the solvent at reduced pressure (water aspirator) afforded 75 mg (0.12 mmol, 12%) of **8** as a yellow oil, which slowly solidified in a refrigerator (4 °C) as yellow crystals: ^{1}H NMR (200 MHz, $CDCl_3$, chair conformation) δ 5.30 (1 H, H-2, d, $J_{2,3}$ = 6.6 Hz), 4.71 (1 H, H-3, dd, $J_{3,2}$ = 6.4 Hz, $J_{3,4e}$ = 4.0 Hz), 4.41 (1 H, H-5a, dt, $J_{5a,6a}$ = 8.5 Hz, $J_{5a,4e} = J_{5a,6e}$ = 5.5 Hz), 3.31 (3 H, MeO, s), 2.42 (1 H, H-4e, at least a 12-line m, $J_{4e,Me}$ = 7.0 Hz, $J_{4e,5a}$ = 5.5 Hz, $J_{4e,3}$ = 4.0 Hz), 2.19 (1 H, H-6e, dd, $J_{6e,6a}$ = 15.9 Hz, $J_{6e,5a}$ = 5.5 Hz), 2.05 (1 H, septet, J = 6.8 Hz), 1.41 (1 H, H-6a, dd, $J_{6a,6e}$ = 15.9 Hz, $J_{6a,5a}$ = 8.8 Hz), 1.18 (6 H, d, J = 6.8 Hz), 0.92 (3 H, MeC-4, d, J = 7.0 Hz); homonuclear decoupling, irradiation at δ 5.30 collapsed the signal at δ 4.71 to a d, irradiation at δ 4.71 collapsed the signals at δ 5.30 to a s and at δ 2.42 to a quintet, irradiation at δ 4.41 collapsed the signals at δ 2.42 to a qd, at δ 2.19 to a d, and at δ 1.41 to a d, irradiation at δ 2.42 collapsed the signals at δ 4.71 to a d, at δ 4.41 to a dd, and at δ 0.92 to a s, irradiation at δ 2.19 collapsed the signals at δ 4.41 to a dd (superficial t) and at δ 1.41 to a d, irradiation at δ 2.05 collapsed the signal at δ 1.18 to a s, irradiation at δ 1.41 collapsed the signals at δ 4.41 to a dd and at δ 2.19 to a d, and irradiation at δ 0.92 collapsed the signal at δ 2.42 to a superficial t.

Di-μ-chlorobis[(1,2,3-η)-5-methoxy-2-isopropyl-5-methyl-2-cyclohexen-1-yl]dipalladium (9). To a cold (−74 °C, dry ice–acetone in a Dilvac Dewar bath), stirred yellow slurry of 650 mg (2.50 mmol) of bis(acetonitrile)palladium dichloride, 217 mg (2.17 mmol) of $KHCO_3$, and 72 mg (0.42 mmol) of cupric chloride

(17) High-pressure liquid chromatography (HPLC) was performed on a Waters Associates Model M-45 instrument (differential refractometer detector) with a micro-Porasil column (silica, 10-μm packing, 0.4 × 30 cm). 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 chemical shifts are expressed in δ values (ppm) relative to a Me_4Si internal standard. The ^{1}H NMR spectra were determined at 200 MHz with a Bruker Model WP 200 Fourier transform spectrometer. The ^{13}C NMR spectra were determined at 50.3 MHz and noise broad-band proton) decoupled spectra were collected for most products. In addition, off-resonance proton-decoupled, selective decoupled, gated proton-decoupled, or attached proton test spectra were collected for these 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. The methoxycarbonylation products were further purified, after flash chromatography, for elemental analysis by bulb-to-bulb distillation on a Büchi Model GKR-50 Kugelrohr apparatus, and the bp temperature cited was the oven temperature. Microanalyses were performed by Centrala Analyslaboratoriet Kemikum or Mikro Kemi AB, Uppsala, Sweden.

(18) Kharasch, M. S.; Seyler, R. C.; Mayo, F. R. *J. Am. Chem. Soc.* **1938**, *60*, 882–884.

(19) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.

Table I. *trans*-Bis(5-methoxy-1-3-η^3-cyclohexenyl)palladium Complexes by Palladium(II)-Promoted Addition of Methanol to 1,4-Cyclohexadienes[a]

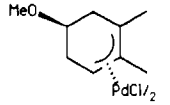
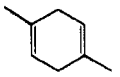
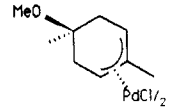
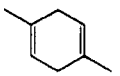
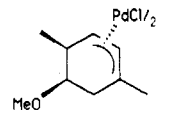
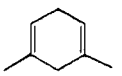
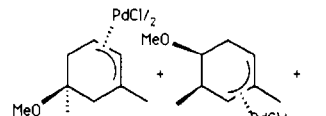
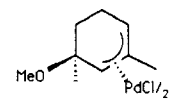
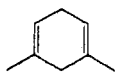
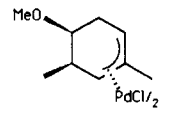
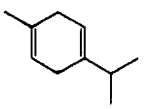
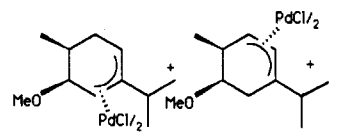
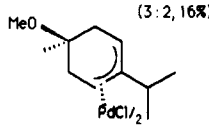
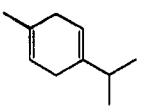
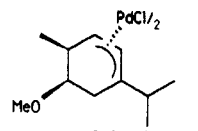
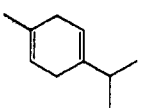
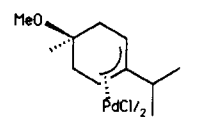
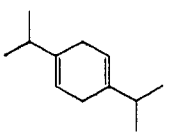
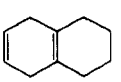
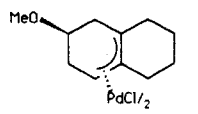
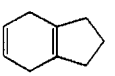
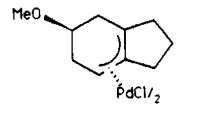
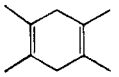
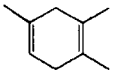
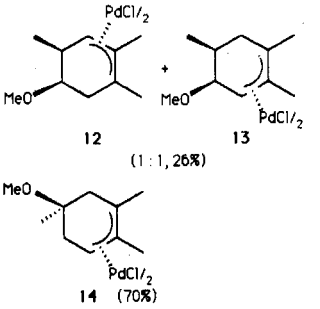
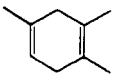
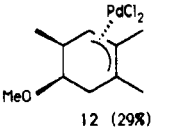
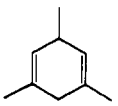
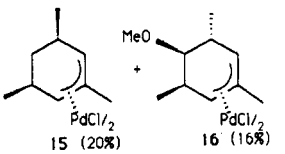
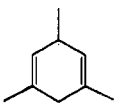
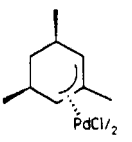
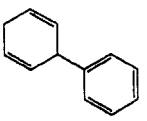
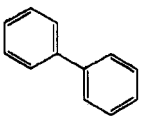
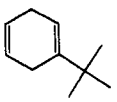
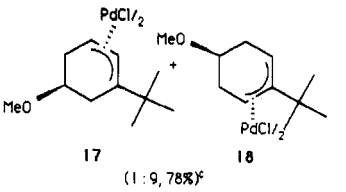
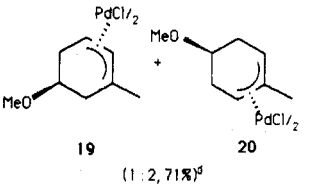
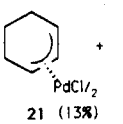
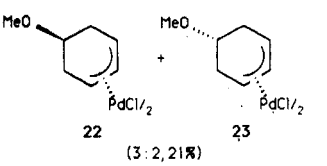
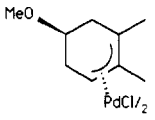
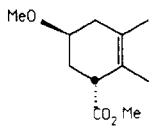
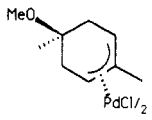
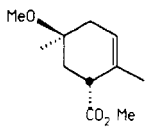
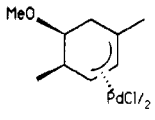
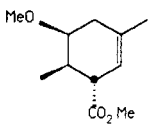
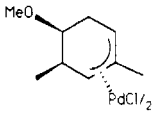
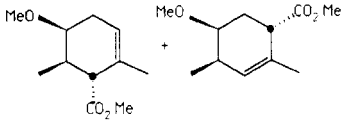
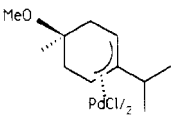
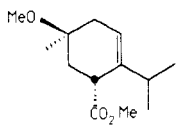
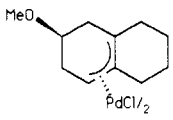
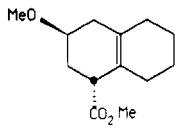
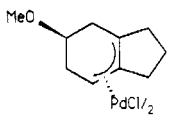
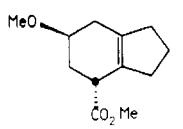
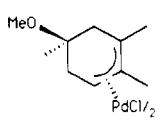
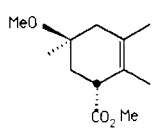
entry	diene	base	temp, °C	time, h	product (ratio, % yield)[b]
1		$KHCO_3$	−10 to 20	19	 1 (88%)
2		$KHCO_3$	−10 to 20	21	 2 (81%)
3			−10 to 20	22	 3 (44%)
4		$KHCO_3$	−10 to 20	22	 4 5  6 (2:1:1, 53%)
5			−68 to 12	24	 5 (39%)
6		$KHCO_3$	20	24	 7 8 (3:2, 16%)  9 (63%)
7			−78 to 15	26	 8 (12%)
8		$KHCO_3$	−74 to 15	22	 9 (53%)
9			−10 to 17	60	no reaction
10		$KHCO_3$	−10 to 20	19	 10 (87%)
11		$KHCO_3$	20	23	 11 (83%)

Table I (Continued)

entry	diene	base	temp, °C	time, h	product (ratio, % yield)[b]
12		$KHCO_3$	−79 to 19	20	labile mixture
13		$KHCO_3$	16	28	no reaction
14		$KHCO_3$	17	21	 12 13 (1:1, 26%) 14 (70%)
15			−78 to 20	120	 12 (29%)
16		$KHCO_3$	20	24	 15 (20%) 16 (16%)
17		$KHCO_3$	−76 to 17	24	 15 (30%)
18		$KHCO_3$	−70 to 20	48	 (97%)
19		$KHCO_3$	16	15	 17 18 (1:9, 78%)[c]
20		$KHCO_3$	16	24	 19 20 (1:2, 71%)[d]
21		$KHCO_3$	−78 to −18	117	 21 (13%)  22 23 (3:2, 21%)

[a] Details are in the Experimental Section. [b] Ratio of products when a mixture was formed. Isolated yield after flash chromatography. [c] See footnote 20. [d] See footnote 21.

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

palladium complex	product (% yield)[b]
 1	 24 (63%, 64%)
 2	 25 (95%, 43%)
 3	 26 (66%, 35%)
 5	 27 28 (2 : 1, 87%, -)
 9	 29 (83%, -)
 10	 30 (85%, 80%)
 11	 31 (89%, 41%)
 14	 32 (72%, -)

[a] Details are in the Experimental Section. [b] Isolated yields after flash chromatography. The first yield, in the bracket, is the one-step procedure from the palladium complex. The second yield is the tandem two-step sequence from the 1,4-cyclohexadiene.

in 15 mL of MeOH was added (dropwise, 5 min) a solution of 276 mg (2.03 mmol) of 1-isopropyl-4-methyl-1,4-cyclohexadiene in 10 mL of MeOH. After 22 h—the temperature of the slurry had slowly risen to 15 °C—the yellow slurry was filtered through a 5-mm pad of Celite (dry packed) and the filter rinsed first with 25 mL of MeOH and then with 100 mL of EtOAc. The yellow filtrate—a yellow-brown precipitate remained on the filter—was concentrated in vacuo at water aspiratory pressure on a rotary evaporator to afford a yellow-brown oil that was immediately slurried in 2–3 mL of EtOAc and flash chromatographed through a 2 × 15 cm SiO_2 column packed with EtOAc–petroleum ether (2:3) and eluted with the same solvent mixture. Removal of the solvent at reduced pressure (water aspirator) afforded 331 mg (0.54 mmol, 53%) of **9** as yellow crystals: ^{1}H NMR (200 MHz, $CDCl_3$, boat conformation) δ 4.65 (2 H H-1 and H-3, d, $J_{1,6e} = J_{3,4e}$ = 5.9 Hz), 2.98 (3 H, MeO, s), 2.42 (1 H, septet, J = 6.9 Hz), 2.09 (2 H, H-4e and H-6e, dd, $J_{4e,4a} = J_{6e,6a}$ = 18.5 Hz, $J_{6e,1} = J_{4e,3}$ = 6.0 Hz), 1.85 (2 H, H-4a and H-6a, d, $J_{4a,4e} = J_{6a,6e}$ = 18.5 Hz), 1.17 (6 H, d, J = 6.9 Hz), 1.07 (3 H, MeC-5, s); homonuclear decoupling, irradiation at δ 4.65 collapsed the signal at δ 2.09 to a d, and irradiation at δ 2.42 collapsed the signal at δ 1.17 to a s; ^{13}C NMR (50 MHz, $CDCl_3$, broad-band proton and off-resonance proton decoupling) 128.35 (s), 70.22 (s), 68.25 (2 C, d), 49.27 (q), 40.19 (2 C, t), 33.39 (d), 23.10 (q), 22.48 (2 C, q) ppm.

Di-μ-chlorobis[(1,4a,8a-η)-1,2,3,4,5,6,7,8-octahydro-3-methoxy-1-naphthalenyl]dipalladium (10). To a cold (−10 °C, salt–ice in a Dilvac Dewar bath), stirred yellow slurry of 607 mg (2.34 mmol) of bis(acetonitrile)palladium dichloride, 204 mg (2.04 mmol) of $KHCO_3$, and 51 mg (0.30 mmol) of cupric chloride in 15 mL of MeOH was added (dropwise, 5 min) a solution of 267 mg (1.99 mmol) of 1,2,3,4,5,8-hexahydronaphthalene in 10 mL of MeOH. After 19 h—the temperature of the slurry had risen to 20 °C—the yellow supernatant with a yellow flocculent precipitate was filtered through a 5-mm pad of Celite (dry packed) and the filter was rinsed first with 25 mL of MeOH and then with 100 mL of EtOAc. The yellow filtrate—a pale green precipitate remained on the filter—was concentrated in vacuo at water aspirator pressure on a rotary evaporator to afford 605 mg of a yellow-brown oil that was immediately diluted with 2–3 mL of EtOAc and flash chromatographed through a 2 × 15 cm SiO_2 column packed with EtOAc–petroleum ether (1:1) and eluted with the same solvent mixture. Removal of the solvent at reduced pressure (water aspirator) afforded 529 mg (0.86 mmol, 87%) of **10** as a yellow oil, which slowly crystallized in a refrigerator (4 °C) as yellow crystals: ^{1}H NMR (200 MHz, $CDCl_3$, chair conformation) δ 4.43 (1 H, H-1, t, $J_{1,2a} = J_{1,2e}$ = ca. 3.3 Hz) superimposed on 4.48–4.33 (1 H, H-3a, m), 3.29 (3 H, MeO, s), 2.50 (1 H, H-4e, dd, $J_{4e,4a}$ = ca. 15.4 Hz, $J_{4e,3a}$ = ca. 6.1 Hz) superimposed on 2.65–2.40 (2 H, m), 2.36 (1 H, H-2e, ddd, $J_{2e,2a}$ = 15.4 Hz, $J_{2e,3a}$ = 5.9 Hz, $J_{2e,1}$ = ca. 4.0 Hz), 2.05–1.45 (5 H, m), 1.31 (1 H, H-4a, dd, $J_{4a,4e}$ = 14.9 Hz, $J_{4a,3a}$ = 8.8 Hz) superimposed on 1.37–1.25 (1 H, m), 1.09 (1 H, H-2a, ddd, $J_{2a,2e}$ = 15.4 Hz, $J_{2a,3a}$ = 8.3 Hz, $J_{2a,1}$ = 2.7 Hz); homonuclear decoupling, irradiation at δ 4.43 collapsed the signals at δ 2.50, 2.36, 1.31, and 1.09 to d, irradiation at δ 2.50 collapsed the signals at δ 4.43 and 1.31 to d and slightly simplified the m at δ 2.05–1.45, irradiation at δ 2.36 collapsed the signals at δ 4.43 to a d and at δ 1.09 to a dd and simplified the m at δ 4.48–4.33, irradiation at δ 1.31 simplified the signal at δ 4.48–4.33 and collapsed the signal at δ 2.50 to a d, and irradiation at δ 1.09 collapsed the signal at δ 4.43 to a d and at δ 2.36 to a dd, and simplified the m at δ 4.48–4.33; ^{13}C NMR (50 MHz, $CDCl_3$, broad-band proton and off-resonance proton decoupling) 114.21 (s), 93.39 (s), 74.32 (d), 68.73 (d), 56.04 (q), 40.33 (dd), 33.82 (dd), 32.60 (dd), 28.92 (t), 22.12 (t), 21.84 (t) ppm.

Di-μ-chlorobis[(3a,4,7a-η)-2,3,4,5,6,7-hexahydro-6-methoxy-1*H*-inden-4-yl]dipalladium (11). Similar treatment of 640 mg (2.47 mmol) of bis(acetonitrile)palladium dichloride, 207 mg

Table III. Vicinal Coupling Constants for Methyl *trans*-5-Methoxy-2,3-dimethyl-2-cyclohexene-1-carboxylate (24)[a]

vicinal coupling	coupling constant, Hz	assignment
$J_{6a,1}$	6.1	a,e
$J_{6e,1}$	3.2	e,e
$J_{6a,5}$	9.3	a,a
$J_{6e,5}$	5.1	e,a
$J_{4a,5}$	ca. 8	a,a
$J_{4e,5}$	3.8	e,a

[a] NMR details are in the Experimental Section.

(2.07 mmol) of $KHCO_3$, and 57 mg (0.30 mmol) of cupric chloride with 237 mg (1.98 mmol) of 4,7-dihydroindan, as described for **7**, **8**, and **9**, afforded 543 mg of a yellow-brown oil that was diluted in 2–3 mL of EtOAc and flash chromatographed through a 2 × 15 cm SiO_2 column packed with EtOAc–petroleum ether (1:1) and eluted with the same solvent mixture. Removal of the solvent at reduced pressure (water aspirator) afforded 483 mg (0.82 mmol, 83%) of **11** as a yellow oil, which solidified to yellow crystals in a refrigerator (4 °C): ^{1}H NMR (200 MHz, $CDCl_3$, chair conformation) δ 4.73 (1 H, H-4, t, $J_{4,5a} = J_{4,5e}$ = ca. 3.3 Hz), 4.41 (1 H, H-6a, tt, $J_{6a,5a} = J_{6a,7a}$ = 8.2 Hz, $J_{6a,5e} = J_{6a,7e}$ = 5.9 Hz), 3.30 (3 H, MeO, s), 2.55–2.39 (2 H, m) on which is superimposed 2.59 (1 H, H-7e, dd, $J_{7e,7a}$ = 16.0 Hz, $J_{7e,6a}$ = 6.0 Hz) and 2.37 (1 H, H-5e, ddd, $J_{5e,5a}$ = 15.4 Hz, $J_{5e,6a}$ = 5.6 Hz, $J_{5e,4}$ = 3.7 Hz), 2.14–1.84 (3 H, complex overlapping m), 1.23 (1 H, H-7a, dd, $J_{7a,7e}$ = ca. 15 Hz, $J_{7a,6a}$ = ca. 7 Hz) superimposed on 1.39–1.24 (1 H, m) and on 1.16 (1 H, H-5a, ddd, $J_{5a,5e}$ = 16.1 Hz, $J_{5a,6a}$ = 8.3 Hz, $J_{5a,4}$ = 2.7 Hz); homonuclear decoupling, irradiation at δ 4.73 collapsed the signals at δ 2.37 and 1.16 to dd, irradiation at δ 4.41 collapsed the signals at δ 2.59 and 1.23 to d and at δ 2.37 and 1.16 to dd, irradiation at δ 2.59 collapsed the signals at δ 4.41 to a td and at δ 1.23 to a d, and irradiation at δ 2.37 collapsed the signals at δ 4.73 to a d, at δ 4.41 to a td, and at δ 1.16 to a dd; ^{13}C NMR (50 MHz, $CDCl_3$, broad-band proton and off-resonance proton decoupling) 121.59 (s), 97.75 (s), 74.69 (d), 65.36 (d), 56.28 (q), 36.57 (dd), 36.50 (dd), 33.90 (dd), 32.67 (t), 23.70 (t) ppm.

Di-μ-chlorobis[(1,2,3-η)-5-methoxy-1,2,4-trimethyl-2-cyclohexen-1-yl]dipalladium (12), Di-μ-chlorobis[(1,2,3-η)-4-methoxy-1,2,5-trimethyl-2-cyclohexen-1-yl]dipalladium (13), and Di-μ-chlorobis[(1,2,3-η)-5-methoxy-1,2,5-trimethyl-2-cyclohexen-1-yl]dipalladium (14). Similar treatment of 642 mg (2.47 mmol) of bis(acetonitrile)palladium dichloride, 224 mg (2.24 mmol) of $KHCO_3$, and 94 mg (0.55 mmol) of cupric chloride with 221 mg (1.81 mmol) of 1,2,4-trimethyl-1,4-cyclohexadiene at 17 °C for 21 h, as described for **7**, **8**, and **9**, afforded a yellow oil that was diluted in 2–3 mL of EtOAc and flash chromatographed through a 2.5 × 26 cm SiO_2 column packed with EtOAc–petroleum ether (2:3) and eluted with this solvent mixture. Removal of the solvent at reduced pressure (water aspirator) afforded first 124 mg (0.24 mmol, 26%) of a 1:1 mixture of **12** and **13** as a yellow oil, followed by 328 mg (0.63 mmol, 70%) of **14** as a yellow oil that solidified to yellow crystals in a refrigerator (4 °C). Separation of **12** and **13** was achieved by HPLC (EtOAc–petroleum ether, 1:9), which afforded **12** followed by **13**, both as yellow oils. (η^3-Cyclohexenyl)palladium complex **13**: ^{1}H NMR (200 MHz, $CDCl_3$, chair conformation) δ 4.62 (1 H, H-3, d, $J_{3,4e}$ = 3.7 Hz), 3.52 (1 H, H-4e, superficial t, $J_{4e,3} = J_{4e,5a}$ = 4.2 Hz), 3.39 (3 H, MeO, s), 3.06–2.95 (1 H, H-5, m, at least a nine-line pattern), 2.09 (3 H, MeC-2, s) overlapping 2.04 (1 H, H-6e, dd, $J_{6e,6a}$ = 14.6 Hz, $J_{6e,5a}$ = 6.0 Hz), 1.36 (3 H, MeC-1, s), 1.02 (1 H, H-6a, dd, $J_{6a,6e}$ = 16.3 Hz, $J_{6a,5a}$ = 10.7 Hz), 0.85 (3 H, MeC-5, d, J = 6.8 Hz); homonuclear decoupling, irradiation at δ 4.62 collapsed the signal at δ 3.52 to a d, irradiation at δ 3.52 collapsed the signals at δ 4.62 to a s and at δ 3.06–2.95 to an apparent septet, irradiation a δ 3.01 collapsed the signals at δ 3.52 to a d, at δ 2.04 to a d, at δ 1.02 to a d, and at δ 0.85 to a s, irradiation at δ 2.04 collapsed the signals at δ 3.06–2.95 to an apparent septet and at δ 1.02 to a d, irradiation at δ 1.02 simplified the signals at δ 3.06–2.95 and collapsed the signal at δ 2.04 to a d, and irradiation at δ 0.85 collapsed the signal at δ 3.06–2.95 to an apparent q. (η^3-Cyclohexenyl)palladium complex **14**: ^{1}H NMR (200 MHz, $CDCl_3$, boat conformation) δ 4.48 (1 H, H-3, d, $J_{3,4e}$ = 6.3 Hz), 2.98 (3 H, MeO, s), 2.24 (1 H, H-6e, d, $J_{6e,6a}$ = 17.9 Hz), 2.05 (3 H, MeC-2, s) superimposed on 2.15-1.93 (2 H, H-4a and H-4e, m), 1.79 (1 H, H-6a, d, $J_{6a,6e}$ = 18.3 Hz), 1.42 (3 H, MeC-1, s), 1.09 (3 H, MeC-5, s); ^{13}C NMR (50 MHz, $CDCl_3$, broad-band proton and off-resonance proton decoupling) 115.48 (s), 84.72 (s), 70.79 (s), 69.40 (d), 49.46 (q), 47.72 (t), 39.95 (t), 23.23 (q), 22.11 (q), 18.53 (q) ppm.

Di-μ-chlorobis[(1,2,3-η)-5-methoxy-1,2,4-trimethyl-2-cyclohexen-1-yl]dipalladium (12). Similar treatment of 650 mg (2.50 mmol) of bis(acetonitrile)palladium dichloride and 58 mg (0.38 mmol) of cupric chloride with 242 mg (1.98 mmol) of 1,2,4-trimethyl-1,4-cyclohexadiene, as described for **8** except that after the mixture was allowed to warm from −78 to 20 °C over a 24-h period the mixture was then stirred for an additional 96 h at 20 °C, afforded a red oil with black particles that was slurried in 2–3 mL of EtOAc and flash chromatographed through a 2 × 15 SiO_2 column packed and eluted with EtOAc–petroleum ether (2:3). Removal of the solvent at reduced pressure (water aspirator) afforded 167 mg (0.32 mmol, 29%) of **12** as a yellow oil that solidified to yellow crystals in a refrigerator (4 °C): ^{1}H NMR (200 MHz, $CDCl_3$, chair conformation) δ 4.47 (1 H, H-3, d, $J_{3,4e}$ = 3.7 Hz) superimposed on 4.49–4.39 (1 H, H-5a, m), 3.29 (3 H, MeO, s), 2.46 (1 H, H-4e, apparent qt, $J_{4e,Me}$ = 6.8 Hz, $J_{4e,3} = J_{4e,5a}$ = 3.8 Hz), 2.29 (1 H, H-6e, dd, $J_{6e,6a}$ = 15.5 Hz, $J_{6e,5a}$ = 5.8 Hz), 2.06 (3 H, MeC-2, s), 1.37 (3 H, MeC-1, s), 1.23 (1 H, H-6a, dd, $J_{6a,6e}$ = 16.0 Hz, $J_{6a,5a}$ = 9.2 Hz), 0.87 (3 H, MeC-4, d, J = 7.0 Hz); homonuclear decoupling, irradiation at δ 4.47 collapsed the signals at δ 2.46 to a q, at δ 2.29 to a d, and at δ 1.23 to a d, irradiation at δ 2.46 collapsed the signals at δ 4.47 and 0.87 to s and simplified the m at δ 4.49–4.39, irradiation at δ 2.29 simplified the m at δ 4.49–4.39 and collapsed the signal at δ 1.23 to a d, irradiation at ca. δ 1.23 simplified the signals at δ 4.49–4.39 and at δ 2.29, and irradiation at δ 0.87 collapsed the signal at δ 2.46 to a t; ^{13}C NMR (50 MHz, $CDCl_3$, broad-band proton and off-resonance proton decoupling) 112.20 (s), 88.61 (s), 79.13 (d), 76.42 (d), 56.07 (q), 38.05 (dd), 36.78 (d), 21.78 (q), 19.53 (q), 15.22 (q) ppm.

Di-μ-chlorobis[(1,2,3-η)-2,4,6-trimethyl-2-cyclohexen-1-yl]dipalladium (15) and Di-μ-chlorobis[(1,2,3-η)-5-methoxy-2,4,6-trimethyl-2-cyclohexen-1-yl]dipalladium (16). Similar treatment of 651 mg (2.51 mmol) of bis(acetonitrile)palladium dichloride, 220 mg (2.20 mmol) of $KHCO_3$, and 79 mg (0.46 mmol) of cupric chloride with 223 mg (1.83 mmol) of 1,3,5-trimethyl-1,4-cyclohexadiene as described for **7**, **8**, and **9**, afforded a gray-green slurry with some black particles that was immediately slurried in 2–3 mL of EtOAc and flash chromatographed through a 2 × 15 cm SiO_2 column packed and eluted with EtOAc–petroleum ether (3:7). Removal of the solvent at reduced pressure (water aspirator) afforded first 97 mg (0.18 mmol, 20%) of **15** as yellow crystals followed by 84 mg (0.14 mmol, 16%) of **16** as a yellow oil. (η^3-Cyclohexenyl)palladium complex **16**: ^{1}H NMR (200 MHz, $CDCl_3$, chair conformation) δ 4.74 (1 H, H-3, dd, $J_{3,4e}$ = 4.6 Hz, $J_{3,1}$ = 1.7 Hz), 4.48 (1 H, H-1, br s), 4.03 (1 H, H-5a, apparent t, $J_{5a,4e} = J_{5a,6a}$ = ca. 6 Hz), 3.31 (3 H, MeO, s), 2.59 (1 H, H-4e, at least a nine-line m), 2.06 (3 H, MeC-2, s), 1.32 (3 H, MeC-6, d, $J_{Me,6a}$ = 6.1 Hz) superimposed on 1.30–1.13 (1 H, H-6a, m), 0.88 (3 H, MeC-4, d, $J_{Me,4e}$ = 6.8 Hz); homonuclear decoupling, irradiation at δ 4.74 collapsed the signal at δ 2.59 to a q, irradiation at δ 4.03 collapsed the signal at δ 1.30–1.13 to a q, irradiation at δ 2.59 collapsed the signals at δ 4.74 to a d, at δ 4.03 to an apparent d, and at δ 0.88 to a s, irradiation at δ 1.21 collapsed the signal at δ 1.32 to a s, and irradiation at δ 0.88 collapsed the signal at δ 2.59 to a t.

Di-μ-chlorobis[(1,2,3-η)-2,4,6-trimethyl-2-cyclohexen-1-yl]dipalladium (15). Similar treatment of 655 mg (2.52 mmol) of bis(acetonitrile)palladium dichloride, 225 mg (2.25 mmol) of $KHCO_3$, and 72 mg (0.42 mmol) of cupric chloride with 246 mg (2.02 mmol) of 1,3,5-trimethyl-1,4-cyclohexadiene, as described for **9**, afforded a red-brown oil that was diluted with 2–3 mL of EtOAc and flash chromatographed through a 2 × 15 cm SiO_2 column packed and eluted with EtOAc–petroleum ether (3:7). Removal of the solvent at reduced pressure (water aspirator) afforded 157 mg (0.30 mmol, 30%) of **15** as yellow crystals: ^{1}H NMR (200 MHz, $CDCl_3$, boat conformation) δ 4.69 (2 H, H-1 and H-3, s), 2.10 (2 H, H-4 and H-6, dqd), 2.00 (3 H, MeC-2, s), 1.54 (1 H, H-5e, dt, $J_{5e,5a}$ = 12.5 Hz, $J_{5e,4} = J_{5e,6}$ = 5.2 Hz), 1.04 (6 H, MeC-4 and MeC-6, d, $J_{Me,4} = J_{Me,6}$ = 7.0 Hz), 0.04 (1 H, H-5a, q, $J_{5a,6} = J_{5a,4} = J_{5a,5e}$ = 11.7 Hz); homonuclear decoupling, irradiation at δ 2.10 collapsed the signals at δ 1.54 and 0.04 to d and at δ 1.04 to a s, irradiation at δ 1.54 collapsed the signal at δ 2.10 to a dq and at δ 0.04 to a t, irradiation at δ 1.04 collapsed the signal at δ 2.10 to a dd, and irradiation at δ 0.04 affected the signal at δ 2.10 and collapsed the signal at δ 1.54 to a t; ^{13}C NMR (50 MHz, $CDCl_3$, broad-band proton and off-resonance proton decoupling) 115.25 (s), 83.56 (2 C, d), 37.22 (dd), 35.62 (2 C, d), 22.51 (2 C, q), 22.41 (q) ppm.

Di-μ-chlorobis[(1,2,3-η)-5-methoxy-1-*tert*-butyl-2-cyclohexen-1-yl]dipalladium (17) and Di-μ-chlorobis[(1,2,3-η)-5-methoxy-2-*tert*-butyl-2-cyclohexen-1-yl]dipalladium (18). Similar treatment of 657 mg (2.53 mmol) of bis(acetonitrile)-palladium dichloride, 212 mg (2.12 mmol) of $KHCO_3$, and 52 mg

(0.30 mmol) of cupric chloride with 270 mg (1.98 mmol) of 1-*tert*-butyl-1,4-cyclohexadiene at 16 °C for 15 h, as described for **7**, **8**, and **9**, afforded a yellow-brown oil. The yellow-brown oil was diluted in 2–3 mL of EtOAc and flash chromatographed on a 2.5 × 25 cm SiO_2 column packed and eluted with EtOAc–petroleum ether (2:3) to afford first 13 mg (0.02 mmol, 2%) of a 3:2 mixture of di-μ-chlorobis[(1,2,3-η)-1-*tert*-butyl-2-cyclohexen-1-yl]dipalladium and di-μ-chlorobis[(1,2,3-η)-2-*tert*-butyl-2-cyclohexen-1-yl]dipalladium[20] as a pale yellow oil, which was inseparable on HPLC, followed by 477 mg (0.77 mmol, 78%) of a 1:9 mixture of **17** and **18**, which was also inseparable on HPLC, as a yellow oil that solidified in a refrigerator (4 °C). (η^3-Cyclohexenyl)palladium complex **17**: Partial ^{1}H NMR (200 MHz, $CDCl_3$, chair conformation, from a 1:9 mixture of **17** and **18**) δ 3.27 (3 H, MeO, s), 1.23 (9 H, (Me_3C, s). (η^3-Cyclohexenyl)palladium complex **18**, which slowly crystallized from a **17**–**18** mixture in Et_2O at 4 °C: ^{1}H NMR (200 MHz, $CDCl_3$, chair conformation) δ 4.78 (2 H, H-1 and H-3, apparent t, J = 2.7 Hz), 4.10 (1 H, H-5a, apparent quintet, overlapping tt, $J_{5a,4a} = J_{5a,6a}$ = 7.2 Hz, $J_{5a,4e} = J_{5a,6c}$ = 5.7 Hz), 3.24 (3 H, MeO, s), 2.36 (2 H, H-4e and H-6e, ddd, $J_{4e,4a} = J_{6e,6a}$ = 16.1 Hz, $J_{4e,5a} = J_{6e,5a}$ = 5.0 Hz, $J_{4e,3} = J_{6e,1}$ = 3.6 Hz), 1.39 (2 H, H-4a and H-6a, ddd, $J_{4a,4e} = J_{6a,6e}$ = 16.2 Hz, $J_{4a,5a} = J_{6a,5a}$ = 7.2 Hz, $J_{4a,3} = J_{6a,1}$ = 3.5 Hz), 1.21 (9 H, Me_3C, s); homonuclear decoupling, irradiation at δ 4.78 collapsed the signals at δ 2.36 and 1.39 to dd, irradiation at δ 4.10 collapsed the signals at δ 2.36 and 1.39 to dd, irradiation at δ 2.36 collapsed the signals at δ 4.78 to a d, at δ 4.10 to a t, and at δ 1.39 to an apparent dd, and irradiation at ca. δ 1.39 simplified the signals at δ 4.78, 4.10 and 2.36; ^{13}C NMR (50 MHz, $CDCl_3$, broad-band proton and off-resonance proton decoupling) 128.73 (s), 73.48 (d), 69.24 (2 C, d), 55.87 (q), 34.52 (s), 34.40 (2 C, t), 29.47 (3 C, q) ppm.

Di-μ-chlorobis[(1,2,3-η)-5-methoxy-1-methyl-2-cyclohexen-1-yl]dipalladium (19) and Di-μ-chlorobis[(1,2,3-η)-5-methoxy-2-methyl-2-cyclohexen-1-yl]dipalladium (20). Similar treatment of 653 mg (2.52 mmol) of bis(acetonitrile)-palladium dichloride, 214 mg (2.14 mmol) of $KHCO_3$, and 64 mg (0.38 mmol) of cupric chloride with 192 mg (2.04 mmol) of 1-methyl-1,4-cyclohexadiene, as described for **7**, **8**, and **9**, afforded a yellow oil. The yellow oil was diluted with 2–3 mL of EtOAc and flash chromatographed on a 2 × 15 cm SiO_2 column packed and eluted with EtOAc–petroleum ether (2:3) to afford first 40 mg (0.08 mmol, 8%) of a 1:2 mixture of di-μ-chlorobis[([1,2,3-η)-1-methyl-2-cyclohexen-1-yl]dipalladium and di-μ-chlorobis-[(1,2,3-η)-2-methyl-2-cyclohexen-1-yl]dipalladium[21] as a yellow oil, which was separable on HPLC, followed by 387 mg (0.72 mmol, 71%) of a 1:2 mixture of **19** and **20** as a yellow oil. Separation of **19** and **20** was achieved by HPLC (EtOAc–petroleum ether, 1:3), which afforded **19** followed by **20**, both as yellow oils. (η^3-Cyclohexenyl)palladium complex **19**: ^{1}H NMR (200 MHz, $CDCl_3$, chair conformation) δ 5.34 (1 H, H-2, d, $J_{2,3}$ = 6.7 Hz), 4.74 (1 H, H-3, dt, $J_{3,2}$ = 6.6 Hz, $J_{3,4a} = J_{3,4e}$ = 3.3 Hz), 4.24 (1 H, H-5a, tt, $J_{5a,4a} = J_{5a,6a}$ = 7.3 Hz, $J_{5a,4e} = J_{5a,6e}$ = 5.9 Hz), 3.29 (3 H, MeO, s), 2.43 (1 H, H-6e, $J_{6e,6a}$ = 16.4 Hz, $J_{6e,5a}$ = 5.7 Hz), 2.24 (1 H, H-4e, ddd, $J_{4e,4a}$ = 16.3 Hz, $J_{4e,5a}$ = 5.8 Hz, $J_{4e,3}$ = 3.4 Hz), 1.44 (3 H, MeC-1, s), 1.32 (1 H, H-6a, dd, $J_{6a,6e}$ = 16.3 Hz, $J_{6a,5a}$ = 7.3 Hz) overlapping ca. 1.32–1.14 (1 H, H-4a, m). (η^3-Cyclohexenyl)palladium complex **20**: ^{1}H NMR (200 MHz, $CDCl_3$, chair conformation) δ 4.70 (2 H, H-1 and H-3, t, $J_{1,6a} = J_{1,6e} = J_{3,4a} = J_{3,4e}$ = ca. 2.7 Hz), 4.16 (1 H, H-5a, tt, $J_{5a,4a} = J_{5a,6a}$ = 7.3 Hz, $J_{5a,4e} = J_{5a,6e}$ = 5.8 Hz), 3.27 (3 H, MeO, s), 2.34 (2 H, H-4e and H-6e, ddd, $J_{4e,4a} = J_{6e,6a}$ = 16.1 Hz, $J_{4e,5a} = J_{6e,5a}$ = 5.4 Hz, $J_{6e,1} = J_{4e,3}$ = 3.4 Hz), 2.07 (3 H, MeC-2, s), 1.34 (2 H, H-4a and H-6a, ddd, $J_{4a,4e} = J_{6a,6e}$ = 16.0 Hz, $J_{4a,5a} = J_{6a,5a}$ = 7.5 Hz, $J_{6a,1} = J_{4a,3}$ = 2.9 Hz); homonuclear decoupling, irradiation at δ 4.16 collapsed the signals at δ 2.34 and 1.34 to dd, irradiation at δ 2.34 collapsed the signals at δ 4.70 to a d, at δ 4.16 to a t, and at δ 1.34 to a dd, and irradiation at δ 1.34 collapsed the signals at δ 4.70 to a d, at δ 4.16 to an apparent t, and at δ 2.34 to an apparent dd.

Di-μ-chlorobis[(1,2,3-η)-2-cyclohexen-1-yl]dipalladium (21), *trans*-22, and *cis*-Di-μ-chlorobis[(1,2,3-η)-5-methoxy-2-cyclohexen-1-yl]dipalladium (23). To a cold (−78 °C, dry ice–acetone in a Dilvac Dewar bath), stirred yellow slurry of 650 mg (2.51 mmol) of bis(acetonitrile)palladium dichloride, 230 mg (2.30 mmol) of $KHCO_3$, and 73 mg (0.43 mmol) of cupric chloride in 15 mL of MeOH was slowly added (dropwise, 5 min) a solution of 165 mg (2.06 mmol) of 1,4-cyclohexadiene in 10 mL of MeOH, and then the reaction vessel containing the yellow slurry was sealed and placed in a freezer at −18 °C. After 117 h, the yellow-brown slurry was filtered through a 5-mm pad of Celite (dry packed) and the filter was rinsed with 10 mL of EtOAc. The yellow-brown filtrate—a yellow-brown precipitate remained on the filter—was concentrated in vacuo at water aspirator pressure to afford a red-brown oil that was immediately diluted in 2–3 mL of EtOAc and flash chromatographed through a 2 × 15 cm SiO_2 column packed and eluted with EtOAc–petroleum ether (3:2). Removal of solvent at reduced pressure (water aspirator) afforded first 59 mg (0.13 mmol, 13%) of **21** as pale yellow crystals follows by 111 mg (0.22 mmol, 21%) of a 57:43 mixture of **22** and **23** as a yellow oil, which was inseparable on HPLC. (η^3-Cyclohexenyl)palladium complex **21**:[22] ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.50 (1 H, H-2, t, $J_{2,1} = J_{2,3}$ = 6.4 Hz), 5.20 (2 H, H-1 and H-3, apparent dt, $J_{1,2} = J_{3,2}$ = 6.2 Hz, $J_{1,6a} = J_{3,4a} = J_{1,6e} = J_{3,4e}$ = 4.3 Hz), 1.80 (5 H, br s, $w_{1/2}$ = ca. 13 Hz), 1.12 (1 H, H-5e, m); homonuclear decoupling, irradiation at δ 5.50 collapsed the signal at δ 5.20 to an apparent t, irradiation at δ 5.20 collapsed the signal at δ 5.50 to a s, and irradiation at δ 1.80 collapsed the signal at δ 5.20 to a d. *trans*-(η^3-Cyclohexenyl)palladium complex **22**: ^{1}H NMR (200 MHz, $CDCl_3$, chair conformation, from a ca. 57:43 mixture of **22** and **23**) δ 5.53 (1 H, H-2, $J_{2,1} = J_{2,3}$ = 6.6 Hz), 5.04–4.95 (2 H, H-1 and H-3, m), 4.13 (1 H, H-5a, tt, $J_{5a,4a} = J_{5a,6a}$ = 6.8 Hz, $J_{5a,4e} = J_{5a,6e}$ = 5.6 Hz), 3.28 (3 H, MeO, s), 2.28 (2 H, H-4e and H-6e, ddd, $J_{4e,4a} = J_{6e,6a}$ = 16.7 Hz, $J_{4e,5a} = J_{6e,5a}$ = 5.4 Hz, $J_{6e,1} = J_{4e,3}$ = 3.4 Hz), 1.44 (2 H, H-4a and H-6a, ddd, $J_{4a,4e} = J_{6a,6e}$ = 16.5 Hz, $J_{4a,5a} = J_{6a,5a}$ = 6.8 Hz, $J_{6a,1} = J_{4a,3}$ = 3.5 Hz); homonuclear decoupling, irradiation at δ 5.53 collapsed the signal at δ 5.04–4.95 to an apparent t, irradiation at ca. δ 5.00 collapsed the signals a δ 5.53 to a s and at δ 2.28 and 1.44 to dd, irradiation a δ 4.13 collapsed the signals at δ 2.28 and 1.44 to dd, irradiation at δ 2.28 collapsed the signals at δ 5.04–4.95 to an apparent dd, at δ 4.13 to an apparent t, and δ 1.44 to a dd, and irradiation at δ 1.44 collapsed the signals at δ 5.04–4.95, at δ 4.13, and at δ 2.28. *cis*-(η^3-Cyclohexenyl)palladium complex **23**: ^{1}H NMR (200 MHz, $CDCl_3$, boat conformation, from a ca. 57:43 mixture of **22** and **23**) δ 5.50 (1 H, H-2, t, $J_{2,1} = J_{2,3}$ = 6.5 Hz), 5.00 (2 H, H-1 and H-3, t, $J_{1,2} = J_{3,2} = J_{3,4e} = J_{1,6e}$ = 6.3 Hz), 3.30 (3 H, MeO, s), 3.03 (1 H, H-5a, tt, $J_{5a,4a} = J_{5a,6a}$ = 8.8 Hz, $J_{5a,4e} = J_{5a,6e}$ = 5.4 Hz), 2.20 (2 H, H-4e and H-6e, dt, $J_{4e,4a} = J_{6e,6a}$ = 18.6 Hz, $J_{6e,1} = J_{4e,3} = J_{4e,5a} = J_{6e,5a}$ = 5.4 Hz), 1.80 (2 H, H-4a and H-6a, dd, $J_{4a,4e} = J_{6a,6e}$ = 17.9 Hz, $J_{4a,5a} = J_{6a,5a}$ = 8.7 Hz); homonuclear decoupling, irradiation at δ 5.50 collapsed the signal at δ 5.00 to a d, irradiation at δ 5.00 collapsed the signals at δ 5.50 to a s and at δ 2.19 to a dd, irradiation at δ 3.03 collapsed the signals at δ 2.19 to a dd and at δ 1.80 to a d, irradiation at ca. δ 2.19 collapsed the signals at δ 5.00 to a d, at δ 3.03 to a t, and at δ 1.80 to a d, and irradiation at ca. δ 1.80 collapsed the signals at δ 3.03 and 2.19 to apparent t.

Methyl *trans*-5-Methoxy-2,3-dimethyl-2-cyclohexene-1-carboxylate (24). Upon pressurizing a sealed 90-mL Fischer & Porter pressure tube containing a stirred gold-yellow slurry of 439 mg (0.78 mmol) of (η^3-cyclohexenyl)palladium complex **1** and 755 mg (7.86 mmol) of sodium propionate in 22 mL of MeOH to 3.8 atm with carbon monoxide, the mixture immediately turned black as a flocculent black precipitate formed. After 24 h the black slurry was filtered through a 1-cm pad of Celite (dry packed) and the filter rinsed with 50 mL of EtOAc to reveal a pale yellow filtrate that clouded as the EtOAc was introduced. Removal of

(20) ^{1}H NMR (200 MHz, $CDCl_3$, from the 3:2 mixture) of di-μ-chlorobis[(1,2,3-η)-1-*tert*-butyl-2-cyclohexen-1-yl]dipalladium: δ 5.39 (1 H, H-2, d, $J_{2,3}$ = 6.6 Hz), 5.00–4.92 (1 H, H-3, m), 2.05–1.92 (2 H, m), 1.92–1.63 (4 H, m), 1.22 (9 H, s). Di-μ-chlorobis[(1,2,3-η)-2-*tert*-butyl-2-cyclohexen-1-yl]dipalladium: δ 5.02 (2 H, H-1 and H-3, d, J = 4.2 Hz), 2.05–1.92 (2 H, m), 1.92–1.63 (4 H, m), 1.19 (9 H, s).

(21) ^{1}H NMR (200 MHz, $CDCl_3$) of di-μ-chlorobis[(1,2,3-η)-1-methyl-2-cyclohexen-1-yl]dipalladium: δ 5.31 (1 H, H-2, d, $J_{2,3}$ = 6.4 Hz), 4.98–4.90 (1 H, H-3, m), 2.2–1.5 (6 H), 1.45 (3 H, s). Di-μ-chlorobis-[(1,2,3-η)-2-methyl-2-cyclohexen-1-yl]dipalladium: δ 4.93 (2 H, H-1 and H-3, d, J = 4.6 Hz), 2.02 (3 H, s), 2.05–1.55 (6 H, m).

(22) Trost, B. M.; Strege, P. E.; Weber, L.; Fullerton, T J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3407–3415.

the solvent at reduced pressure (water aspirator) on a rotary evaporator afforded a white crystalline residue, which was triturated with 20 mL of petroleum ether and the slurry filtered through a second pad of Celite and the filter rinsed with 50 mL of petroleum ether. Removal of the petroleum ether from the filtrate at reduced pressure afforded 306 mg of a pale yellow oil that was flash chromatographed on a 2 × 15 cm SiO_2 column packed and eluted with EtOAc–petroleum ether (1:4) to afford 196 mg (0.99 mmol, 63%) of **24** as a colorless oil: ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.70 (3 H, CO_2Me, s) superimposed on 3.77–3.57 (1 H, H-5, complex m), 3.36 (3 H, OMe, s), 3.16 (1 H, H-1, m, $w_{1/2}$ = 11 Hz), 2.36 (1 H, H-4e, apparent dd with further fine splitting, $J_{4e,4a}$ = ca. 17 Hz, $J_{4e,5a}$ = 3.8 Hz), 2.10 (1 H, H-6e, dddd, $J_{6e,6a}$ = 12.9 Hz, $J_{6e,5a}$ = 5.1 Hz, $J_{6e,1e}$ = 3.2 Hz, $J_{6e,4e}$ = 1.2 Hz), 1.96 (1 H, H-4a, dd with further fine splitting, $J_{4a,4e}$ = ca. 17 Hz, $J_{4a,5a}$ = ca. 8 Hz), 1.79 (1 H, H-6a, ddd, $J_{6a,6e}$ = 12.7 Hz, $J_{6a,5a}$ = 9.3 Hz, $J_{6a,1e}$ = 6.1 Hz), and two overlapping Me multiplets with signals at 1.67, 1.66, 1.65, and 1.64 (6 H, MeC-2 and MeC-3); homonuclear decoupling, irradiation at δ 3.64 collapsed the signals at δ 2.36 and 1.96 to d and at δ 2.10 and 1.79 to dd, irradiation at δ 3.16 collapsed the signals at δ 2.10 and 1.79 to dd, irradiation at δ 2.36 collapsed the signals at δ 3.77–3.57 to an apparent ddd and at δ 1.96 to a d, irradiation at δ 2.10 collapsed the signals at δ 3.77–3.57 to an apparent ddd, at δ 3.16 to a d, and at δ 1.79 to an apparent dd, irradiation at δ 1.79 collapsed the signals at δ 3.77–3.57 to an apparent ddd, at δ 3.16 to a br s, and at δ 2.10 to an apparent dd.

Methyl *trans*-5-Methoxy-2,3-dimethyl-2-cyclohexene-1-carboxylate (24). Tandem Reaction. After stirring a yellow slurry of 639 mg (2.46 mmol) of bis(acetonitrile)palladium dichloride, 208 mg (2.08 mmol) of $KHCO_3$, 68 mg (0.40 mmol) of cupric chloride, and 218 mg (2.02 mmol) of 1,2-dimethyl-1,4-cyclohexadiene in 25 mL of MeOH in a 90 mL Fischer & Porter pressure tube under N_2 for 24 h, 968 mg (10.07 mmol) of sodium propionate was added, the walls of the tube were rinsed down with 10 mL of MeOH, and then the tube was sealed and pressurized to 4 atm with carbon monoxide. After 40 h the black slurry was filtered through a 5-mm pad of Celite (dry packed) and the filter rinsed first with 25 mL of MeOH and then with 50 mL of EtOAc. Removal of the solvent at reduced pressure (water aspirator) on a rotary evaporator afforded a white crystalline residue, which was partitioned between 25 mL of Et_2O and 25 mL of H_2O. The aqueous phase was subsequently extracted twice with 25-mL portions of Et_2O and the combined organic phase was dried ($MgSO_4$), filtered, and concentrated at water-aspirator pressure to afford 551 mg of a pale yellow oil. Following flash chromatography, 257 mg (1.30 mmol, 64%) of **24** was obtained as a colorless oil.

Methyl *trans*-5-Methoxy-2,5-dimethyl-2-cyclohexene-1-carboxylate (25). Upon pressurizing a sealed 90-mL Fischer & Porter pressure tube containing a stirred gold-yellow slurry of 243 mg (0.43 mmol) of (η^3-cyclohexenyl)palladium complex **2** and 415 mg (4.32 mmol) of sodium propionate in 30 mL of MeOH to 4 atm with carbon monoxide, the mixture immediately turned black as a flocculent black precipitate formed. After 120 h the black slurry was filtered through a 5-mm pad of Celite (dry packed) and the filter rinsed first with 25 mL of MeOH and then with 50 mL of EtOAc. Removal of the solvent at reduced pressure (water aspirator) on a rotary evaporator afforded a white crystalline residue, which was partitioned between 25 mL of Et_2O and 25 mL of H_2O. The aqueous phase was subsequently extracted twice with 25-mL portions of Et_2O, and the combined organic phase was dried ($MgSO_4$), filtered, and concentrated at water-aspirator pressure to afford a pale yellow oil. Following flash chromatography on a 2 × 15 cm SiO_2 column packed and eluted with EtOAc–petroleum ether (1:9), 162 mg (0.82 mmol, 95%) of **25** was obtained as a colorless oil: ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.44 (1 H, H-3, apparent ddd, J = 5.0, 2.4, 1.1 Hz), 3.71 (3 H, CO_2Me, s), 3.20 (3 H, MeO, s) superimposed on 3.33–3.13 (1 H, H-1, m), 2.22–2.03 (3 H, H-6e, H-4e, H-4a, three overlapping m), 1.77 (1 H, H-6a, dd, $J_{6a,6e}$ = 13.2 Hz, $J_{6a,1}$ = 11.2 Hz), 1.68 (3 H, MeC-2, apparent dd, J = 2.3, 1.2 Hz), 1.20 (3 H, MeC-5, s); homonuclear decoupling, irradiation at δ 5.44 simplified the signals at δ 2.22–2.03 and 1.68, irradiation at δ 3.23 simplified the signal at δ 2.22–2.03 and collapsed the signal at δ 1.77 to a d, irradiation at ca. δ 2.12 collapsed the signal at δ 5.44 to a br s, collapsed the m at δ 3.33–3.13, and affected the signal at δ 1.77, irradiation at δ 1.77 affected the signals at δ 3.33–3.13 and 2.22–2.03.

Methyl *trans*-5-Methoxy-2,5-dimethyl-2-cyclohexene-1-carboxylate (25). Tandem Reaction. After allowing a cold (−11 °C, salt–ice in a Dilvac Dewar bath), stirred yellow slurry of 601 mg (2.32 mmol) of bis(acetonitrile)palladium dichloride, 200 mg (2.00 mmol) of $KHCO_3$, 49 mg (0.29 mmol) of cupric chloride, and 216 mg (2.00 mmol) of 1,4-dimethyl-1,4-cyclohexadiene in 20 mL of MeOH in a 90-mL Fischer & Porter pressure tube under N_2 to slowly warm to 12 °C over a 22-h period, 974 mg (10.15 mmol) of sodium propionate was added, the walls of the tube were rinsed down with 5 mL of MeOH, and then the tube was sealed and pressurized to 3.5 atm with carbon monoxide. After 50 h the black slurry was filtered through a 1-cm pad of Celite (dry packed) and the filter rinsed with 50 mL of EtOAc to reveal a pale blue filtrate that clouded when the EtOAc was introduced. Removal of the solvent at water-aspirator pressure on a rotary evaporator afforded 2.05 g of a pale blue solid, which was triturated with 20 mL of petroleum ether and the slurry filtered through a second 1-cm pad of Celite and the filter rinsed with 50 mL of petroleum ether. Removal of the petroleum ether at water-aspirator pressure afforded 416 mg of a blue oil that was flash chromatographed on a 2 × 13 cm SiO_2 column packed and eluted with EtOAc–petroleum ether (1:9) to afford 171 mg (0.86 mmol, 43%) of **25** as a colorless oil.

Methyl (1α,5β,6β)-5-Methoxy-3,6-dimethyl-2-cyclohexene-1-carboxylate (26). Upon pressurizing a sealed 90-mL Fischer & Porter pressure tube containing a stirred gold-yellow slurry of 287 mg (0.51 mmol) of (η^3-cyclohexenyl)palladium complex **3** and 480 mg (5.0 mmol) of sodium propionate in 25 mL of MeOH to 3.5 atm with carbon monoxide, the mixture immediately turned black as a flocculent black precipitate formed. After 20 h the black slurry was filtered through a 1-cm pad of Celite (dry packed) and the filter rinsed with 50 mL of EtOAc to reveal a colorless filtrate that clouded as the EtOAc was introduced. Removal of the solvent at reduced pressure (water aspirator) on a rotary evaporator afforded 638 mg of a white solid, which was triturated with 25 mL of petroleum ether, and the slurry was filtered through a second 5-mm pad of Celite and the filter rinsed with 50 mL of petroleum ether. Removal of the petroleum ether from the filtrate at reduced pressure afforded 174 mg of a pale yellow oil that was flash chromatographed on a 2 × 13 cm SiO_2 column packed and eluted with EtOAc–petroleum ether (1:9) to afford 133 mg (0.67 mmol, 66%) of **26** as a colorless oil: ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.35 (1 H, H-2, dq, $J_{2,1}$ = 3.3 Hz, $J_{2,Me}$ = 1.7 Hz), 3.70 (3 H, CO_2Me, s), 3.52 (1H, H-5, td, $J_{5,4}$ = 5.4 Hz, $J_{5,6}$ = 2.9 Hz), 3.57 (3 H, MeO, s), 2.98 (1 H, H-1, at least a 10-line m), 2.27 (1 H, H-6, quintet of d, $J_{6,Me}$ = $J_{6,1}$ = 6.6 Hz, $J_{6,5}$ = 2.9 Hz), 2.11 (2 H, H-4, br s, $w_{1/2}$ = ca. 11 Hz), 1.71 (3 H, MeC-3, br s, $w_{1/2}$ = 4.5 Hz), 0.97 (3 H, MeC-6, d, J = 7.1 Hz); homonuclear decoupling, irradiation at δ 5.35 collapsed the signals at δ 2.98 to a dq and at δ 1.71 to a t, irradiation at δ 3.52 collapsed the signal at δ 2.27 to a quintet and affected the signal at δ 2.11, irradiation at δ 2.98 collapsed the signals at δ 5.35 to a q and at δ 2.27 to a qd, and affected the signal at δ 2.11, irradiation at δ 2.27 collapsed the signals at δ 3.52 to a t and at δ 0.97 to a s, and simplified the m at δ 2.98, irradiation at δ 2.11 collapsed the signals at δ 3.52 to a d and at δ 1.71 to a t, irradiation at δ 1.71 collapsed the signals at δ 5.35 to a dt and at δ 2.98 to an apparent dq and provided fine structure (apparent td) to the signal at δ 2.98, and irradiation at δ 0.97 collapsed the signal at δ 2.27 to a dd.

Methyl (1α,5β,6β)-5-Methoxy-3,6-dimethyl-2-cyclohexene-1-carboxylate (26). Tandem Reaction. After allowing a cold (−13 °C, salt–ice in a Dilvac Dewar bath), stirred yellow slurry of 623 mg (2.41 mmol) of bis(acetonitrile)palladium dichloride, 50 mg (0.29 mmol) of cupric chloride, and 219 mg (2.03 mmol) of 1,4-dimethyl-1,4-cyclohexadiene in 20 mL of MeOH in a 90-mL Fischer & Porter pressure tube under N_2 to slowly warm to 20 °C over a 24-h period, 498 mg (5.19 mmol) of sodium propionate was quickly added and then the tube was sealed and pressurized to 3.5 atm with carbon monoxide. After 20 h the black slurry was filtered through a 1-cm pad of Celite (dry packed) and the filter rinsed with 65 mL of EtOAc to reveal a colorless filtrate that clouded as the EtOAc was introduced. Refiltration through a second pad of Celite afforded a colorless filtrate, which also clouded when the filter was rinsed with 50 mL of EtOAc. Removal

of the solvent at water-aspirator pressure on a rotary evaporator afforded 415 mg of a yellow oil containing brown particles, which was triturated five times with 15-mL portions of petroleum ether and the triturates filtered through a third pad of Celite. Removal of the petroleum ether at water-aspirator pressure afforded 248 mg of a pale green oil that after flash chromatography afforded 142 mg (0.72 mmol, 35%) of **26** as a colorless oil.

Methyl (1α,5β,6β)-5-Methoxy-2,6-dimethyl-2-cyclohexene-1-carboxylate (27) and Methyl (1α,4β,5β)-5-Methoxy-2,4-dimethyl-2-cyclohexene-1-carboxylate (28). Similar treatment of 320 mg (0.57 mmol) of (η^3-cyclohexenyl)palladium complex **5** and 543 mg (5.66 mmol) of sodium propionate, as described for **26**, afforded 214 mg of a pale yellow oil that was flash chromatographed to afford 196 mg (0.99 mmol, 87%) of a colorless oil, which was a 2:1 mixture (GLC and NMR) of **27** and **28**. Methyl cyclohexenecarboxylate **27**: ^{1}H NMR (200 MHz, $CDCl_3$, from a 2:1 mixture) δ 5.47–5.40 (1 H, H-3, m), 3.71 (3 H, CO_2Me, s), 3.57–3.47 (1 H, H-5, m), 3.33 (3 H, MeO, s), 2.90 (1 H, H-1, d, J = 5.4 Hz), 2.31–2.01 (3 H, H-4 and H-6, overlapping m), 1.68 (3 H, MeC-2, br s with fine splitting, $w_{1/2}$ = 5.7 Hz), 0.97 (3 H, MeC-6, d, J = 6.8 Hz). Methyl cyclohexenecarboxylate **28**: ^{1}H NMR (200 MHz, $CDCl_3$, from a 2:1 mixture) δ 5.47–5.40 (1 H, H-3, m), 3.71 (3 H, CO_2Me, s), 3.57–3.47 (1 H, H-5, m), 3.36 (3 H, MeO, s), 3.12 (1 H, H-1, t, J = 5.4 Hz), 2.57–2.41 (1 H, H-4, m), 2.25 (1 H, H-6e, ddd, J = 12.9, 6.8, 3.1 Hz), 1.87 (1 H, H-6a, ddd, J = 12.6, 6.3, 3.1 Hz), 1.68 (3 H, MeC-2, br s with fine splitting, $w_{1/2}$ = 5.7 Hz), 0.96 (3 H, MeC-4, d, J = 7.3 Hz).

Methyl *trans*-5-Methoxy-2-isopropyl-5-methyl-2-cyclohexene-1-carboxylate (29). Similar treatment of 319 mg (0.52 mmol) of (η^3-cyclohexenyl)palladium complex **9** and 523 mg of sodium propionate, as described for **24**, afforded 279 mg of a pale yellow oil that was flash chromatographed on a 2 × 15 cm SiO_2 column packed and eluted with EtOAc–petroleum ether (1:9) to afford 194 mg (0.86 mmol, 83%) of **29** as a colorless oil: ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.49–5.41 (1 H, H-3, complex m), 3.70 (3 H, CO_2Me, s), 3.42 (1 H, H-1, ddd, $J_{1,6a}$ = 10.9 Hz, $J_{1,6e}$ = 5.5 Hz, $J_{1,3}$ = 2.7 Hz), 3.18 (3 H, MeO, s), 2.3–2.0 (4 H, complex overlapping m), 1.78 (1 H, H-6a, dd, $J_{6a,6e}$ = 13.2 Hz, $J_{6a,1}$ = 11.0 Hz), 1.19 (3 H, Me), 1.05 (3 H, d, J = 6.6 Hz), 1.01 (3 H, d, J = 6.8 Hz); homonuclear decoupling, irradiation at δ 5.45 affected the signal at δ 2.3–2.0, irradiation at δ 3.42 affected the signal at δ 2.3–2.0 and collapsed the signal at δ 1.78 to a d, irradiation at ca. δ 2.15 collapsed the signals at δ 5.49–5.41 to a s, at δ 3.42 and 1.78 to d, and at δ 1.05 and 1.01 to s, irradiation at δ 1.78 collapsed the signals at δ 3.42 and 2.3–2.0, and irradiation at ca. δ 1.03 affected the signal at δ 2.3–2.0.

Methyl *trans*-1,2,3,4,5,6,7,8-Octahydro-3-methoxy-1-naphthalenecarboxylate (30). Similar treatment of 524 mg (0.86 mmol) of (η^3-cyclohexenyl)palladium complex **10** and 820 mg (8.53 mmol) of sodium propionate, as described for **25** except the reaction was performed at 5 atm of carbon monoxide pressure for only 3 h, afforded 467 mg of a colorless oil that was flash chromatographed to afford 325 mg (1.45 mmol, 85%) of **30** as a colorless oil: ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.70 (3 H, CO_2Me, s) superimposed on 3.78–3.60 (1 H, H-3a, complex m), 3.37 (3 H, MeO, s), 3.10 (1 H, H-1, apparent t, $w_{1/2}$ = 11 Hz), 2.30 (1 H, H-4e, apparent dd, $J_{4e,4a}$ = ca. 18 Hz, $J_{4e,3a}$ = ca. 3 Hz), 2.12 (1 H, H-2e, dddd, $J_{2e,2a}$ = 12.9 Hz, $J_{2e,1e}$ = 5.1 Hz, $J_{2e,3a}$ = 3.2 Hz, $J_{2e,4e}$ = 1.2 Hz), 1.94 (4 H, H-5, H-8, br s, $w_{1/2}$ = 8 Hz) superimposed on 1.98 (1 H, H-4a, m), 1.82 (1 H, H-2a, ddd, $J_{2a,2e}$ = 12.9 Hz, $J_{2a,3a}$ = 9.3 Hz, $J_{2a,1e}$ = 6.1 Hz), and two overlapping multiplets with signals at 1.64, 1.63, 1.62, 1.60 (4 H, H-6 and H-7); homonuclear decoupling, irradiation at δ 3.10 collapsed the signals at δ 2.12 and 1.82 to d, irradiation at δ 2.30 simplified the signal at δ 3.78–3.60, irradiation at δ 2.12 simplified the signal at δ 3.78–3.60, collapsed the signals at δ 3.10 to an apparent d and at δ 1.82 to a dd, and irradiation at δ 1.82 simplified the signals at δ 3.10 to an apparent d and at δ 2.12 to a ddd.

Methyl *trans*-1,2,3,4,5,6,7,8-Octahydro-3-methoxy-1-naphthalenecarboxylate (30). Tandem Reaction. Similar treatment of a mixture of 655 mg (2.53 mmol) of bis(acetonitrile)palladium dichloride, 216 mg (2.16 mmol) of $KHCO_3$, 74 mg (0.43 mmol) of cupric chloride, and 270 mg (2.01 mmol) of 1,2,3,4,5,8-hexahydronaphthalene after 24 h with 960 mg (10.00 mmol) of sodium propionate, as described for **24** (tandem reaction) except the second reaction was performed at 5 atm of carbon monoxide pressure for 18 h, afforded 724 mg of a pale yellow oil that was flash chromatographed on a 2 × 15 cm SiO_2 column packed and eluted with EtOAc–petroleum ether (1:9) to afford 359 mg (1.26 mm, 80%) of **30** as a colorless oil.

Methyl *trans*-2,3,4,5,6,7-Hexahydro-6-methoxy-1*H*-indene-4-carboxylate (31). Similar treatment of 296 mg (0.51 mmol) of (η^3-cyclohexenyl)palladium complex **11** and 506 mg (5.27 mmol) of sodium propionate, as described for **24**, afforded 225 mg of a pale yellow oil that was flash chromatographed on a 2 × 15 cm SiO_2 column packed and eluted with EtOAc–petroleum ether (1:9) to afford 189 mg (0.90 mmol, 89%) of **31** as a colorless oil: ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.70 (3 H, CO_2Me, s) superimposed on 3.81–3.68 (1 H, H-6, m), 3.39 (3 H, MeO, s), 3.22 (1 H, H-4, apparent t, $w_{1/2}$ = 13 Hz), 2.45–2.20 (5 H, H-1, H-3, and H-7, m), 2.12 (1 H, H-5, ddd, $J_{5e,5a}$ = 13.2 Hz, $J_{5,4}$ = 5.9 Hz, $J_{5,6}$ = 2.9 Hz), 1.99–1.78 (4 H, H-2, H-7a, and H-5a, m); homonuclear decoupling, irradiation at δ 3.75 collapsed the signal at δ 2.12 to a dd and simplified the signals at δ 2.45–2.20 and 1.99–1.78, irradiation at δ 3.22 collapsed the signal at δ 2.12 to a dd and simplified the signals at δ 1.99–1.78, irradiation at δ 2.35 collapsed the signal at δ 3.81–3.68 to an apparent ddd and affected the signals at δ 1.99–1.78, irradiation at δ 2.12 collapsed the signal at δ 3.81–3.68 to an apparent ddd, at δ 3.22 to a br s and affected the signals at δ 1.99–1.78, and irradiation at δ 1.89 collapsed the signals at δ 3.81–3.68 to an apparent dd, at δ 3.22 to an apparent d, and affected the signals at δ 2.45–2.20 and 2.12.

Methyl *trans*-2,3,4,5,6,7-Hexahydro-6-methoxy-1*H*-indene-4-carboxylate (31). Tandem Reaction. Similar treatment of a mixture of 652 mg (2.51 mmol) of bis(acetonitrile)palladium dichloride, 229 mg (2.29 mmol) of $KHCO_3$, 72 mg (0.42 mmol) of cupric chloride, and 243 mg (2.02 mmol) of 4,7-dihydroindan after 25 h with 963 mg (10.00 mmol) of sodium propionate, as described for **24** (tandem reaction) except the second reaction was performed at 4 atm of carbon monoxide pressure for 70 h, afforded a pale yellow oil that after flash chromatography on a 3 × 29 cm SiO_2 column packed and eluted with EtOAc–petroleum ether (1:9) afforded 173 mg (0.83 mmol, 41%) of **31** as a colorless oil.

Methyl *trans*-5-Methoxy-2,3,5-trimethyl-2-cyclohexene-1-carboxylate (32). Similar treatment of 320 mg (0.54 mmol) of (η^3-cyclohexenyl)palladium complex **14** and 594 mg (6.18 mmol) of sodium propionate, as described for **24** except the reaction was performed at 3.7 atm of carbon monoxide pressure for 54 h, afforded 210 mg of a pale yellow oil that after flash chromatography on a 2 × 15 cm SiO_2 column packed and eluted with EtOAc–petroleum ether (1:9) afforded 165 mg (0.78 mmol, 72%) of **32** as a colorless oil: ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.69 (3 H, CO_2Me, s), 3.19 (3 H, MeO, s) superimposed on 3.30–3.12 (1 H, H-1, m), 2.09 (2 H, H-4, br s, $w_{1/2}$ = 8 Hz) overlapping ca. 2.1 (1 H, H-6e, dd, $J_{6e,6a}$ = ca. 13 Hz, $J_{6e,1}$ = ca. 6 Hz), 1.70 (1 H, H-6a, dd, $J_{6a,6e}$ = 12.8 Hz, $J_{6a,1}$ = 11.2 Hz) overlapping 1.65 (3 H, s), 1.62 (3 H, s), 1.19 (3 H, MeC-5, s); homonuclear decoupling, irradiation at ca. δ 3.2 collapsed the signals at δ 2.1 and 1.70 to apparent d, irradiation at ca. δ 2.1 collapsed the signals at δ 3.30–3.12 and 1.70 to apparent d, and irradiation at δ 1.70 collapsed the signals at δ 3.30–3.12 and 2.1 to apparent d.

Acknowledgment. We are grateful to the Swedish Board for Technical Development, the Swedish Natural Science Research Council, the Rutgers University Research Council, and the Rutgers University Faculty Academic Study Program for supporting this research. We also thank S. Hanson, A. Vitagliano, and K. Zetterberg for NMR data, T. H. O. Eriksson for MS data, and G. Hammarberg for IR spectra.

Registry No. 1, 91443-64-0; 2, 91443-65-1; 3, 91443-66-2; 4, 91466-43-2; 5, 91443-67-3; 6, 114300-90-2; 7, 114300-91-3; 8, 114300-92-4; 9, 114300-93-5; 10, 114300-94-6; 11, 114300-95-7; 12, 114300-96-8; 13, 114300-97-9; 14, 114300-98-0; 15, 114300-99-1; 16, 114301-00-7; 17, 114301-01-8; 18, 114301-02-9; 19, 114301-03-0; 20, 114301-04-1; 21, 12090-09-4; 22, 114301-05-2; 23, 114376-25-9; 24, 111026-08-5; 25, 114300-81-1; 26, 114300-82-2; 27, 114300-83-3; 28, 114300-84-4; 29, 114300-85-5; 30, 114300-86-6; 31, 114300-87-7; 32, 114300-88-8; bis(acetonitrile)palladium dichloride, 14592-56-4; di-μ-chlorobis[(1,2,3-η)-1-*tert*-butyl-2-cyclohexen-1-yl]dipalladium,

114301-06-3; di-μ-chlorobis[(1,2,3-η)-2-*tert*-butyl-2-cyclohexen-1-yl]dipalladium, 114301-07-4; di-μ-chlorobis[(1,2,3-η)-1-methyl-2-cyclohexen-1-yl]dipalladium, 96981-64-5; di-μ-chlorobis[(1,2,3-η)-2-methyl-2-cyclohexen-1-yl]dipalladium, 32915-13-2; 1,2-dimethyl-1,4-cyclohexadiene, 17351-28-9; 1,4-dimethyl-1,4-cyclohexadiene, 4074-22-0; 1,5-dimethyl-1,4-cyclohexadiene, 4190-06-1; 1-isopropyl-4-methyl-1,4-cyclohexadiene, 99-85-4; 1,4-diisopropyl-1,4-cyclohexadiene, 114300-89-9; 1,2,3,4,5,8-hexahydronaphthalene, 36231-13-7; 2,3,4,7-tetrahydro-1*H*-indene, 7603-37-4; bicyclo[4.2.0]octa-1(6),3-diene, 38325-66-5; 1,2,4,5-tetramethyl-1,4-cyclohexadiene, 26976-92-1; 1,2,4-trimethyl-1,4-cyclohexadiene, 72985-36-5; 1,3,5-trimethyl-1,4-cyclohexadiene, 4074-23-1; 3-phenyl-1,4-cyclohexadiene, 4794-05-2; 1-*tert*-butyl-1,4-cyclohexadiene, 94625-86-2; 1-methyl-1,4-cyclohexadiene, 4313-57-9; 1,4-cyclohexadiene, 628-41-1; biphenyl, 92-52-4.

Supplementary Material Available: Melting points, IR, and elemental analyses (C, H) data for (η^3-cyclohexenyl)palladium complexes **7–16**, **18** and **20**, boiling points, IR, ^{13}C NMR, mass spectra, and elemental analyses (C, H) data for methyl cyclohexenecarboxylates **24–32**, and experimental details and NMR data for 1-isopropyl-4-methyl-1,4-cyclohexadiene, 1,4-diisopropyl-1,4-cyclohexadiene, 1,2,3,4,5,8-hexahydronaphthalene, 4,7-dihydroindan, 1,2,3,6-tetrahydrobenzocyclobutene, 1,2,4-trimethyl-1,4-cyclohexadiene, 1,3,5-trimethyl-1,4-cyclohexadiene, 3-phenyl-1,4-cyclohexadiene, 1-*tert*-butyl-1,4-cyclohexadiene, and 1-methyl-1,4-cyclohexadiene (11 pages). Ordering information is given on any current masthead page.

(Cycloalkylidenemethyl)triphenylphosphonium Salts as Versatile Intermediate Reagents

Toru Minami,* Shoji Shikita, Shuichiro So, Minoru Nakayama, and Izumi Yamamoto

Department of Industrial Chemistry, Kyushu Institute of Technology, Sensuicho, Tobata, Kitakyushu 804, Japan

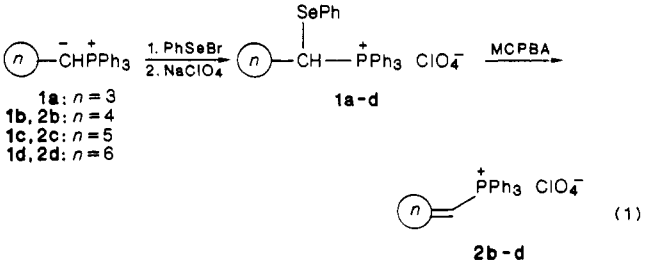
Received August 27, 1987

The (cycloalkylidenemethyl)triphenylphosphonium salts **2b–d** were synthesized in high yields by phenylselenylation of (cycloalkylmethylene)triphenylphosphoranes with benzeneselenenyl bromide to the [cycloalkyl(phenylseleno)methyl]triphenylphosphonium salts **1b–d** and subsequent oxidative elimination of the phenylseleno moiety, while the synthesis of the (cyclopropylidenemethyl)triphenylphosphonium salt **2a** was unsuccessful. Hydrolysis of **2b–d** in aqueous THF and methanol containing sodium hydroxide was studied. The reactions of the (cyclohexylidenemethyl)phosphonium salt **2d** and 1.1 equiv of butyllithium with aldehydes **9** gave alkenylcyclohexenes **10d–f** in 56–81% yields, whereas similar reactions using 1.5 equiv and 2 equiv of butyllithium produced allenes **11d–f** as major products together with small amounts of **10d,e**. Similar reactions of the (cyclopentylidenemethyl)phosphonium salt **2c** and butyllithium with **9** gave alkenylcyclopentenes **10a–c** in 56–80% yields, regardless of the amount of butyllithium used. The formation mechanism of **10** and **11** was discussed.

We have recently reported the synthesis and synthetic applications of 1-cycloalkenyltriphenylphosphonium salts.[1] Of these salts, the 1-cyclobutenyltriphenylphosphonium salt has been well-studied owing to its high reactivity and versatility.[2] On the other hand, (cycloalkylidenemethyl)triphenylphosphonium salts, a new type of related phosphonium salts, are similarly expected to be versatile intermediate reagents for the synthesis of functionalized cycloalkanes and fused cycloalkane compounds, but their syntheses have, to our knowledge, not been reported to date. Furthermore, in comparison with the 1-cycloalkenyltriphenylphosphonium salts, we became interested in the influence of ring sizes of the (cycloalkylidenemethyl)triphenylphosphonium salts on chemical and physical properties. We report herein the synthesis and synthetic utilization of small-ring to medium-ring (cycloalkylidenemethyl)phosphonium salts.

Results and Discussion

According to the established procedure,[1a,2a] the [cycloalkyl(phenylseleno)methyl]triphenylphosphonium salts **1a–d** were prepared in good yields from phenylselenylation of (cycloalkylmethylene)triphenylphosphoranes with benzeneselenenyl bromide. Oxidative elimination of the phenylseleno moiety in **1b–d** successfully produced the corresponding (cycloalkylidenemethyl)triphenylphosphonium perchlorates **2b–d**, while similar treatment of the [cyclopropyl(phenylseleno)methyl]triphenylphosphonium salt **1a** did not lead to the expected (cyclopropylidenemethyl)phosphonium salt **2a**; only an unidentified salt[3] was obtained. The structures of **2b–d** are



(1)

clearly derivable from their ^1H NMR (Experimental Section) and ^{13}C NMR spectral data (Table I). Thus, for **2d**, the ^1H NMR spectrum showed characteristically a vinylic proton at δ 6.15 as a doublet ($^2J_{P-H}$ = 23.7 Hz), and the ^{13}C NMR spectrum exhibited two olefinic carbons at δ 99.5 ($^1J_{^{31}P-^{13}C}$ = 88.5 Hz, C-1) and δ 178.0 (C-2), two allylic carbons to phosphorus at δ 35.0 ($^3J_{^{31}P-^{13}C}$ = 7.7 Hz, C-3)

(1) (a) Saleh, G.; Minami, T.; Ohshiro, Y.; Agawa, T. *Chem. Ber.* **1979**, *112*, 355. (b) Minami, T.; Hanamoto, T.; Hirao, I. *J. Org. Chem.* **1985**, *50*, 1278.

(2) (a) Minami, T.; Sako, H.; Ikehira, T.; Hanamoto, T.; Hirao, I. *J. Org. Chem.* **1983**, *48*, 2569. (b) Minami, T.; Chikugo, T.; Hanamoto, T. *J. Org. Chem.* **1986**, *51*, 2210. (c) Minami, T.; Harui, N.; Taniguchi, Y. *J. Org. Chem.* **1986**, *51*, 3572. (d) Minami, T.; Okada, Y.; Nomura, R.; Hirota, S.; Nagahara, Y.; Fukuyama, K. *Chem. Lett.* **1986**, 613. (e) Okada, Y.; Minami, T.; Yahiro, S.; Kaku, H.; Ishiyama, M. *Nippon Kagaku Kaishi* **1987**, 1244.

(3) The ^{13}C NMR spectrum showed only sp^2 carbons at δ 111–137, which could not be assigned.

0022-3263/88/1953-2937$01.50/0