($CDCl_3$, 300 MHz) $\delta_H$ 8.09 (d, $J$ = 7 Hz, 2 H), 7.93 (d, $J$ = 7.2 Hz, 2 H), 7.90 (d, $J$ = 8.5 Hz, 2 H), 7.63 (s, 4 H), 7.63-7.47 (m, 8 H); $^{13}C$ NMR ($CDCl_3$ $\delta_C$ 125.4, 125.8, 126.08, 126.11, 127.1, 127.7, 128.3, 130.0, 131.7, 133.9, 139.7, 140.0.

**Acknowledgment.** We acknowledge grants from the Research Committee of the New Zealand Universities Grants Committee.

**Registry No.** **9**, 103-05-9; **10**, 4912-92-9; **13**, 68426-07-3; **14** 5-sulfonyl fluoride, 124620-37-7; **14** 6-sulfonyl fluoride, 124620-32-2; **14** 7-sulfonyl fluoride, 124620-38-8; **15**, 124620-30-0; **17**, 380-18-7; **19**, 20480-66-4; **20**, 79235-09-9; **24**, 79297-74-8; **25**, 70561-39-6; **26**, 101740-77-6; **28**, 124620-39-9; **29**, 124620-40-2; **30**, 67476-28-2; **33**, 124620-33-3; **34**, 124620-28-6; **36**, 124620-34-4; **37**, 101100-11-2; **38**, 109445-09-2; **39**, 124620-29-7; **40**, 124620-35-5; **41**, 38229-94-6; **42**, 124751-28-6; **43**, 124751-29-7; **45**, 124620-36-6; **47**, 30078-89-8; **48**, 58978-27-1; **49**, 3018-20-0; **50**, 52376-43-9; **51**, 124620-31-1; **52** (isomer 1), 124620-41-3; **52** (isomer 2), 124620-42-4; **53**, 64065-97-0; lithium phenylacetylide, 4440-01-1; camphor, 76-22-2; 2-(phenylethynyl)isoborneol, 124620-27-5; 2-methylcyclohexanone, 583-59-5; (3-phenylpropyl)magnesium chloride, 54812-94-1; terephthaldehyde, 623-27-8; fluorosulfuric acid, 7789-21-1.

**Supplementary Material Available:** $^1H$ and $^{13}C$ NMR spectra for compound **36** (2 pages). Ordering information is given on any current masthead page.

(35) Hart, H.; Harada, K.; Du, C. J. F. *J. Org. Chem.* **1985**, *50*, 3104.

# *trans*-Bis(5-acetoxy-1,2,3-$\eta^3$-cyclohexenyl)palladium Complexes by Palladium(II)-Promoted Addition of Acetate to 1,4-Cyclohexadienes[1]

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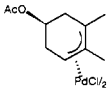
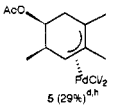
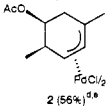
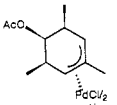
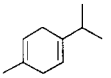
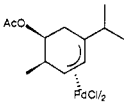
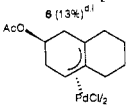
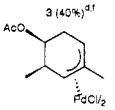
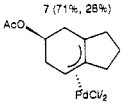
Acetate adds to alkyl-substituted 1,4-cyclohexadienes in the presence of bis(acetonitrile)palladium dichloride to yield the corresponding *trans*-bis(5-acetoxy-1,2,3-$\eta^3$-cyclohexenyl)palladium complexes. This highly stereoselective and regioselective palladium(II)-promoted distal addition is achieved in either acetic acid or acetonitrile solvents.

($\eta^3$-Allyl)palladium complexes have become useful synthons in organic synthesis.[2,3] Standard preparation procedures include insertion of palladium(0) into the carbon-heteroatom bond of allylic systems,[4] direct substitution of the allylic hydrogen of alkenes by palladium(II),[5] and palladium(II)-promoted addition of nucleophiles and palladium across 1,3-dienes.[6] Both Larock's group with acyclic nonconjugated dienes[7] and this group with 1,4-cyclohexadienes[1,8] demonstrated that nonconjugated dienes afford ($\eta^3$-allyl)palladium complexes via the initial addition

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

| 1,4-cyclohexadiene | product (% yield)[b] | 1,4-cyclohexadiene | product (% yield)[b] |
|---|---|---|---|
|  |  1 (92%, 73%)[c] |  |  5 (29%)[d,h] |
|  |  2 (56%)[d,e] |  |  6 (13%)[d,i] |
|  |  3 (40%)[d,f] |  |  7 (71%, 28%) |
|  |  4 (36%)[d,g] |  |  8 (67%, 29%) |

[a] Details in the Experimental Section. [b] The first isolated yield is in acetic acid; a second is in acetonitrile. [c] See ref 9. [d] Hydride-addition complex formation was avoided by slowly adding (2 h, syringe pump) the diene to the mixture. [e] Similar results (53-54%) were obtained by adding (15 min, syringe or addition funnel) the diene to a mixture containing $CuCl_2$. [f] *p*-Cymene was also formed (7%). [g] *m*-Xylene was also formed (23%). [h] 1,2,4-Trimethylbenzene was also formed (53%). [i] 1,3,5-Trimethylbenzene was also formed (33%).

(1) (a) 1,4-Diene-Derived ($\eta^3$-Allyl)palladium Complexes. 5. Part 4: Åkermark, B.; Söderberg, B. C.; Hall, S. S. *J. Org. Chem.* **1989**, *54*, 1110-1116. (b) Taken in part from the Ph.D. (Teknisk Doktor) Dissertation of B.C.S., The Royal Institute of Technology, Dec 1987. (c) Initially disclosed at the 196th National Meeting of the American Chemical Society, Los Angeles, CA, Sept 1988, paper ORGN 197.

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

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

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

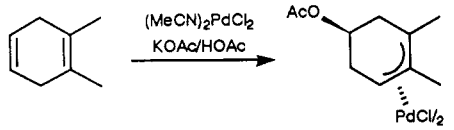
(5) (a) Hüttel, R.; Dietl, H.; Christ, H. *Chem. Ber.* **1964**, *97*, 2037-2045. (b) Trost, B. M.; Strege, P. E.; Weber, L.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3407-3415. (c) Hartley, F. R. *The Chemistry of Palladium and Platinum*; Applied Science: London, 1973;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

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

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

0022-3263/90/1955-1344$02.50/0 

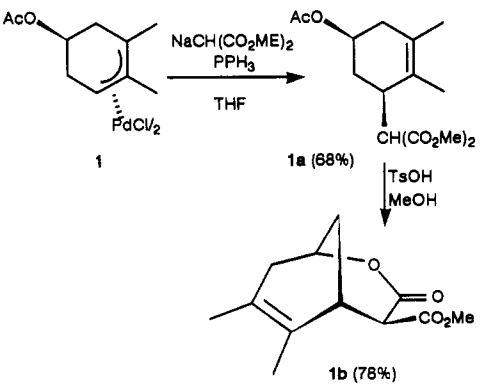
of palladium(II) and a nucleophile across the less hindered double bond. Subsequent migration of the metal toward the remaining double bond generates the ($\eta^3$-allyl)palladium system. These previous studies demonstrated that *trans*-bis(5-alkoxy- and 5-hydroxy-1,2,3-$\eta^3$-cyclohexenyl)-palladium complexes can be stereoselectively and regioselectively formed by the palladium(II)-promoted distal addition of nucleophiles such as alcohols and water to a variety of alkyl-substituted 1,4-cyclohexadienes.[1,8] Herein is described the palladium(II)-promoted addition of acetate to a selection of alkyl-substituted 1,4-cyclohexadienes to prepare the corresponding *trans*-bis(5-acetoxy-1,2,3-$\eta^3$-cyclohexenyl)palladium complexes.




1

Stirring a yellow slurry of 1,2-dimethyl-1,4-cyclohexadiene (1.00 mmol) and bis(acetonitrile)palladium dichloride (1.25 mmol) in acetic acid, in the presence of potassium bicarbonate (5.00 mmol), for 22 h at ambient temperature (20 °C) afforded *trans*-bis(5-acetoxy-1,2-dimethyl-1,2,3-$\eta^3$-cyclohexenyl)palladium chloride (**1**, 92%).[9] Similar results were also obtained when the reaction was carried out in acetonitrile for 21 h using acetic acid (5.00 mmol) and sodium bicarbonate (5.00 mmol) as reagents, in the presence of cupric chloride (0.12 mmol), albeit, in ca. 20% lower yield. These latter conditions provide the versatility to introduce any acylate at the C-5 site. Table I compiles the alkyl-substituted 1,4-cyclohexadienes that were subjected to the reaction conditions in acetic acid (**1–8**)[10,11] and acetonitrile (**1**, **7**, **8**). In all of these examples, the acetate added in a distal manner to the less-hindered terminus of the less substituted double bond of the 1,4-cyclohexadiene system. Initially, 1,4-dimethyl-1,4-cyclohexadiene in acetic acid afforded a mixture of the acetate–addition complex **2**, as well as the hydride–addition complex bis(1,4-dimethyl-1,2,3-$\eta^3$-cyclohexenyl)palladium chloride (**2a**).[12] The formation of **2a** was subsequently avoided either by slow addition of the 1,4-cyclohexadiene solution to the reaction mixture using a syringe pump or more conveniently by normal addition of the 1,4-cyclohexadiene solution (with a syringe or addition funnel) to a reaction mixture that also contained cupric chloride (ca. 10–20%). One of these two techniques was employed for the remaining table entries that were executed in acetic acid.

The structure and relative stereochemistry of *trans*-bis(5-acetoxy-1,2-dimethyl-1,2,3-$\eta^3$-cyclohexenyl)palladium chloride (**1**) was confirmed by a two-step transformation to the bicyclic lactone 4-*exo*-carbomethoxy-6,7-dimethyl-2-oxabicyclo[3.3.1]non-6-en-3-one (**1b**), a compound previously prepared in a related series.[1a] The first step employed an alkylation with dimethyl malonate anion to yield the acetoxy malonate derivative dimethyl *cis*-5-acetoxy-2,3-dimethyl-2-cyclohexene-1-malonate (**1a**). Dimethyl malonate anion alkylations occur directly at carbon on the face of the $\eta^3$-allyl unit distal to the palladium.[13] In addition, with the ($\eta^3$-cyclohexenyl)palladium complexes, alkylation with dimethyl malonate anion occurs regioselectively at the less substituted terminus of the $\eta^3$-cyclohexenyl system.[1a]




1 **1a** (68%) **1b** (78%)

Since the acetoxypalladation to form the *trans*-bis(5-acetoxy-1,2,3-$\eta^3$-cyclohexenyl)palladium complexes is a distal addition process[14] and the alkylation with malonate anion is an inversion, the relative stereochemistry of the malonate and the acetoxy groups is expected to be cis, which was corroborated by the subsequent lactonization. NMR analysis of **1a** indicates that the acetoxy group prefers the equitorial position ($J_{5a,4a} = J_{5a,6a} = 8.8$ Hz and

(8) (a) Söderberg, B. C.; Åkermark, B.; Hall, S. S. *J. Org. Chem.* **1988**, *53*, 2925–2937. (b) Åkermark, B.; Söderberg, B. C.; Hall, S. S. *Organometallics* **1987**, *6*, 2608–2610. (c) Hall, S. S.; Åkermark, B. *Organometallics* **1984**, *3*, 1745–1748.

(9) In a parallel experiment, which was performed exactly as **1** (HOAc) except that cupric chloride (0.20 mmol) had been added to the reaction mixture as oxidant to recycle any generated Pd(0), the yield of **1** after only 1 h was already 79% (isolated).

(10) Similar treatment of 80 mg (1.00 mmol) of 1,4-cyclohexadiene, as described for **1** (HOAc) except the reaction was performed for only 15 min, afforded 29 mg (0.06 mmol, 13%) of di($\mu$-chloro)bis[(1,2,3-$\eta$)-2-cyclohexen-1-yl]dipalladium (**9a**),[5b,8a,22] followed by 27 mg (0.05 mmol, 10%) of di($\mu$-chloro)bis[(1,2,3-$\eta$)-5-acetoxy-2-cyclohexen-1-yl]dipalladium (**9**) as a partially separable mixture. Complex **9**: $^1$H NMR (200 MHz, from a mixture of **9a** and **9**) $\delta$ 5.61 (1 H, H-2, t, $J_{2,1} = J_{2,3} = 6.5$ Hz), 5.32 (1 H, H-5e, quintet, $J_{5e,4a} = J_{5e,4e} = J_{5e,6a} = J_{5e,6e} = 4.8$ Hz), 5.02 (2 H, H-1 and H-3, ddd, $J_{1,2} = J_{3,2} = 6.5$ Hz, $J_{1,6e} = J_{3,4e} = 4.4$ Hz, $J_{1,6a} = J_{3,4a} = 2.1$ Hz), 2.27 (2 H, H-4a, H-6a, ddd, $J_{4a,4e} = J_{6a,6e} = 17.8$ Hz, $J_{4a,5e} = J_{6a,5e} = 5.2$ Hz, $J_{4a,3} = J_{6a,1} = 2.0$ Hz), 1.99 (3 H, s), 1.78 (2 H, H-4e, H-6e, dt with further fine splitting, $J_{4e,4a} = J_{6e,6a} = 17.7$ Hz, $J_{4e,3} = J_{4e,5e} = J_{6e,5e} = J_{6e,1} = 4.7$ Hz); homonuclear decoupling, irradiation at $\delta$ 5.61 collapsed the signal at $\delta$ 5.02 to a dd, irradiation at $\delta$ 5.32 collapsed the signals at $\delta$ 2.27 and 1.78 to dd, irradiation at $\delta$ 5.02 collapsed the signals at $\delta$ 5.61 to a s and at $\delta$ 2.27 and 1.78 to dd, irradiation at $\delta$ 2.27 collapsed the signals at $\delta$ 5.32 to a br m and at $\delta$ 5.02 and 1.78 to dd, irradiation at $\delta$ 1.78 collapsed the signals at $\delta$ 5.32 to a t and at $\delta$ 5.02 and 2.27 to dd; $^{13}$C NMR (100 MHz, from a mixture of **9a** and **9**) 170.32 (CO, s), 101.82 (C-1, d), 73.68 (2 C, C-2 and C-6, d), 65.00 (C-4, d), 33.90 (2 C, C-3 and C-5, t), 21.20 (MeCO, q) ppm.

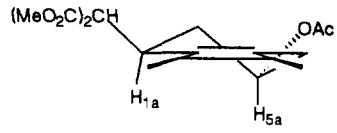
(11) Attempted palladium(II)-promoted addition of acetate to 3-phenyl-1,4-cyclohexadiene, using the reaction conditions described for **1** (HOAc), afforded only biphenyl (34%). A similar result had been observed in an attempted methanol addition.[8a]

(12) Similar treatment of 108 mg (1.00 mmol) of 1,4-dimethyl-1,4-cyclohexadiene, as described for **1** (HOAc) except the reaction was performed for only 80 min, afforded di($\mu$-chloro)bis[(1,2,3-$\eta$)-1,4-dimethyl-2-cyclohexen-1-yl]dipalladium (**2a**, yellow oil, 18%),[23] followed by **2** (37%). Complex **2a**: IR (film) 2950, 2915, 2865, 1440, 1430, 1370, 1030, 1015, 915, 735 cm$^{-1}$; $^1$H NMR (200 MHz) $\delta$ 5.26 (1 H, H-2, d, $J_{2,3} = 6.4$ Hz), 4.68 (1 H, H-3, dd, $J_{3,2} = 6.4$ Hz, $J_{3,4e} = 1.2$ Hz), 2.14–1.91 (2 H, H-4e, H-6e, complex m), 1.86–1.63 (2 H, H-5e, H-6a, complex m), 1.44 (3 H, MeC-1, s), 1.00 (3 H, MeC-4, d, $J = 6.9$ Hz), 0.74–0.52 (1 H, H-5a, complex m); homonuclear decoupling, irradiation at $\delta$ 5.26 collapsed the signal at $\delta$ 4.68 to an apparent s, irradiation at $\delta$ 4.68 collapsed the signal at $\delta$ 5.26 to a s, irradiation at $\delta$ 2.03 collapsed the signals at $\delta$ 4.68 to a d and at $\delta$ 1.00 to a s and simplified the signals at $\delta$ 1.86–1.63 and 0.74–0.52, irradiation at $\delta$ 1.75 sharpened the signal at $\delta$ 4.68 to a resolved dd and simplified the signals at $\delta$ 2.14–1.91 and 0.74–0.52, irradiation at $\delta$ 1.00 simplified the signal at $\delta$ 2.14–1.91, irradiation at $\delta$ 0.74–0.52 simplified the signals at $\delta$ 2.14–1.91 and 1.86–1.63; $^{13}$C NMR (100 MHz) 100.86 (C-2, d), 95.26 (C-1, s), 80.41 (C-3, d), 34.52 (t), 34.34 (C-4, d), 28.30 (dd), 24.99 (MeC-1, q), 22.21 (MeC-4, q) ppm. Similar treatment of 108 mg (1.00 mmol) of 1,4-dimethyl-1,4-cyclohexadiene, as described for **1** (HOAc) except that $Na_2PdCl_4$ (367 mg, 1.25 mmol) was used, afforded a mixture of *p*-xylene (17%), **2a** (23%), and **2** (21%).

(13) (a) Trost, B. M.; Weber, L. *J. Am. Chem. Soc.* **1975**, *97*, 1611–1612. (b) Collins, D. J.; Jackson, W. R.; Timms, R. N. *Tetrahedron Lett.* **1976**, 495–496. (c) Trost, B. M.; Weber, L.; Strege, P. E.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3416–3426.

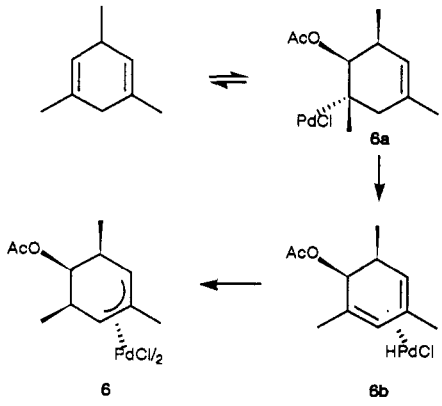
(14) (a) Henry, P. M.; Ward, G. A. *J. Am. Chem. Soc.* **1971**, *93*, 1494–1497. (b) Wolfe, S.; Campbell, P. G. C. *Ibid.* **1971**, *93*, 1497–1499.

$J_{5a,4e} = J_{5a,6e} = 5.9$ Hz) and the dimethyl malonate group the pseudoequitorial position, thus the preferred conformation for **1a** is shown.

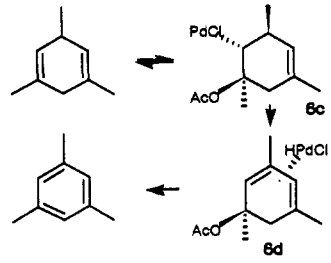



**1a**

The mechanism[1,8] for the formation of these *trans*-bis(5-acetoxy-1,2,3-$\eta^3$-cyclohexenyl)palladium complexes, using complex **6** as an example, involves the distal addition of acetate to the less hindered terminus of the less substituted double bond of the alkyl-substituted 1,4-cyclohexadiene and palladium(II)[14] to the more hindered terminus to afford $\sigma$-cyclohexenylpalladium complex **6a**.[15] Subsequent $\beta$-elimination of hydride from the allylic carbon generates 5-acetoxy-1,3-cyclohexadienylpalladium complex **6b**, and readdition of palladium hydride from the same face[16] affords the *trans*-bis(5-acetoxy-1,2,3-$\eta^3$-cyclohexenyl)palladium complex **6**. The mechanism dictates not only the relative stereochemistry of the nucleophile (in this case, acetate) and the metal, but also the stereochemistry of a substituent at the C-4 position since the hydride is delivered from the metal (proximal) as the palladium ratchets around the $\alpha$-face of the cyclohexadiene system to secure a stable position. It is interesting to note in this case that the palladium(II) also prefers to be distal to the methyl at the C-3 position in its initial approach to the 1,3,5-trimethyl-1,4-cyclohexadiene, which ultimately secures the stereochemistry of the C-6 methyl in complex **6**.

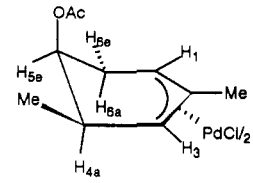



(15) It is conceivable that for the di- and trialkyl-substituted 1,4-cyclohexadienes, where there is at least one alkyl group on each double bond, the initial acetoxypalladation may not be regioselective. After the possible alternative $\sigma$-cyclohexenylpalladium complex **6c** eliminates palladium hydride ($\beta$-elimination), the tertiary 5-acetoxy-1,3-cyclohexadienylpalladium complex **6d** could eliminate acetic acid to form 1,3,5-trimethylbenzene, rather than reaccepting palladium hydride to generate a *trans*-bis(5-acetoxy-1,2,3-$\eta^3$-cyclohexenyl)palladium complex.




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

The *trans*-bis(5-acetoxy-1,2,3-$\eta^3$-cyclohexenyl)palladium complexes appear to prefer half-boat conformations (see the example conformation for complex **4**) with the 5-acetoxy group at the axial site, which positions the group as far away from the metal as possible. For the *trans*-bis(5-acetoxy-1,2,3-$\eta^3$-cyclohexenyl)palladium chloride series **1–5**, the average vicinal coupling constant between the C-5 and the C-4 and C-6 protons is $J_{5e,4a} = J_{5e,6a} = J_{5e,4e} = J_{5e,6e} = 5.1$ Hz, and the average vicinal coupling constants between C-1 and C-6 and between C-3 and C-4 protons are $J_{1,6e} = J_{3,4e} = 4.5$ Hz and $J_{1,6a} = J_{3,4a} = 2.2$ Hz.[17] Another diagnostic feature of the half-boat conformation is the average C-6 and C-4 geminal proton coupling values of $J_{4e,4a} = J_{6e,6a} = 17.4$ Hz for this series (**1–5**).



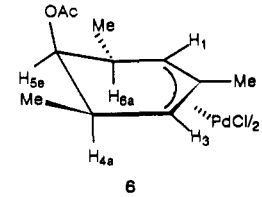

**4**

Other useful NMR characterization features of the *trans*-bis(5-acetoxy-1,2,3-$\eta^3$-cyclohexenyl)palladium complexes **1–9** include the resonances for the protons of the methyl group attached to C-1 at $\delta$ 1.43 and to C-2 at $\delta$ 2.06, and for protons attached to C-1 and C-3 at $\delta$ 4.60 and to C-2 at $\delta$ 5.47, as well as the vicinal proton couplings through the (1,2,3-$\eta^3$-cyclohexenyl)palladium system, which are $J_{1,2} = J_{2,3} = 6.5$ Hz and $J_{1,3} = 2.0$ Hz.

## Experimental Section[18]

All reactions to generate ($\eta^3$-cyclohexenyl)palladium complexes were performed under a static $N_2$ atmosphere in oven-dried, 25- or 50-mL, two-neck, round-bottomed flasks equipped with magnetic stir bars. Palladium dichloride was from Engelhard and Johnson Matthey, Inc. Bis(acetonitrile)palladium dichloride was prepared by the general method of Kharasch et al.[19] The preparations of the alkyl-substituted 1,4-cyclohexadienes have

(17) The exception is the symmetrical complex **6**, which is probably a flattened half-boat since the vicinal coupling constants between both the C-5 and the C-4 and C-6 protons ($J_{5e,4a} = J_{5e,6a}$ = ca. 4 Hz) and between the C-1 and C-6 and between the C-3 and C-4 protons ($J_{1,6a} = J_{3,4a} < 1$ Hz) are smaller.




**6**

(18) Melting points (uncorrected) were determined with a Büchi Model 510 apparatus. The IR spectra were determined with a Perkin-Elmer Model 257 grating spectrophotometer and the FT-IR spectra with a Nicolet Model 5ZDX Fourier transform infrared spectrophotometer. All NMR spectra were determined in $CDCl_3$ and the chemical shifts are expressed in $\delta$ values (ppm) relative to a $Me_4Si$ internal standard. The $^1H$ NMR spectra were determined at 200 MHz with a Bruker Model WP 200 and an IBM Model WP-200SY and at 400 MHz with a Bruker Model AM 400 and a Varian Model VXR-400S Fourier transform spectrometers, and proton assignments were confirmed by homonuclear decoupling studies. The $^{13}C$ NMR spectra were determined at 50 and 100 MHz, and broad-band proton-decoupled and off-resonance proton-decoupled spectra were collected for all new products. Mass spectra were determined on a Finnigan Model 4000 spectrometer (70 eV) with Finnigan Model 9610 GLC and Data General Model Nova 3 data system attachments. Bulb-to-bulb distillations were accomplished on a Büchi Model GKR-50 Kugelrohr apparatus, and the boiling point temperature cited was the oven temperature. Microanalyses were performed by Mikro Kemi AB, Uppsala, Sweden, and Hoffmann-La Roche Inc., Nutley, NJ.

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

been described.[1,8] Acetic acid (glacial, 99.8%), dimethyl malonate, triphenylphosphine, *p*-toluenesulfonic acid, and sodium hydride (80% dispersion in mineral oil) were from Aldrich Chemical Co. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl radical, and acetonitrile was dried over molecular sieves (4-Å) prior to use. Slow continuous addition of 1,4-cyclohexadiene solutions was achieved using a Sage Instruments Model 355 syringe pump. Flash chromatography was performed on silica gel 60 (230–400 mesh, E. Merck).[20] It is recommended that the entire reaction sequence to generate the ($\eta^3$-cyclohexenyl)palladium complexes and the subsequent flash chromatography be performed without interruption to remove the product complex as quickly as possible from the impurities. Once pure, these ($\eta^3$-cyclohexenyl)palladium complexes are relatively stable and are not air-sensitive, but as a precaution they were usually stored neat as oils or as crystals at −18 °C under $N_2$. See ref 1 and 8 for other general experimental comments.

**Di(μ-chloro)bis[(1,2,3-η)-5-acetoxy-1,2-dimethyl-2-cyclohexen-1-yl]dipalladium (1, HOAc).** Within 15 min after a solution of 108 mg (1.00 mmol) of 1,2-dimethyl-1,4-cyclohexadiene in 6 mL of acetic acid was added (dropwise, 5 min) to a stirred yellow slurry of 325 mg (1.25 mmol) of bis(acetonitrile)palladium dichloride and 500 mg (5.00 mmol) of potassium bicarbonate in 10 mL of acetic acid at 20 °C a clear yellow solution formed. After 22 h, the yellow solution was poured into 25 mL of water, and the resulting yellow-white suspension was extracted twice with 50-mL portions of chloroform. The combined organic phase was washed twice with 50-mL portions of sodium bicarbonate solution (10%) and dried ($MgSO_4$), and the solvent was removed at reduced pressure (water aspirator) on a rotary evaporator to afford a yellow oil, which was diluted with 1–2 mL of EtOAc and flash chromatographed (1.5 × 15-cm column packed and eluated with EtOAc–petroleum ether, 3:7). Removal of solvent at reduced pressure (water aspirator) afforded 284 mg (0.46 mmol, 92%) of 1 as a yellow oil, which solidified to yellow crystals in a freezer (−18 °C): mp 99 °C (with decomposition to black particles); IR (KBr) 2950, 2840, 1735, 1435, 1390, 1375, 1360, 1305, 1245, 1130, 1030, 980, 895 $cm^{-1}$; $^1H$ NMR (200 MHz) δ 5.34 (1 H, H-5e, quintet, $J_{5e,4a} = J_{5e,4e} = J_{5e,6a} = J_{5e,6e}$ = 5.2 Hz), 4.53 (1 H, H-3, dd, $J_{3,4e}$ = 4.2 Hz, $J_{3,4a}$ = 2.1 Hz), 2.54 (1 H, H-6a, dd, $J_{6a,6e}$ = 17.2 Hz, $J_{6a,5e}$ = 5.2 Hz), 2.28 (1 H, H-4a, ddd, $J_{4a,4e}$ = 16.9 Hz, $J_{4a,5e}$ = 5.6 Hz, $J_{4a,3}$ = 2.0 Hz), 2.06 (3 H, MeC-2, s), 1.96 (3 H, s), 1.70–1.54 (2 H, H-6e, H-4e, overlapping m), 1.42 (3 H, MeC-1, s); irradiation at δ 5.34 collapsed the signals at δ 2.54 to a d and at δ 2.88 to a br d and simplified the signal at δ 1.70–1.54, irradiation at δ 4.53 collapsed the signals at δ 2.28 to a dd and at δ 1.70–1.54 to an apparent dt, irradiation at δ 2.54 collapsed the signal at δ 5.34 to a q and simplified the signal at δ 1.70–1.54, irradiation at δ 2.28 affected the signal at δ 5.34 and collapsed the signals at δ 4.53 to a d and at δ 1.70–1.54 to an apparent dd, irradiation at ca. δ 1.6 collapsed the signals at δ 5.34 to a br t and at δ 4.53 and 2.54 to d and at δ 2.28 to a dd; $^{13}C$ NMR (50 MHz) 169.25 (CO, s), 113.11 (C-2, s), 85.50 (C-1, s), 70.20 (d), 66.02 (d), 40.97 (t), 34.10 (t), 21.87 (q), 21.07 (q), 18.74 (q) ppm. Anal. Calcd for $(C_{10}H_{15}O_2PdCl)_2$: C, 38.86; H, 4.89. Found: C, 38.90; H, 4.90.

**Di(μ-chloro)bis[(1,2,3-η)-5-acetoxy-1,2-dimethyl-2-cyclohexen-1-yl]dipalladium (1, MeCN, $CuCl_2$).** To a cold (0 °C, ice–water in a Dewar bath), stirred yellow slurry of 289 mg (1.11 mmol) of bis(acetonitrile)palladium dichloride, 420 mg (5.00 mmol) of sodium bicarbonate, and 21 mg (0.12 mmol) of cupric chloride (dihydrate) in 10 mL of acetonitrile was added (dropwise, 5 min) a solution of 108 mg (1.00 mmol) of 1,2-dimethyl-1,4-cyclohexadiene in 5 mL of acetonitrile, followed 10 min later by the addition (dropwise, 5 min) or a solution of 300 mg (5.00 mmol) of acetic acid in 5 mL of acetonitrile, which turned the mixture to a green slurry within 10 min. The green slurry was then allowed to warm slowly to ambient temperature, and after 22 h the now yellow slurry was filtered through a 5-mm pad of $MgSO_4$ on a 5-mm pad of Celite 545 (dry packed), and the filter was rinsed first with 25 mL of EtOAc and then with 50 mL of $Et_2O$. The yellow filtrate was concentrated in vacuo (water aspirator pressure) on a rotary evaporator to afford a brown oil, which was diluted in 1–2 mL of EtOAc and flash chromatographed (3.5 × 15-cm column packed and eluated with EtOAc–petroleum ether, 1:2). Removal of solvent at reduced pressure (water aspirator) afforded 225 mg (0.36 mmol, 73%) of 1 as a yellow solid: mp 102–114 °C (with decomposition to black particles).

**Di(μ-chloro)bis[(1,2,3-η)-5-acetoxy-1,4-dimethyl-2-cyclohexen-1-yl]dipalladium (2, HOAc).**[12] To a stirred yellow slurry of 325 mg (1.25 mmol) of bis(acetonitrile)palladium dichloride and 500 mg (5.00 mmol) of potassium bicarbonate in 10 mL of acetic acid at 20 °C was slowly added (syringe pump, 110 min) a solution of 108 mg (1.00 mmol) of 1,4-dimethyl-1,4-cyclohexadiene in 6 mL of acetic acid. After 48 h the resultant yellow solution containing black particles [palladium(0)] was poured into 50 mL of water and extracted twice with 25-mL portions of dichloromethane. The combined yellow organic phase was washed twice with 25-mL portions of sodium bicarbonate solution (10%) and dried ($MgSO_4$), and the solvent was removed at reduced pressure (water aspirator) on a rotary evaporator to afford yellow crystals, which were dissolved in 1–2 mL of EtOAc and flash chromatographed (1.5 × 15-cm column packed and eluated with EtOAc–petroleum ether, 3:7). Removal of solvent at reduced pressure (water aspirator) afforded 174 mg (0.28 mmol, 56%) of 2 as yellow crystals: mp 101 °C (with decomposition to black particles); IR (KBr) 2965, 2920, 2840, 1735, 1450, 1380, 1245, 1085, 1040, 1025, 1000, 970, 900 $cm^{-1}$; $^1H$ NMR (200 MHz) δ 5.45 (1 H, H-5e, q, $J_{5e,4a} = J_{5e,6a} = J_{5e,6e}$ = 5.3 Hz), 5.38 (1 H, H-2, d, $J_{2,3}$ = 6.5 Hz), 4.61 (1 H, H-3, dd, $J_{3,2}$ = 6.5 Hz, $J_{3,4a}$ = 2.5 Hz), 2.49–2.32 (1 H, H-4a, m) on which is superimposed 2.37 (1 H, H-6a, dd, $J_{6a,6e}$ = 18.0 Hz, $J_{6a,5e}$ = 4.7 Hz), 2.00 (3 H, s), 1.67 (1 H, H-6e, dd, $J_{6e,6a}$ = 17.4 Hz, $J_{6e,5e}$ = 5.9 Hz), 1.46 (3 H, MeC-1, s), 0.99 (3 H, MeC-4, d, $J$ = 7.1 Hz); irradiation at δ 5.45 collapsed the signals at δ 2.37 and 1.67 to d and affected the signal at δ 2.49–2.30, irradiation at δ 5.38 collapsed the signal at δ 4.61 to a d and affected the signals at δ 2.37 and 1.67, irradiation at δ 4.61 collapsed the signal at δ 5.38 to a s and simplified the signal at δ 2.49–2.30, irradiation at δ 2.40 collapsed the signals at δ 5.45 to a m and at δ 4.61 to a d and at δ 0.99 to a s, irradiation at δ 2.37 collapsed the signals at δ 5.45 to a br s and at δ 4.61 and 1.67 to d and at δ 0.99 to a s, irradiation at δ 1.67 affected the signal at δ 5.45 and collapsed the signal at δ 2.37 to a d, irradiation at δ 0.99 collapsed the signal at δ 2.49–2.30 to a dd; $^{13}C$ NMR (50 MHz) 169.21 (CO, s), 100.11 (C-2, d), 90.31 (C-1, s), 75.59 (d), 68.10 (d), 38.59 (C-6, t), 36.58 (C-4, d), 24.71 (MeC-1, q), 20.85 (MeCO, q), 16.56 (MeC-4, q) ppm. Anal. Calcd for $(C_{10}H_{15}O_2PdCl)_2$: C, 38.86; H, 4.89. Found: C, 38.50; H, 4.80.

**Di(μ-chloro)bis[(1,2,3-η)-5-acetoxy-1,4-dimethyl-2-cyclohexen-1-yl]dipalladium (2, HOAc, $CuCl_2$).** To a stirred yellow-green slurry of 325 mg (1.25 mmol) of bis(acetonitrile)palladium dichloride, 500 mg (5.00 mmol) of potassium bicarbonate, and 32 mg (0.19 mmol) of cupric chloride (dihydrate) in 10 mL of acetic acid at 20 °C was slowly added (syringe or addition funnel, 15 min) a solution of 108 mg (1.00 mmol) of 1,4-dimethyl-1,4-cyclohexadiene in 6 mL of acetic acid. After 24 h the green slurry with suspended black particles was filtered through a 5-mm pad of Celite 545 (dry packed), and the filter containing a black residue was rinsed with 50 mL of $CH_2Cl_2$. The filtrate was washed twice with 25-mL portions of water and then twice with 25-mL portions of sodium bicarbonate solution (10%) and dried ($MgSO_4$), and the solvent was removed at reduced pressure (water aspirator) on a rotary evaporator to afford 186 mg of a yellow-brown solid, which was dissolved with 1–2 mL of EtOAc and flash chromatographed (3.5 × 15-cm column packed and eluted with EtOAc–hexane, 3:7). Removal of solvent at reduced pressure afforded 166 mg (0.27 mmol, 54%) of 2 as a yellow crystals: mp 100–102 °C (with decomposition to black particles).

**Di(μ-chloro)bis[(1,2,3-η)-5-acetoxy-4-methyl-1-(methylethyl)-2-cyclohexen-1-yl]dipalladium (3, HOAc).** Similar treatment of 136 mg (1.00 mmol) of 1-methyl-4-(methylethyl)-1,4-cyclohexadiene, as described for 2 (HOAc) except that the reaction was performed for 44 h, afforded first 10 mg (7%) of *p*-cymene followed by 136 mg (0.20 mmol, 40%) of 3 as yellow crystals: mp 95 °C (with decomposition to black particles); IR (KBr) 2960, 2930, 2875, 1730, 1450, 1435, 1380, 1260, 1210, 1035, 1015, 975, 920 $cm^{-1}$; $^1H$ NMR (200 MHz) δ 5.41 (1 H, H-2, d, $J_{2,3}$ = 6.6 Hz), 5.30 (1 H, H-5e, q, $J_{5e,4a} = J_{5e,6a} = J_{5e,6e}$ = 4.6 Hz), 4.58 (1 H, H-3, dd, $J_{3,2}$ = 6.6 Hz, $J_{3,4a}$ = 1.7 Hz), 2.37 (1 H, H-4a, qdd, $J_{4a,Me}$ = 7.0 Hz, $J_{4a,5e}$ = 4.7 Hz, $J_{4a,3}$ = 2.0 Hz) partially superim-

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

posed on 2.26 (1 H, H-6a, dd, $J_{6a,6e}$ = 17.6 Hz, $J_{6a,5e}$ = 4.5 Hz), 2.08 (1 H, septet, $J$ = 6.9 Hz), 1.98 (3 H, s) superimposed on 1.97 (1 H, H-6e, dd, $J_{6e,6a}$ = 17.6 Hz, $J_{6e,5e}$ = 4.7 Hz), 1.16 (6 H, d, $J$ = 6.8 Hz), 1.02 (3 H, MeC-4, d, $J_{Me,4a}$ = 7.2 Hz); homonuclear decoupling, irradiation at δ 5.41 collapsed the signal at δ 4.58 to a d and seemed to affect the signals at δ 2.37 and 2.26 and 1.97, irradiation at δ 5.30 collapsed the signals at δ 2.37 to a br q and at δ 2.26 and 1.97 to d, irradiation at δ 4.58 collapsed the signals at δ 5.41 to a s and at δ 2.37 to a qd, irradiation at δ 2.37 collapsed the signals at δ 5.30 to br t and at δ 4.58 to a d and at δ 1.02 to a s, irradiation at δ 2.26 collapsed the signals at δ 5.30 to a br t and at δ 1.97 to a d, irradiation at δ 1.97 collapsed the signals at δ 5.30 to a br t and at δ 2.26 to a d, irradiation at δ 1.16 collapsed the signal at δ 2.08 to a s, irradiation at δ 1.02 collapsed the signal at δ 2.37 to a dd; $^{13}$C NMR (50 MHz) 169.59 (CO, s), 100.93 (C-1, s), 97.81 (C-2, d), 75.77 (d), 68.60 (d), 37.77 (C-4, d), 35.97 (C-6, t), 35.16 ($CHMe_2$, d), 21.31 (q), 21.10 (q), 20.08 (q), 16.88 (q) ppm. Anal. Calcd for $(C_{12}H_{18}O_2PdCl)_2$: C, 42.88; H, 5.39. Found: C, 42.80; H, 5.70.

**Di(μ-chloro)bis[(1,2,3-η)-5-acetoxy-2,4-dimethyl-2-cyclohexen-1-yl]dipalladium (4, HOAc).**[21] Similar treatment of 108 mg (1.00 mmol) of 1,5-dimethyl-1,4-cyclohexadiene, as described for **2** (HOAc) except the reaction was performed for 53 h, afforded first 24 mg (23%) of *m*-xylene followed by 117 mg (0.19 mmol, 38%) of **4** as a yellow oil, which solidified to yellow crystals in a freezer (−18 °C): mp 55–61 °C (with decomposition to black particles); IR (KBr) 2970, 2930, 2870, 1735, 1435, 1375, 1240, 1035, 995, 970, 905 cm$^{-1}$; $^1$H NMR (200 MHz) δ 5.29 (1 H, H-5e, q, $J_{5e,4a}$ = $J_{5e,6a}$ = $J_{5e,6e}$ = 4.9 Hz), 4.70 (1 H, H-1, dt, $J_{1,6e}$ = 4.6 Hz, $J_{1,6a}$ = $J_{1,3}$ = 2.3 Hz), 4.54 (1 H, H-3, t, $J_{3,4a}$ = $J_{3,1}$ = 2.0 Hz), 2.50 (1 H, H-4a, qdd, $J_{4a,Me}$ = 7.1 Hz, $J_{4a,5e}$ = 4.9 Hz, $J_{4a,3}$ = 2.1 Hz), 2.19 (1 H, H-6a, ddd, $J_{6a,6e}$ = 17.3 Hz, $J_{6a,5e}$ = 5.0 Hz, $J_{6a,1}$ = 2.1 Hz), 2.07 (3 H, MeC-2, s), 1.99 (3 H, s), 1.72 (1 H, H-6e, dt, $J_{6e,6a}$ = 17.4 Hz, $J_{6e,5e}$ = $J_{6e,1}$ = 4.9 Hz), 1.00 (3 H, MeC-4, d, $J_{Me,4a}$ = 7.1 Hz); homonuclear decoupling, irradiation at δ 5.29 collapsed the signals at δ 2.50 to a qd and at δ 2.19 and 1.72 to dd, irradiation at δ 4.70 collapsed the signals at δ 4.54 to a d and at δ 2.19 and 1.72 to dd, irradiation at δ 4.54 collapsed the signals at δ 4.70 to a br d and at δ 2.50 to a qd, irradiation at δ 2.50 collapsed the signals at δ 5.29 to a t and at δ 4.54 to a d and at δ 1.00 to a s, irradiation at δ 2.19 collapsed the signals at δ 5.29 and 1.72 to t and at δ 4.70 to a dd, irradiation at δ 1.72 collapsed the signals at δ 5.29 and 4.70 to br t and at δ 2.19 to a dd, irradiation at δ 1.00 collapsed the signal at δ 2.50 to a dd; $^{13}$C NMR (100 MHz) 170.18 (CO, s), 116.01 (C-2, s), 78.85 (d), 72.31 (d), 68.37 (d), 37.95 (C-4, d), 33.17 (C-6, t), 21.99 (q), 20.93 (q), 16.58 (q) ppm. Anal. Calcd for $(C_{10}H_{15}O_2PdCl)_2$: C, 38.86; H, 4.89. Found: C, 38.90; H, 4.90.

**Di(μ-chloro)bis[(1,2,3-η)-5-acetoxy-1,2,4-trimethyl-2-cyclohexen-1-yl]dipalladium (5, HOAc).** Similar treatment of 122 mg (1.00 mmol) of 1,2,4-trimethyl-1,4-cyclohexadiene, as described for **2** (HOAc), afforded first 64 mg (53%) of 1,2,4-trimethylbenzene followed by 94 mg (0.15 mmol, 29%) of **5** as yellow crystals: mp 50–55 °C (with decomposition to black particles); IR (film) 2970, 2930, 1735, 1455, 1375, 1240, 1200, 1135, 1080, 1025, 790, 765 cm$^{-1}$; $^1$H NMR (200 MHz) δ 5.35 (1 H, H-5e, q, $J_{5e,4a}$ = $J_{5e,6a}$ = $J_{5e,6e}$ = 5.1 Hz), 4.36 (1 H, H-3, d, $J_{3,4a}$ = 2.2 Hz), 2.58–2.39 (1 H, H-4a, m) on which is superimposed 2.43 (1 H, H-6a, dd, $J_{6a,6e}$ = 17.3 Hz, $J_{6a,5e}$ = 4.9 Hz), 2.06 (3 H, MeC-2, s), 1.98 (3 H, s), 1.68 (1 H, H-6e, dd, $J_{6e,6a}$ = 17.3 Hz, $J_{6e,5e}$ = 5.4 Hz), 1.41 (3 H, MeC-1, s), 0.98 (3 H, MeC-4, d, $J_{Me,4a}$ = 7.1 Hz); homonuclear decoupling, irradiation at δ 5.35 collapsed the signals at δ 2.58–2.39 to a qd and at δ 2.43 and 1.68 to d, irradiation at δ 4.36 collapsed the signal at δ 2.58–2.39 to a qd, irradiation at δ 2.49 collapsed the signals at δ 5.35 to a br t and at δ 4.36 and 0.98 to s, irradiation at δ 2.43 collapsed the signals at δ 5.35 to a br t and at δ 1.68 to a d, irradiation at δ 1.68 collapsed the signals at δ 5.35 to a br t and at δ 2.43 to a d, irradiation at δ 0.98 collapsed the signal at δ 2.58–2.39 to a d; $^{13}$C NMR (50 MHz) 169.58 (CO, s), 112.94 (C-2, s), 85.64 (C-1, s), 77.00 (C-3, d), 69.10 (C-5, d), 40.28 (C-6, t), 38.16 (C-4, d), 22.21 (q), 21.25 (q), 19.28 (q), 16.98 (q) ppm. Anal. Calcd for $(C_{11}H_{17}O_2PdCl)_2$: C, 40.89; H, 5.30. Found: C, 40.50; H, 5.10.

**Di(μ-chloro)bis[(1,2,3-η)-5-acetoxy-2,4,6-trimethyl-2-cyclohexen-1-yl]dipalladium (6, HOAc).** Similar treatment of 122 mg (1.00 mmol) of 1,3,5-trimethyl-1,4-cyclohexadiene, as described for **2** (HOAc), afforded first 40 mg (33%) of 1,3,5-trimethylbenzene followed by 43 mg (0.07 mmol, 13%) of **6** as yellow crystals: mp 99 °C (with decomposition to black particles); IR (KBr) 2965, 2925, 2870, 1735, 1450, 1375, 1250, 1155, 1025, 990, 945, 915, 860 cm$^{-1}$; $^1$H NMR (200 MHz) δ 4.97 (1 H, H-5e, t, $J_{5e,4a}$ = $J_{5e,6a}$ = 3.7 Hz), 4.41 (2 H, H-1, H-3, s), 2.35 (2 H, H-4a, H-6a, qd, $J_{4a,Me}$ = $J_{6a,Me}$ = 7.2 Hz, $J_{4a,5e}$ = $J_{6a,5e}$ = ca. 4.2 Hz), 2.06 (3 H, MeC-2, s), 2.01 (3 H, s), 1.02 (6 H, MeC-4, MeC-6, d, $J$ = 7.2 Hz); homonuclear decoupling, irradiation at δ 4.97 collapsed the signal at δ 2.35 to a q, irradiation at δ 2.35 collapsed the signals at δ 4.97 and 1.02 to s, irradiation at δ 1.02 collapsed the signal at δ 2.35 to a br s; $^{13}$C NMR (100 MHz) 170.74 (CO, s), 116.38 (C-2, s), 77.22 (2 C, C-1 and C-3, d), 70.89 (C-5, d), 39.55 (2 C, C-4 and C-6, d), 21.72 (q), 20.60 (q), 17.25 (2 C, MeC-4, MeC-6, q) ppm. Anal. Calcd for $(C_{11}H_{17}O_2PdCl)_2$: C, 40.89; H, 5.30. Found: C, 40.70; H, 5.30.

**Di(μ-chloro)bis[(1,4a,8a-η)-1,2,3,4,5,6,7,8-octahydro-3-acetoxy-1-naphthalenyl]dipalladium (7, HOAc, $CuCl_2$).** Similar treatment of 137 mg (1.02 mmol) of 1,2,3,4,5,8-hexahydronaphthalene, as described for **2** (HOAc, $CuCl_2$), produced 282 mg of a yellow oil, which after flash chromatography afforded 238 mg (0.36 mmol, 71%) of **7** as a yellow solid: mp 126–130 °C (with decomposition to black particles); FT-IR ($CH_2Cl_2$) 3061, 3055, 2982, 1733, 1608, 1376, 1285, 1251, 1024 cm$^{-1}$; $^1$H NMR (200 MHz) δ 5.50 (1 H, H-3e, quintet, $J_{3e,2a}$ = $J_{3e,4a}$ = $J_{3e,2e}$ = $J_{3e,4e}$ = 5.8 Hz), 4.45 (1 H, H-1, apparent t, $J_{1,2a}$ = $J_{1,2e}$ = ca. 3.3 Hz), 2.61 (1 H, H-4a, dd, $J_{4a,4e}$ = 16.7 Hz, $J_{4a,3e}$ = 5.8 Hz) superimposed on 2.67–2.55 (1 H, H-8a, m), 2.44 (1 H, H-5a, dt, $J_{5a,5e}$ = 17.6 Hz, $J$ = 5.4 Hz), 2.32 (1 H, H-2a, ddd, $J_{2a,2e}$ = 16.7 Hz, $J_{2a,3e}$ = 5.7 Hz, $J_{2a,1}$ = 2.7 Hz), 1.97 (3 H, s) superimposed on 2.08–1.77 (3 H, overlapping m), 1.62 (1 H, H-4e, dd, $J_{4e,4a}$ = 16.8 Hz, $J_{4e,3e}$ = 5.3 Hz) superimposed on 1.77–1.56 (1 H, m), 1.48 (1 H, H-2e, ddd, $J_{2e,2a}$ = 16.6 Hz, $J_{2e,3e}$ = 5.8 Hz, $J_{2e,1}$ = 3.8 Hz) superimposed on 1.56–1.44 (1 H, m), 1.29 (1 H, H-7a, apparent dtt, $J$ = 17.0, 8.5, 2.8 Hz); homonuclear decoupling, irradiation at δ 5.50 collapsed the signals at δ 2.61 and 1.62 to d and at δ 2.32 and 1.48 to dd, irradiation at δ 4.45 collapsed the signals at δ 2.32 and 1.48 to dd; $^{13}$C NMR (100 MHz) 170.42 (CO, s), 114.79 (C-8a, s), 92.08 (C-4a, s), 67.40 (C-1, d), 66.87 (C-3, d), 40.25 (t), 33.90 (t), 32.99 (t), 28.70 (t), 22.24 (t), 21.82 (t), 21.31 (q) ppm. Anal. Calcd for $(C_{12}H_{17}O_2PdCl)_2$: C, 43.01; H, 5.11. Found: C, 42.90; H, 5.17.

**Di(μ-chloro)bis[(1,4a,8a-η)-1,2,3,4,5,6,7,8-octahydro-3-acetoxy-1-naphthalenyl]dipalladium (7, MeCN, $CuCl_2$).** Similar treatment of 136 mg (1.01 mmol) of 1,2,3,4,5,8-hexahydronaphthalene, as described for **1** (MeCN, $CuCl_2$) except that the reaction was performed for 45 h, afforded a yellow-brown filtrate. The filtrate was washed twice with 25-mL portions of sodium bicarbonate solution (0.1 M) saturated with NaCl and dried ($MgSO_4$), and the solvent was removed at reduced pressure (water aspirator) on a rotary evaporator to afford 151 mg of a brown oil, which was diluted with 1–2 mL of EtOAc and flash chromatographed (3.5 × 15-cm column packed and eluted with EtOAc–hexane, 3:7). Removal of solvent at reduced pressure (water aspirator) afforded 96 mg (0.14 mmol, 28%) of **7** as a yellow oil, which solidified to yellow crystals in a freezer (−18 °C): mp 125–130 °C (with decomposition to black particles).

**Di(μ-chloro)bis[(3a,4,7a-η)-2,3,4,5,6,7-hexahydro-6-acetoxy-1*H*-inden-4-yl]dipalladium (8, HOAc, $CuCl_2$).** Similar treatment of 124 mg (1.03 mmol) of 4,7-dihydroindan, as described for **2** (HOAc, $CuCl_2$), produced 250 mg of a brown oil, which after flash chromatography afforded 215 mg (0.34 mmol, 67%) of **8** as a yellow oil solid: mp 128–134 °C (with decomposition to black particles); FT-IR ($CH_2Cl_2$) 3062, 3053, 2982, 1733, 1608, 1376, 1291, 1240 cm$^{-1}$; $^1$H NMR (200 MHz) δ 5.50 (1 H, H-6e, quintet, $J_{6e,5a}$ = $J_{6e,7a}$ = $J_{6e,5e}$ = $J_{6e,7e}$ = 5.5 Hz), 4.76 (1 H, H-4, apparent t, $J_{4,5e}$ = ca. 3.5 Hz, $J_{4,5a}$ = ca. 2.9 Hz), 2.60 (1 H, H-7a, dd, $J_{7a,7e}$ = 17.0

(21) Similar treatment of 108 mg (1.00 mmol) of 1,5-dimethyl-1,4-cyclohexadiene, as described for **1** (HOAc) except the reaction was performed for 19 h, afforded di(μ-chloro)bis[(1,2,3-η)-2,4-dimethyl-2-cyclohexen-1-yl]dipalladium (**4a**, yellow oil, 7%), followed by **4** (20%). Complex **4a**: $^1$H NMR (200 MHz, partial) δ 4.94 (1 H, H-1, m), 4.71 (1 H, H-3, s), 2.01 (3 H, MeC-2, s), 1.05 (3 H, MeC-4, d, $J$ = 6.9 Hz).

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Hz, $J_{7a,6e}$ = 5.3 Hz), 2.53 (1 H, H-3a, dd, $J_{3a,3e}$ = 14.8 Hz, $J_{3a,2a}$ = 7.8 Hz), 2.43 (1 H, H-1a, dd, $J_{1a,1e}$ = 18.5 Hz, $J_{1a,2a}$ = 8.9 Hz), 2.35 (1 H, H-5a, ddd, $J_{5a,5e}$ = 17.1 Hz, $J_{5a,6e}$ = 5.6 Hz, $J_{5a,4}$ = 2.6 Hz), 2.16–1.98 (2 H, H-1e, H-3e, m), 1.96 (3 H, s) superimposed on 1.98–1.88 (1 H, H-2e, m), 1.61 (1 H, H-7e, dd, $J_{7e,7a}$ = 17.7 Hz, $J_{7e,6e}$ = 5.4 Hz), 1.53 (1 H, H-5e, dt, $J_{5e,5a}$ = 17.5 Hz, $J_{5e,6e}$ = $J_{5e,4}$ = 4.9 Hz), 1.39–1.13 (1 H, H-2a, m); homonuclear decoupling, irradiation at δ 5.50 collapsed the signals at δ 2.60 and 1.61 to d and at δ 2.35 and 1.53 to dd, irradiation at δ 4.76 collapsed the signals at δ 2.35 and 1.53 to dd; $^{13}$C NMR (100 MHz) 170.31 (CO, s), 122.35 (C-3a, s), 96.08 (C-7a, s), 67.15 (C-4, d), 64.36 (C-6, d), 36.75 (2 C, t), 33.99 (t), 32.56 (t), 23.79 (C-2, t), 21.22 (q) ppm. Anal. Calcd for $(C_{11}H_{15}O_2PdCl)_2$: C, 41.15; H, 4.71. Found: C, 41.10; H, 4.80.

**Di(μ-chloro)bis[(3a,4,7a-η)-2,3,4,5,6,7-hexahydro-6-acetoxy-1*H*-inden-4-yl]dipalladium (8, MeCN, $CuCl_2$).** Similar treatment of 122 mg (1.02 mmol) of 4,7-dihydroindan, as described for 7 (MeCN, $CuCl_2$) except that the reaction was performed for 48 h, produced 143 mg of a brown oil, which after flash chromatography afforded 94 mg (0.15 mmol, 29%) of 8 as a yellow oil, which solidified to yellow crystals in a freezer (−18 °C): mp 128–134 °C (with decomposition to black particles).

**Dimethyl *cis*-5-Acetoxy-2,3-dimethyl-2-cyclohexene-1-malonate (1a).** To a stirred, yellow solution of 278 mg (0.45 mmol) of ($\eta^3$-cyclohexenyl)palladium complex 1 and 471 mg (1.80 mmol) of triphenylphosphine in 25 mL of anhydrous THF (freshly distilled from sodium benzophenone ketyl radical) under a $N_2$ atmosphere was added a solution containing 1.80 mmol of sodium dimethyl malonate in 15 mL of anhydrous THF.[13] After 19 h at 22 °C, the resulting red solution with black particles was poured into 100 mL of water and extracted twice with 100-mL portions of $Et_2O$. The combined organic phase was washed with 100 mL of water and dried ($MgSO_4$), and the solvent was removed at reduced pressure (water aspirator) on a rotary evaporator to afford a red-black oil, which was flash chromatographed (2.5 × 13-cm column packed and eluted with EtOAc–hexane, 2:3). Removal of solvent at reduced pressure (water aspirator) afforded 181 mg (0.61 mmol, 68%) of 1a as a yellow oil. Subsequent bulb-to-bulb distillation (220 °C, 0.4 Torr) for analytical purposes afforded 112 mg (0.38 mmol, 42%) of 1a as a colorless oil: IR (film) 2990, 2950, 2850, 1735, 1435, 1365, 1245, 1145, 1030 cm$^{-1}$; $^1$H NMR (200 MHz) δ 4.88 (1 H, H-5a, tt, $J_{5a,4a}$ = $J_{5a,6a}$ = 8.8 Hz, $J_{5a,4e}$ = $J_{5a,6e}$ = 5.9 Hz), 3.85 (1 H, $CH(CO_2Me)_2$, d, $J$ = 5.5 Hz), 3.74 (3 H, OMe, s), 3.70 (3 H, OMe, s), 3.06–2.91 (1 H, H-1, br m), 2.35–2.08 (2 H, H-4e, H-4a, complex m), 2.03 (3 H, MeCO, s), 1.96 (2 H, H-6a, H-6e, superficial t or dd, $J_{6a,1a}$ = $J_{6a,5a}$ = 8.1 Hz, $J_{6e,1a}$ = $J_{6e,5a}$ = 5.5 Hz), 1.63 (3 H, br s), 1.59 (3 H, br s); homonuclear decoupling, irradiation at δ 4.88 collapsed the signals at δ 2.35–2.08 to an apparent dd and at δ 1.96 to a d, irradiation at δ 3.85 collapsed the signal at 3.06–2.91 to an apparent t, irradiation at δ 2.99 collapsed the signals at δ 3.85 to a s and at δ 1.96 to a d, irradiation at δ 2.22 collapsed the signal at δ 4.88 to an apparent t, irradiation at δ 1.96 simplified the signals at δ 4.88 and 3.06–2.91; $^{13}$C NMR (50 MHz) 170.04 (CO, s), 168.90 (CO, s), 168.02 (CO, s), 126.94 (s), 124.31 (s), 69.71 (C-5, d), 53.43 (d), 52.66 (q), 52.23 (q), 41.20 (C-1, d), 37.36 (C-4, t), 30.80 (C-6, t), 21.70 (q), 20.32 (q), 16.66 (q) ppm. Anal. Calcd for $C_{15}H_{22}O_6$: C, 60.43; H, 7.43. Found: C, 60.30; H, 7.30.

**4-*exo*-Carbomethoxy-6,7-dimethyl-2-oxabicyclo[3.3.1]-non-6-en-3-one (1b).** After a solution of 112 mg (0.38 mmol) of malonate 1a and 19 mg (0.04 mmol) of *p*-toluenesulfonic acid in 12 mL of methanol was refluxed for 24 h, the solvent was removed at reduced pressure (water aspirator) on a rotary evaporator and the residue was flash chromatographed (2.5 × 12-cm column packed and eluted with EtOAc–petroleum ether, 2:3). Removal of solvent at reduced pressure (water aspirator) afforded 66 mg (0.29 mmol, 78%) of 1b as a colorless oil.[1a]

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# Stereoselective Addition of Enol Silanes to Nitro Olefins. A Simple Synthesis of Compounds Related to the Insect Antifeedants Azadiradion and Gedunin

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The Lewis acid mediated aldol reactions of 1-[(trimethylsilyl)oxy]cyclohexene (2) and 2,6,6-trimethyl-1-[(trimethylsilyl)oxy]cyclohexene (6) with (*E*)-1-(3-furyl)-2-nitro-1-propene (1) was investigated (Schemes I and II and Chart II). The addition of enol silane 2 to nitro olefin 1 shows a 4:1 selectivity lk/ul; the same relative topicity observed as that of the corresponding reaction of enamines. The addition of enol silane 6 to 1 shows a synthetically useful lk selectivity (100%). This was applied to the preparation of compounds 8a and 12 related to the insect antifeedants azadiradion and gedunin (Chart I) by a short and stereocontrolled synthetic approach (Scheme II).

## Introduction

Azadiradion and gedunin are two potent insect antifeedants, members of the limonoid family, isolated from the neem tree *Azadirachta indica* (A. Juss).[1] This kind of compound could be used in novel pesticides, in view of the growing interest for the industrial development on neem extracts.[2] Despite the widespread occurrence of the limonoids in nature and their interesting biological properties, there are few approaches to the limonoid[3] and re-

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