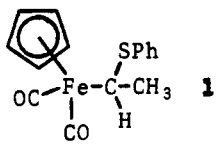
suggested by Still. These modifications are useful for chromatographic separations involving sample sizes of several grams.

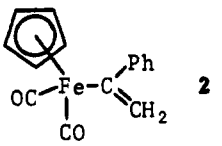
In summary, we have found this modified flash chromatography procedure to be a straightforward, fast, and effective means of purifying air-sensitive compounds.

Experimental Section

Two representative examples of purifications using the technique described in this paper are given below for the iron-containing compounds 1 and 2.



1



2

Purification of Compound 1. Crude 1[3a] (4.5 g) was dissolved in methylene chloride (10–15 mL) and chromatographed according to our procedure using a 1.5:1 mixture of hexanes and methylene chloride (700–1000 mL for elution of the sample in addition to the ca. 500 mL required to set up the column initially) on a 250 × 60 mm column of silica gel (E. Merck No. 9385, 0.040–0.063-mm particle size) with a flow rate of ca. 12 mm/min. An orange band was collected that after concentration in vacuo gave 3.9 g (86% recovery) of 1 as yellow crystals.[3a]

Purification of Compound 2. A sample of highly impure 2[3b] (ca. 5 g) was dissolved in methylene chloride and chromatographed as above by using 4:1 pentane–methylene chloride to give 2.8 g of 2 as a yellow-brown oil.[3b]

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Registry No. 1, 77418-50-9; 2, 83096-21-3.

1,4-Diene-Derived (η^3-Allyl)palladium Complexes. Palladium-Initiated Nucleophilic Addition of Methanol to Dimethyl-1,4-cyclohexadienes

Stan S. Hall*[1] and Björn Åkermark*

Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden

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Dimethyl-1,4-cyclohexadienes in the presence of bis(acetonitrile)palladium dichloride in methanol are stereospecifically converted to (5-methoxy-1-3-η^3-cyclohexenyl)palladium complexes. 1,2-Dimethyl-1,4-cyclohexadiene affords bis(5-methoxy-1,2-dimethyl-1-3-η^3-cyclohexenyl)palladium chloride (1) in the presence or absence of potassium bicarbonate, but the yield improves with the base. In contrast, 1,4-dimethyl-1,4-cyclohexadiene yields bis(5-methoxy-2,5-dimethyl-1-3-η^3-cyclohexenyl)palladium chloride (2) in good yield with base and bis(5-methoxy-1,4-dimethyl-1-3-η^3-cyclohexenyl)palladium chloride (3) without base. 1,5-Dimethyl-1,4-cyclohexadiene affords a mixture of bis(5-methoxy-1,5-dimethyl-1-3-η^3-cyclohexenyl)-palladium chloride (4), bis(5-methoxy-2,4-dimethyl-1-3-η^3-cyclohexenyl)palladium chloride (5), and bis-(4-methoxy-2,4-dimethyl-1-3-η^3-cyclohexenyl)palladium chloride (6) in base; however, only 5 is formed in the absence of base. Configuration and conformation assignments are based on NMR studies. A mechanism for the formation of the (η^3-allyl)palladium complexes is suggested.

Introduction

With palladium(II) as the promoter, 1,3-dienes are generally difunctionalized by a 1,4 addition of nucleophiles.[2] This synthetically useful reaction, which is stereospecific, is extremely versatile since various functionalities may be introduced by the selection of appropriate nucleophiles and have included alcohols,[3] amines,[3,4] carboxylates,[5] chloride,[6] enolates,[7] and malonate anions.[8] This two-step process involves the intermediacy of a (η^3-allyl)palladium complex, which in certain cases can be isolated and characterized. Since rather complex alkyl-substituted 1,4-cyclohexadienes can be prepared by our tandem alkylation–reduction procedures,[9] as well as by simple Birch metal–ammonia reduction of aromatic compounds,[10] it was of interest to examine whether (η^3-al-

(1) Visiting professor at the Royal Institute of Technology and Rutgers University Faculty Academic Study Participant, July 1982–August 1983. Permanent address: Department of Chemistry, Rutgers, The State University of New Jersey, Newark, NJ 07102.

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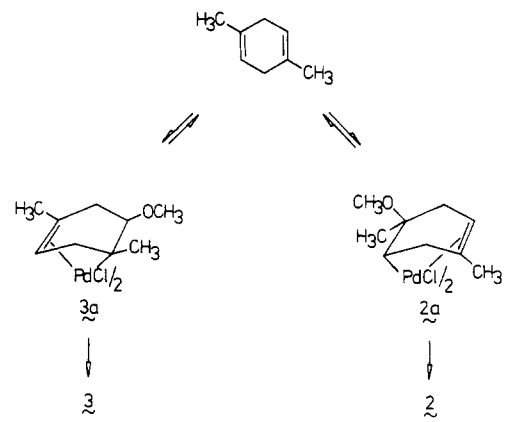
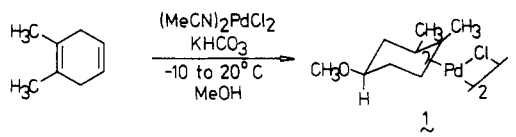
Scheme I



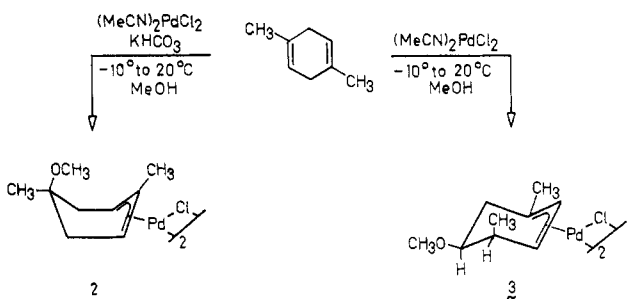
lyl)palladium complexes could be prepared from these dienes.[11] (η^3-Allyl)palladium complexes prepared by such a simple process would have broad potential synthetic applications. Herein is reported our initial study in this area involving three dimethyl-1,4-cyclohexadienes, prepared by reduction of the corresponding xylenes.

Results and Discussion

Allowing a stirred mixture of equimolar amounts of 1,2-dimethyl-1,4-cyclohexadiene, bis(acetonitrile)palladium dichloride, and potassium bicarbonate in methanol to slowly warm from −10 °C to ambient temperature overnight afforded (η^3-allyl)palladium complex **1** in 88% isolated yield. The weak base is important, since when it was omitted, the reaction was not complete and the yield was substantially lower (43%).



Similar treatment of 1,4-dimethyl-1,4-cyclohexadiene afforded (η^3-allyl)palladium complex **2** in 81% isolated yield. In contrast, when this reaction was run in the absence of base, (η^3-allyl)palladium complex **3** was obtained, albeit in a lower yield (44%). The yield of **3** improved



moderately (51%) when the reaction mixture was allowed to warm from −10 °C to ambient temperature overnight and then stirred for 2 additional days.

A proposed mechanism for these results is outlined in Scheme I with 1,4-dimethyl-1,4-cyclohexadiene as the example. In the presence of base, apparently the kinetically preferred nucleophilic addition at the more substituted position affords the (η^3-allyl)palladium complex **2**, presumably via the η^1,η^2-palladium intermediate **2a**. While in the absence of base, the (η^3-allyl)palladium complex **3** arises from an acid-catalyzed equilibrium between the η^1,η^2-palladium complexes **2a** and **3a**, which favors the less sterically congested complex **3a**. In the formation of these intermediate complexes, methanol would be expected to add distal to the palladium atom of the (cyclohexadiene)metal complex to stereospecifically produce the η^1,η^2-palladium intermediates **2a** and **3a**. The anticipated subsequent rearrangement[12]—β-elimination of hydride followed by readdition from the same face[13]—would establish all of the stereocenters of the (η^3-allyl)palladium complexes. These stereochemical assignments have been secured by NMR spectroscopy, which included homonuclear decoupling techniques.

In contrast to the above selective reactions, the last diene in this series 1,5-dimethyl-1,4-cyclohexadiene, using the same basic conditions described above, afforded a 2:1:1 mixture[14] of the three (η^3-allyl)palladium complexes **4**, **5**, and **6** in a total isolated yield of 53%. However in the absence of base *only* (η^3-allyl)palladium complex **5** was formed (39% yield), indicating that this complex is the thermodynamically favored product. The formation of the (η^3-allyl)palladium products **4**[15] and **5** can be rationalized in an analogous fashion as that used for complexes **2** and **3** (Scheme I). (η^3-Allyl)palladium complex **6**,[16] formed in the presence of base, apparently is a secondary product arising from base-catalyzed isomerization of the kinetic product **4**.[17]

(11) (a) Brown and Davidson[5b] isolated trace amounts of a byproduct tentatively assigned a (η^3-allyl)palladium structure in a study with catalytic amounts of palladium acetate and 1,4-cyclohexadiene. (b) Stille and Divakaruni demonstrated palladium(II)-catalyzed carboxylation of various dienes including 1,4-cyclohexadiene: *J. Org. Chem.* **1979**, *44*, 3474–3482. (c) While this work was in progress, Larock and Takagi demonstrated that (η^3-allyl)palladium complexes could be generated from acyclic 1,4-dienes with alkyl- and phenylmercuric chloride and Li_2PdCl_4: *Tetrahedron Lett.* **1983**, 3457–3460.

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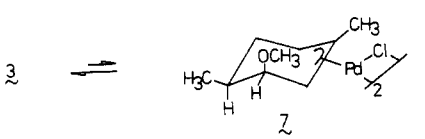
(14) An analogous reaction afforded a 1:1:1 mixture.

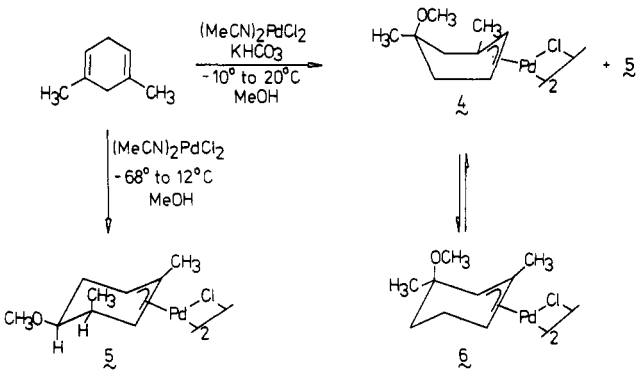
(15) After flash chromatographing a mixture of **4**, **5**, and **6** on a silica gel (less than 0.08 mm, E. Merck) column with EtOAc–petroleum ether (1:1), the column was flushed with EtOAc to afford pure (η^3-cyclohexenyl)palladium complex **4** as a pale yellow solid: IR (KBr) 3020, 2960, 2940, 2910, 2890, 2820, 1455, 1440, 1405, 1370, 1255, 1180, 1150, 1115, 1090, 1070, 1020, 965, 870, 830, 765 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.50 (1 H, H-2, d, $J_{2,3}$ = 6.4 Hz), 4.73 (1 H, H-3, superficial t, $J_{2,3} = J_{3,4a}$ = ca. 6.2 Hz), 3.01 (3 H, CH_3O, s), 2.04 (1 H, H-4a, dd, $J_{4a,4e}$ = 18.5 Hz and $J_{3,4a}$ = ca. 6.7 Hz) superimposed on 2.03 (1 H, H-6a, d, $J_{6a,6e}$ = 18.5 Hz), 1.70 (2 H, H-4e and H-6e, d, $J_{4a,4e} = J_{6a,6e}$ = 19.2 Hz), 1.47 (3 H, CH_3C-1, s), 1.13 (3 H, CH_3C-5, s); homonuclear decoupling, irradiation at δ 5.50 collapsed the signal at δ 4.73 to a d, irradiation at δ 4.73 collapsed the signals at δ 5.50 to a s and at δ 2.04–2.03 to two overlapping d and sharpened the d at δ 1.70, irradiation at ca. δ 2.04 collapsed the signals at δ 4.73 to a d and at δ 1.70 to a s, and irradiation at δ 1.70 sharpened the t at δ 4.73 and collapsed the signals at δ 2.04–2.03 to two overlapping s; ^{13}C NMR (50 MHz, $CDCl_3$, broad-band proton decoupling and attached proton test (APT)) 102.44 (+, C-2), 89.84 (−, C-1), 70.50 (−, C-5), 68.87 (+, C-3), 49.50 (+, CH_3O), 46.54 (−, C-6), 39.02 (−, C-4), 25.00 (+, CH_3C-1), 23.57 (+, CH_3C-5) ppm.

(16) Partial ^1H NMR (200 MHz, $CDCl_3$, from a mixture of **4**, **5**, and **6**) of **6**: δ 3.40 (3 H, CH_3O, s), 2.06 (3 H, CH_3C-2, s), 1.41 (3 H, CH_3C-4, s).

(17) A similar base-catalyzed isomerization (ratchet reaction) was observed with **3** in the presence of K_2CO_3/MeOH to yield a 2:1 mixture of **3** and **7**. ^1H NMR (200 MHz, $CDCl_3$) of **7**: δ 4.85 (1 H, H-1, br m, $W_{1/2}$



= 8 Hz), 4.80 (1 H, H-3, dd, $J_{3,4e}$ = 3.8 Hz and $J_{1,3}$ = 1.6 Hz), 3.57 (1 H, H-4, t, $J_{3,4e} = J_{4e,5e}$ = ca. 4.2 Hz), 3.40 (3 H, CH_3O, s), 2.98–2.82 (1 H, H-5, m), 2.11 (3 H, CH_3C-2, s), 1.97 (1 H, H-6e, ddd, $J_{6a,6e}$ = ca. 16 Hz, $J_{5a,6e}$ = ca. 6 Hz, $J_{1,6e}$ = ca. 4 Hz), ca. 0.96 (1 H, H-6a, m), 0.87 (3 H, CH_3C-5, d, J_{5a,CH_3} = 6.8 Hz).



The NMR data indicate the η^3-cyclohexenyl ring in the palladium complexes **1**, **3**, and **5** is best described as a chair (or pseudochair) conformation, which is analogous to (η^3-cyclohexenyl)molybdenum complexes that were reported recently and analyzed by both X-ray crystallographic and NMR techniques.[18] The axial–axial vicinal coupling values for $J_{4a,5a}$ and $J_{5a,6a}$ were 7.6, 9.2, and 9.1 Hz for complexes **1**, **3**, and **5**, respectively. In contrast, the data for the (η^3-allyl)palladium complex **2** and **4**[15] suggest a boat (or pseudoboat) conformation for the η^3-cyclohexenyl ring. Such a conformation has been previously reported for a (η^3-allyl)palladium complex using X-ray crystallography.[19] One revealing feature is the shielding of the 5-methoxy group by the η^3-allyl system in the boat conformers, which resonates at ca. δ 3.0 (^{1}H) and 49 (^{13}C). The corresponding 5-methoxy signal in the chair conformers of **1**, **3**, and **5** is at ca. δ 3.3 (^{1}H) and 56 (^{13}C). Apparently the boat conformation relieves the serious interaction between the endo-face 5-methyl group and the metal and thereby positions the exo-face 5-methoxy group directly over the shielding region of the η^3-cyclohexenyl system.

Other characteristic NMR features, it was noted, that helped differentiate the chair and boat (η^3-cyclohexenyl)palladium complexes include geminal coupling values for $J_{4a,4e}$ and $J_{6a,6e}$ of ca. 16 Hz for the chair conformers and ca. 18.5 Hz for the boat conformers; and the vicinal $J_{1,6a}$ and $J_{3,4a}$ values are ca. 6 Hz and the $J_{1,6e}$ and $J_{3,4e}$ values are ca. 0 Hz for the boat conformers, while the vicinal $J_{1,6a}$ and $J_{3,4a}$ values are ca. 1.5–3.5 Hz and the $J_{1,6e}$ and $J_{3,4e}$ values are ca. 2.5–4.0 Hz for the chair (η^3-cyclohexenyl)palladium complexes.

This study demonstrates that (η^3-allyl)palladium complexes can be stereospecifically prepared from alkyl-disubstituted 1,4-cyclohexadienes. The distal addition of methanol and palladium and the subsequent migration of palladium—with retention of configuration—proceed with the anticipated stereochemistry. It is remarkable that with this simple two-reaction sequence such structures with defined stereochemistry can be quickly elaborated from benzene derivatives. Since (η^3-allyl)palladium complexes such as these can be subsequently stereospecifically functionalized, the synthetic applications of these reaction sequences are promising and are being examined at this time.

Experimental Section

All reactions were performed in oven-dried, 25-mL, two-neck, round-bottomed flasks equipped with magnetic stir bars under a static N_2 atmosphere. Palladium chloride ($PdCl_2$, 60%) was from Engelhard. Bis(acetonitrile)palladium dichloride was prepared by the general method of Kharasch et al.[20] Cupric chloride (dihydrate) and methanol (0.1% H_2O) was from E. Merck. The Celite was Johns Manville Hyflo Super-cel. Flash chromatography[21] was performed on silica gel 60 (230–400 mesh, E. Merck). Apparently the (η^3-cyclohexenyl)palladium complexes decompose in the presence of Pd(0); consequently it was found that cupric chloride (ca. 10%) is useful to minimize this reaction. It is recommended that the entire reaction sequence and 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 or in crystalline form at −26 °C under N_2. Melting points (uncorrected) were determined with a Reichert micro hot stage 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 $(CH_3)_4Si$ internal standard. The ^{1}H NMR spectra were determined at 200 MHz with a Bruker Model WP 200 Fourier transform NMR spectrometer. The ^{13}C NMR spectra were determined at 50.3 MHz and noise (broad-band proton) decoupled spectra were collected for all products. In addition, off-resonance heteronuclear decoupled, selective decoupled, or attached proton test spectra were collected for all primary products. Microanalyses were performed by Centrala Analyslaboratoriet Kemikum, Uppsala, Sweden.

Bis(5-methoxy-1,2-dimethyl-1-3-η^3-cyclohexenyl)palladium Chloride (1). To a cold (−10 °C, salt–ice in a Dilvac Dewar bath), stirred yellow slurry of 611 mg (2.36 mmol) of bis(acetonitrile)palladium dichloride,[20] 205 mg (2.05 mmol) of $KHCO_3$, and 46 mg (0.27 mmol) of cupric chloride in 15 mL of MeOH was slowly added (dropwise, 5 min) a solution of 219 mg (2.03 mmol) of 1,2-dimethyl-1,4-cyclohexadiene[22] in 10 mL of MeOH. After 19 h—the temperature of the slurry had slowly risen to 21 °C—the yellow supernatant with a yellow flocculent precipitate was filtered through a 5-mm pad of Celite (dry packed) and the filter rinsed first with 25 mL of MeOH and then with 120 mL of EtOAc. The yellow filtrate—a pale yellow-tan precipitate remained on the filter—was concentrated in vacuo at water aspirator pressure to afford 556 mg of a yellow-orange oil–solid that was immediately slurried in 5 mL of EtOAc and flash chromatographed[21] though a 2 × 14 cm SiO_2 column packed with EtOAc–petroleum ether (1:1) and eluted with 350 mL of the same solvent mixture into one receiver. (The yellow band seemed to be entirely flushed from the column after ca. 150 mL of eluant.) Removal of the solvent at reduced pressure (water aspirator) yielded 500 mg (1.78 mmol, 88%) of **1** as a yellow-gold oil, which slowly crystallized from 8 mL of EtOAc–petroleum ether (1:7) in a freezer (−26 °C) as yellow crystals: mp 85–86 °C (decomposition to black particles); IR (KBr) 2980, 2960, 2920, 2880, 2815, 1460, 1435, 1390, 1375, 1365, 1305, 1285, 1235, 1185, 1145, 1130, 1090, 1060, 1040, 1010, 975, 960, 920, 895, 710, 650 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.50 (1 H, H-3, t, $J_{3,4a} = J_{3,4e} = 3.4$ Hz), 4.23 (1 H, H-5, tt, $J_{4a,5a} = J_{5a,6a} = 7.6$ Hz and $J_{4e,5a} = J_{5a,6e} = 5.8$ Hz), 3.27 (3 H, CH_3O, s), 2.47 (1 H, H-6e, dd, $J_{6a,6e} = 15.7$ Hz and $J_{5a,6e} = 5.7$ Hz), 2.31 (1 H, H-4e, ddd, $J_{4a,4e} = 15.9$ Hz, $J_{4e,5a} = 5.6$ Hz, and $J_{3,4e} = 3.6$ Hz), 2.06 (3 H, CH_3C-2,

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(19) Bäckvall, J.-E.; Björkman, E. E. *J. Chem. Soc., Chem. Commun.* **1982**, 693–694.
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(21) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.
(22) Prepared by slowly adding a solution of 5.4 g (50 mmol) of *o*-xylene and 10.4 g (227 mmol) of absolute EtOH in 35 mL of anhydrous Et_2O to a stirred dark blue mixture of 1.6 g (227 mmol, 20 pieces) of lithium wire (0.32-cm diameter) in 150 mL of liquid ammonia. After ca. 3 h the mixture turned gray-white, ca. 3.5 g of NH_4Cl was added as buffer, and then the ammonia was allowed to evaporate. After the residue was partitioned between 100 mL of H_2O and 100 mL of Et_2O, the aqueous layer was extracted four times with 50 mL of Et_2O. The combined organic layer was dried ($MgSO_4$), filtered, and concentrated first on a 60 °C water bath (Vigreaux column) to afford 6.7 g of a pale yellow oil and then for 5 min on a rotary evaporator at water aspirator pressure to yield 4.4 g (83%) of 1,2-dimethyl-1,4-cyclohexadiene as a pale yellow oil:[23] NMR (60 MHz, $CDCl_3$) δ 5.70 (2 H, s), 2.60 (4 H, s), 1.63 (6 H, s).
(23) Paquette, L. A.; Barrett, J. H.; Malmin, J.; Breslow, R. In "Organic Syntheses"; Baumgarten, H. E., Ed.; Wiley: New York, 1973; Coll. Vol. V, pp 467–471.

s), 1.39 (3 H, CH_3C-1, s), 1.28 (1 H, H-6a, dd, $J_{6a,6e}$ = ca. 16 Hz and $J_{5a,6a}$ = ca. 8 Hz) superimposed on δ 1.26 (1 H, H-4a, ddd, $J_{4a,4e}$ = ca. 16 Hz, $J_{4a,5a}$ = ca. 8 Hz, and $J_{3,4a}$ = 3.5 Hz); ^{13}C NMR (50 MHz, $CDCl_3$, off-resonance heteronuclear and broad-band proton decoupling) 113.20 (s), 87.53 (s), 73.80 (d), 72.00 (d), 56.05 (q), 41.21 (t), 34.08 (t), 21.98 (q), 19.08 (q) ppm. Anal. Calcd for $(C_9H_{15}OPdCl)_2$: C, 38.46; H, 5.38. Found: C, 38.68; H, 5.41.

Bis(5-methoxy-2,5-dimethyl-1-3-η^3-cyclohexenyl)palladium Chloride (2). Similar treatment, as described for 1, of 216 mg (2.00 mmol) of 1,4-dimethyl-1,4-cyclohexadiene[24] after 21 h produced a pale yellow-green supernatant with a yellow flocculent precipitate. The entire reaction slurry was filtered through a 5-mm pad of Celite (dry packed) and the filter rinsed with 30 mL of MeOH, followed by 150 mL of EtOAc. The yellow filtrate was concentrated in vacuo (water aspirator pressure) to afford 512 mg of a yellow-brown solid that was immediately slurried, including scrappings from the walls, twice with 5 mL of EtOAc and the slurry flash chromatographed[21] through a 2 × 15 cm SiO_2 column packed with EtOAc–petroleum ether (1:1) and eluted with 700 mL of the same solvent mixture into one receiver. Removal of the solvent at reduced pressure (water aspirator) yielded 456 mg (1.62 mmol, 81%) of **2** as a yellow solid, which slowly crystallized from ca. 80 mL of EtOAc in a freezer (−26 °C) as yellow-gold crystals: mp 96–98 °C (with decomposition to black particles); IR (KBr) 3005, 2960, 2940, 2920, 2900, 2870, 2820, 1455, 1425, 1375, 1370, 1250, 1195, 1180, 1130, 1090, 1070, 920, 810, 735 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.68 (2 H, H-1 and H-3, d, $J_{1,6a} = J_{3,4a}$ = 5.8 Hz), 3.00 (3 H, CH_3O, s), 2.07 (3 H, CH_3C-2, s) that is superimposed on δ 2.10 (2 H, H-4a and H-6a, dd, $J_{4a,4e} = J_{6a,6e}$ = 18.4 Hz and $J_{1,6a} = J_{3,4a}$ = 5.8 Hz), 1.85 (2 H, H-4e and H-6e, d, $J_{4a,4e} = J_{6a,6e}$ = 18.4 Hz), 1.09 (3 H, CH_3C-5, s); homonuclear decoupling, irradiation at δ 4.68 collapsed the signal at δ 2.10 to a d and irradiation at δ 2.10 collapsed the signal at δ 4.68 to a s; ^{13}C NMR (50 MHz, $CDCl_3$, off-resonance heteronuclear and broad-band proton decoupling) 118.27 (s), 71.54 (2 C, d), 70.12 (s), 49.38 (q), 40.31 (2 C, t), 23.25 (q), 21.77 (q) ppm. Anal. Calcd for $(C_9H_{15}OPdCl)_2$: C, 38.46; H, 5.38. Found: C, 38.55; H, 5.36.

Bis(5-methoxy-1,4-dimethyl-1-3-η^3-cyclohexenyl)palladium Chloride (3). Similar treatment, as described for 1 except that no $KHCO_3$ was added, of 216 mg (2.00 mmol) of 1,4-dimethyl-1,4-cyclohexadiene[24] after 22 h produced an orange-red solution. The solution was filtered through a 5-mm pad of Celite (dry packed) and the filter rinsed with 50 mL of EtOAc. The orange-red filtrate was concentrated in vacuo (water-aspirator pressure, water bath temperature 28 °C) to afford 726 mg of a dark brown oil that was immediately taken up in 6 mL of EtOAc and flash chromatographed[21] through a 3 × 15 cm SiO_2 column packed with EtOAc–petroleum ether (1:1) and eluted with 400 mL of the same solvent mixture into one receiver. (The yellow band seemed to be entirely flushed from the column after ca. 200 mL of eluant.) Removal of the solvent at reduced pressure (water aspirator) yielded 247 mg (0.88 mmol, 44%) of **3** as a yellow-gold viscous oil, which crystallized from Et_2O in a freezer (−26 °C) as yellow-gold crystals: mp 114.5–117 °C (with decomposition to black particles); IR (KBr) 2970, 2950, 2920, 2900, 2820, 1490, 1445, 1410, 1375, 1360, 1190, 1180, 1150, 1110, 1090, 1080, 1060, 1035, 980, 935, 905, 830, 700 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.28 (1 H, H-2, d, $J_{2,3}$ = 6.5 Hz), 4.72 (1 H, H-3, dd, $J_{2,3}$ = 6.5 Hz and $J_{3,4e}$ = 4.1 Hz), 4.46 (1 H, H-5, dt, $J_{5a,6a}$ = 9.2 Hz and $J_{4e,5a} = J_{5a,6e}$ = 5.7 Hz), 3.31 (3 H, CH_3O, s), 2.42 (1 H, H-4, at least a 12-line m, J_{4e,CH_3} = 7.0 Hz, $J_{4e,5a}$ = 5.8 Hz, and $J_{3,4e}$ = 4.1 Hz), 2.27 (1 H, H-6e, dd, $J_{6a,6e}$ = 16.0 Hz and $J_{5a,6e}$ = 5.8 Hz), 1.42 (3 H, CH_3C-1, s), 1.26 (1 H, H-6a, dd, $J_{6a,6e}$ = 15.8 Hz and $J_{5a,6a}$ = 9.4 Hz), 0.91 (3 H, CH_3C-4, d, J_{4e,CH_3} = 7.0 Hz); homonuclear decoupling, irradiation at δ 5.28 collapsed the signal at δ 4.72 to a d, irradiation at δ 4.72 collapsed the signals at δ 5.28 to a s and at δ 2.42 to an apparent quintet, irradiation at δ 4.46 collapsed the signals at δ 2.42 to a qd, at δ 2.27 to a d, and at δ 1.26 to a d, irradiation at δ 2.42 collapsed the signals at δ 4.72 to a d, at δ 4.46 to a dd, and at δ 0.91 to a s, irradiation at δ 2.27 collapsed the signals at δ 4.46 to a dd and at δ 1.26 to a d, irradiation at δ 1.26 collapsed the signals at δ 4.46 to a t and at δ 2.27 to a d, and irradiation at δ 0.91 collapsed the signal at δ 2.42 to a dd; ^{13}C NMR (50 MHz, $CDCl_3$, broad-band proton and selective decoupling) 100.09 (d), 93.79 (s), 77.74 (d), 76.11 (d), 56.16 (q), 36.91 (dd), 35.70 (d), 24.81 (q), 15.47 (q) ppm. Anal. Calcd for $(C_9H_{15}OPdCl)_2$: C, 38.46; H, 5.38. Found: C, 38.79; H, 5.37.

Bis(5-methoxy-2,4-dimethyl-1-3-η^3-cyclohexenyl)palladium Chloride (5). To a cold (−68 °C, dry ice–2-propanol in a Dilvac Dewar bath), stirred yellow slurry of 324 mg (1.25 mmol) of bis(acetonitrile)palladium dichloride[20] and 36 mg (0.21 mmol) of cupric chloride in12 mL of MeOH was slowly added (dropwise, 7 min) a solution of 105 mg (0.97 mmol) of 1,5-dimethyl-1,4-cyclohexadiene[25] in 6 mL of MeOH. After 24 h—the temperature of the reaction mixture had slowly risen to 12 °C—the yellow-orange solution was concentrated in vacuo at water aspirator pressure to afford 326 mg of a dark red-brown oil with some black particles. The entire oil sample was diluted with 40 mL of EtOAc–acetone (8:1) and flash chromatographed[21] through a 2 × 11 cm SiO_2 column packed with EtOAc–petroleum ether (4:6) and eluted with 360 mL of the same solvent mixture, followed by 200 mL of EtOAc–petroleum ether (7:3) into the same receiver. Removal of the solvent at reduced pressure (water aspirator) yielded 105 mg (0.37 mmol, 39%) of **5** as a yellow-orange oil with yellow crystals. A second flash chromatography through the same column packed and eluted with EtOAc–petroleum ether (3:7) into 10 25-mL receivers afforded 59 mg (fractions 4–10) of **5** as a yellow oil that solidified to yellow crystals in a freezer (−26 °C): mp 96.5–97.5 °C (with decomposition to black particles); IR (KBr) 3090, 3050, 3020, 2995, 2840, 2820, 1445, 1365, 1205, 1190, 1170, 1150, 1105, 1090, 1030, 1020, 985, 975, 925, 910 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.67 (2 H, H-1 and H-3, broadened d, $J_{1,6e} = J_{3,4e}$ = 2.8 Hz), 4.35 (1 H, H-5, dt, $J_{5a,6a}$ = 9.1 Hz and $J_{4e,5a} = J_{5a,6e}$ = 5.7 Hz), 3.29 (3 H, CH_3O, s), 2.51 (1 H, H-4, at least a 6-line m, $J_{4e,5a}$ = 5.7 Hz), 2.21 (1 H, H-6e, ddd, $J_{6a,6e}$ = 15.7 Hz, $J_{5a,6e}$ = 5.7 Hz, and $J_{1,6e}$ = 2.8 Hz), 2.07 (3 H, CH_3C-2, s), 1.19 (1 H, H-6a, broadened dd, $J_{6a,6e}$ = 15.7 Hz and $J_{5a,6a}$ = 9.0 Hz), 0.91 (3 H, CH_3C-4, d, J_{4e,CH_3} = 7.0 Hz); homonuclear decoupling, irradiation at δ 4.67 collapsed the signals at δ 2.51 to a quintet and at δ 2.21 to a dd and sharpened the dd at δ 1.19, irradiation at δ 4.35 collapsed the signals at δ 2.51 to an apparent q with further fine splitting, at δ 2.21 to a dd, and at δ 1.19 to a br d, irradiation at δ 2.51 collapsed the signals at δ 4.67 to an apparent s, at δ 4.35 to a dd, and at δ 0.91 to a s, irradiation at δ 2.21 collapsed the signals at δ 4.67 to a br s with a shoulder, at δ 4.35 to a dd, and at δ 1.19 to a d, irradiation at δ 1.19 collapsed the signals at δ 4.35 to a dd and at δ 2.21 to a superficial t, and irradiation at δ 0.91 collapsed the signal at δ 2.51 to a superficial t; ^{13}C NMR (50 MHz, $CDCl_3$, off-resonance heteronuclear and broad-band proton decoupling) 115.12 (s), 81.22 (d), 76.58 (d), 75.25 (d), 56.11 (q), 36.86 (d), 31.05 (dd), 22.53 (q), 15.31 (q) ppm. Anal. Calcd for $(C_9H_{15}OPdCl)_2$: C, 38.46; H, 5.38. Found: C, 38.60; H, 5.38.

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Registry No. 1, 91443-64-0; 2, 91443-65-1; 3, 91443-66-2; 4, 91466-43-2; 5, 91443-67-3; 6, 91443-68-4; 7, 91443-69-5; $(MeCN)_2PdCl_2$, 14592-56-4; MeOH, 67-56-1; 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; *o*-xylene, 95-47-6; *p*-xylene, 106-42-3; *m*-xylene, 108-38-3.

(24) Prepared by Li–NH_3–EtOH reduction of *p*-xylene, as described for *o*-xylene in ref 22, afforded 4.6 g (85%) of 1,4-dimethyl-1,4-cyclohexadiene as a pale yellow oil: NMR (60 MHz, $CDCl_3$) δ 5.37 (2 H, br s), 2.53 (4 H, s), 1.65 (6 H, s).

(25) Prepared by Li–NH_3–EtOH reduction of *m*-xylene, as described for *o*-xylene in ref 22, afforded 4.3 g (80%) of 1,5-dimethyl-1,4-cyclohexadiene as a colorless oil: NMR (60 MHz, $CDCl_3$) δ 5.40 (2 H, br s), 2.52 (4 H, br s), 1.70 (6 H, s).