that the amount of Pd/C was increased to 1 mmol and the cupric chloride was omitted. Caution—fire hazard!

The yield of methyl cinnamate prepared by tetrakis(triphenylphosphine)palladium(0) catalysis was determined by GLC analysis on a reaction run at −78° employing methanol (10 ml), styrylmercuric chloride (1 mmol), carbon monoxide, and catalyst (0.1 mmol). No lithium chloride was added. The reaction was allowed to slowly warm on its own to room temperature and stirred overnight before analysis.

Preparation of α,β-Unsaturated Acids. Both preparative and GLC reactions were run in a manner identical with the above ester reactions except that 0.5–5% aqueous THF replaced the alcohol solvent.

The following procedure for the preparation of 4,4-dimethyl-*trans*-2-pentenoic acid is representative. Anhydrous lithium chloride (20 mmol), palladium chloride (10 mmol), 5 ml of water, and 95 ml of THF were added to a 250-ml round-bottom flask containing a septum inlet and carbon monoxide inlet tube (a balloon will suffice). The flask was cooled to −78° and 3,3-dimethyl-*trans*-1-butenylmercuric chloride (10 mmol) was added. The flask was thoroughly flushed with carbon monoxide. The well-stirred reaction mixture was then allowed to slowly warm to room temperature over a 4-hr period and stirred overnight while maintaining a slight positive pressure of carbon monoxide. Ether and activated carbon were added to the reaction mixture, which was filtered, washed with saturated ammonium chloride, and finally extracted several times with saturated sodium bicarbonate solution. The bicarbonate solution was acidified with cold hydrochloric acid and extracted several times with ether. After drying over anhydrous Na_2SO_4 and removal of the solvent, one obtains 1.25 g (98%) of acid (essentially pure by GLC and ^{1}H NMR), mp 62–62.5° (hexane) (lit.[21] mp 61–62°).

The following α,β-unsaturated carboxylic acids were obtained in a similar manner. *trans*-β-Cyclohexylacrylic acid, mp 57° (hexane) (lit.[22] mp 57–58°). Cinnamic acid, mp 132° (H_2O) (lit.[23] mp 132.6–132.8°). *trans*-6-Cyano-2-hexenoic acid: mp 69.5–70°; ir max (neat) 3600–2000, 2240, 1705, 1640, 1310, 1295, and 1210 cm^{-1}; ^{1}H NMR peaks ($DCCl_3$) at δ 1.90 (m, 2 H, CCH_2C), 2.1–2.7 (m, 4 H, $NCCH_2$ and allyl), 5.88 (dt, J = 1 and 16 Hz, 1 H, vinyl), 7.03 (dt, J = 7 and 16 Hz, 1 H, vinyl), and 11.06 (s, 1 H, COOH); *m/e* 121.0524 ± 0.0006 (calcd for $C_7H_9NO_2$, 121.0528). *trans*-β-(1-Cyclohexenyl)acrylic acid: mp 116.5–117.5° (hexane); ir max (KBr) 3300–2000, 1675, 1600, 1410, 1305, and 1275 cm^{-1}; ^{1}H NMR peaks ($DCCl_3$) at δ 1.66 (m, 4 H, CH_2CH_2), 2.18 (m, 4 H, allyl), 5.73 (d, J = 16 Hz, 1 H, CHCO), 6.20 (m, 1 H, vinyl), 7.35 (d, J = 16 Hz, 1 H, vinyl), and 11.28 (br, 1 H, COOH); *m/e* 152.0838 ± 0.0008 (calcd for $C_9H_{12}O_2$, 152.0837).

The catalytic carboxylic acid reactions were run exactly as those of the esters except that 5% aqueous THF was employed as the solvent and saturated ammonium chloride and ether were added to the reaction before GLC analysis.

Acknowledgment. The author gratefully acknowledges the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their generous support of this research. Partial support by the Iowa State Research Foundation is also greatly appreciated. A special debt of gratitude is due Professor George Zweifel, who generously provided numerous authentic samples, and Matthey Bishop, Inc., for a large loan of palladium chloride.

References and Notes

(1) Part V: R. C. Larock, *J. Org. Chem.*, **39**, 3721 (1974).
(2) L. R. Barlow and J. M. Davidson, *J. Chem. Soc. A*, 1609 (1968).
(3) J. M. Davidson, *J. Chem. Soc. A*, 193 (1969).
(4) R. F. Heck, *J. Am. Chem. Soc.*, **90**, 5518 (1968).
(5) P. M. Maitlis, "The Organic Chemistry of Palladium", Vol. II, Academic Press, New York, N.Y., 1971, pp 18–33.
(6) J. K. Stille and P. K. Wong, *J. Org. Chem.*, **40**, 335 (1975).
(7) L. F. Hines and J. K. Stille, *J. Am. Chem. Soc.*, **94**, 485 (1972).
(8) P. M. Henry, *Tetrahedron Lett.*, 2285 (1968).
(9) R. C. Larock and H. C. Brown, *J. Organomet. Chem.*, **36**, 1 (1972).
(10) R. C. Larock, S. K. Gupta, and H. C. Brown, *J. Am. Chem. Soc.*, **94**, 4371 (1972).
(11) H. Staub, K. P. Zeller, and H. Leditschke in Houben-Weyl, "Methoden der Organischen Chemie", Vol. 13, 4th ed, Georg Thieme Verlag, Stuttgart, 1974, Part 2b, pp 192–199.
(12) A. N. Nesmeyanov and N. K. Kochetkov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 76 (1949).
(13) A. N. Nesmeyanov, A. E. Borisov, and V. D. Vil'chevskaya, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1008 (1954).
(14) G. Drefahl, G. Heublein, and A. Wintzer, *Angew. Chem.*, **70**, 166 (1958).
(15) H. C. Brown, D. H. Bowman, S. Misumi, and M. K. Unni, *J. Am. Chem. Soc.*, **89**, 4531 (1967).
(16) G. Zweifel, R. P. Fisher, J. T. Snow, and C. C. Whitney, *J. Am. Chem. Soc.*, **93**, 6309 (1971).
(17) G. Zweifel, G. M. Clark, and N. L. Poston, *J. Am. Chem. Soc.*, **93**, 3395 (1971), and references cited therein.
(18) A. Schoenberg, I. Bartoletti, and R. F. Heck, *J. Org. Chem.*, **39**, 3318 (1974).
(19) J. J. Sudborough and L. L. Lloyd, *J. Chem. Soc.*, **73**, 89 (1898).
(20) Y. Hata, *Nippon Kagaku Zasshi*, **79**, 1531 (1958); *Chem. Abstr.*, **54**, 24620*cd* (1960).
(21) R. T. Arnold, O. C. Elmer, and R. M. Dodson, *J. Am. Chem. Soc.*, **72**, 4359 (1950).
(22) S. S. G. Sircar, *J. Chem. Soc.*, 55 (1928).
(23) K. Kraut, *Justus Liebigs Ann. Chem.*, **147**, 112 (1868).

The Palladium Dichloride Complex of 4-Vinylcyclohexene

W. Todd Wipke*[1a] and G. L. Goeke

Department of Chemistry, Princeton University, Princeton, New Jersey 08540

Received August 27, 1974

In our hands the reported rearrangement of 4-vinylcyclohexene to 1,5-cyclooctadiene upon reaction with bisbenzonitrilepalladium dichloride does not occur. A variety of conditions were explored to try to induce rearrangement. NMR analysis of the product and its reactions with nucleophiles indicate that the product is the unrearranged π,π complex of 4-vinylcyclohexene. The reaction of related alkyl-substituted dienes with bisbenzonitrilepalladium dichloride is discussed.

The ability of transition metals to effect skeletal rearrangements of olefins is well documented.[1b] Wilkinson et al. reported the conversion of 4-vinylcyclohexene to 1,5-cyclooctadiene using an iridium salt.[2] This same conversion was reported using $(PhCN)_2PdCl_2$,[3] but an analogous reaction with Na_2PtCl_4 gave no rearranged product.[4a] In addition, no rearrangement occurred with 4-substituted 4-vinylcyclohexenes via the palladium complex.[4b]

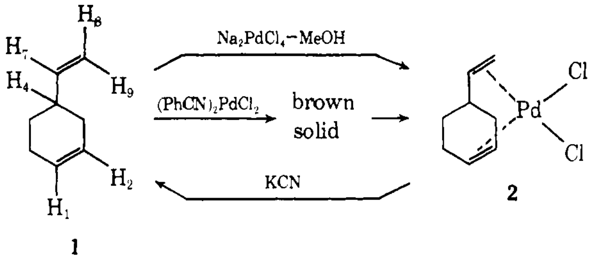
In connection with our studies on the effect of diene structure on nucleophilic additions to palladium complexes, we investigated the reaction of 4-vinylcyclohexene with $(PhCN)_2PdCl_2$ and now report that the palladium complex remains unrearranged, in contrast to earlier reports.[3] We also report on the tendency of some related dienes to complex with palladium.

Results

The reaction between 4-vinylcyclohexene and bisbenzonitrilepalladium dichloride [$(PhCn)_2PdCl_2$] in benzene immediately produces a dark brown solid, which on standing at room temperature is transformed into a gold-colored solid, in agreement with Frye's observation.[3] However, in our hands, decomposition of this solid with KCN gave 4-vinylcyclohexene as the only organic product, and not 1,5-cyclooctadiene as Frye reported. The gold-colored solid could also be prepared in acetone or chloroform without the intermediacy of the brown solid.

Paiaro reported the formation of 2 from 4-vinylcyclohexene and Na_2PdCl_4.[5] We repeated this reaction and found the product to be identical with our gold-colored solid. These results are depicted in Scheme I.

Scheme I



Since Frye's observation has been widely cited as one of a few samples of a rearrangement initiated by palladium, we examined possible ways to induce this rearrangement: allowing the brown solid to stand in the presence of trace amounts of acetic acid, methanol, NaOH, excess diene, PhCN, $CHCl_3$, or acetone always resulted in the same transformation to 2. In addition, heating a benzene solution of this solid to reflux with traces of PhCN, $CHCl_3$, or excess 4-vinylcyclohexene likewise produced 2.

NMR analysis of 2 further supports the unrearranged π,π structure. Figure 1 depicts the olefinic region of 2 as well as a deuterated and a methyl derivative (5 and 7, respectively). These were prepared as shown in Scheme II.

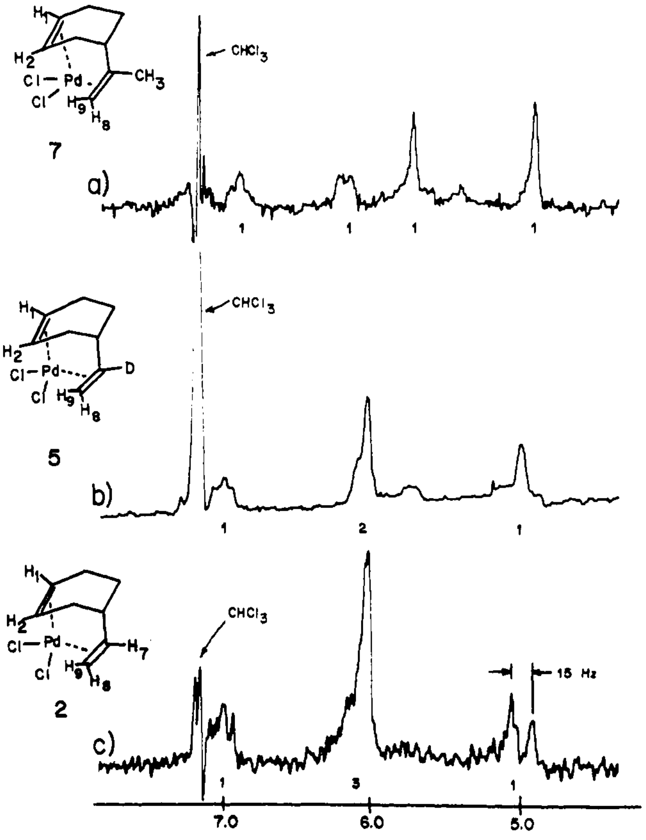
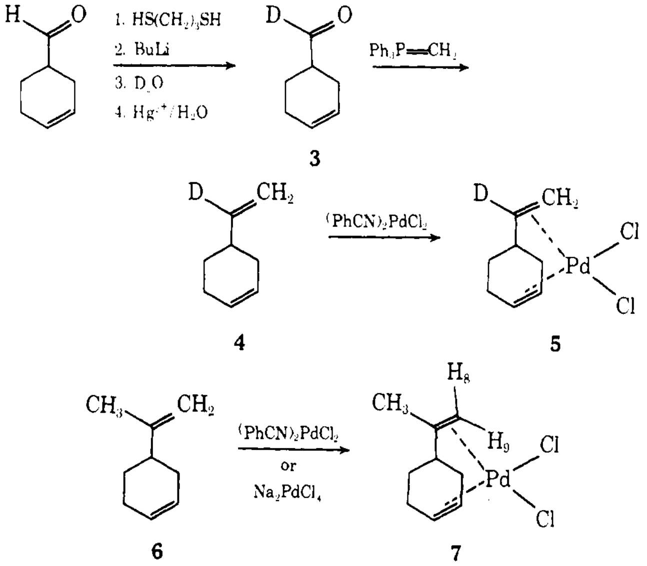


Figure 1. NMR spectra (100 MHz) of the olefinic region of complexes (a) 7, (b) 5, and (c) 2 in $CDCl_3$ with Me_4Si as internal standard after 70 scans with CAT.

Scheme II

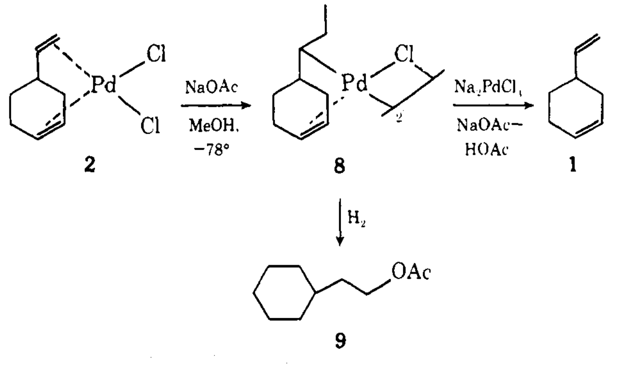


The magnetically nonequivalent cyclohexene protons in compound 7 (Figure 1a) appear as broad absorptions at δ 6.82 and 6.14 ppm. The sharper absorptions at δ 5.62 and 4.70 ppm are H_8 and H_9, respectively. The increased shielding of H_9 arises from the diamagnetic anisotropy of the C-5–C-6 bond, above which it is constrained to lie in order for the diene to be favorably aligned for π,π-complex formation.[6]

Compounds 2 and 5 (Figures 1c and 1b) likewise display broad absorptions for the cyclohexene protons at δ 7.01 and 6.0 ppm. Replacement of H_7 by deuterium results in a disappearance of the absorption at δ 6.01 ppm and in a loss of coupling (J = 15 Hz) in the doublet at δ 5.0 ppm in 2; this doublet is assigned to H_9. The splitting arises from trans coupling with H_7.[6] The remaining resonance at δ 6.01 ppm in 2 may be assigned to H_8. The cis coupling between H_7 and H_8 cannot be discerned because of the accidental equivalence of H_7, H_8, and $H_{1(2)}$.

Reaction of 2 with acetate ion lends additional supports for our structural assignment.[5] In methanol at room temperature, reduction to the metal occurs. However, at −78°, a light, gray solid forms which can be isolated by filtering in the cold. An identical solid results from reaction of 4-vinylcyclohexene with Na_2PdCl_4 in HOAc–NaOAc at room temperature. Elemental analysis of this solid indicates the empirical formula $C_{10}H_{15}ClO_2Pd$, and reduction with hydrogen affords 2-cyclohexylethyl acetate (9). These results suggest that complex 2 has undergone nucleophilic attack by acetate ion to give complex 8 (Scheme III).

Scheme III



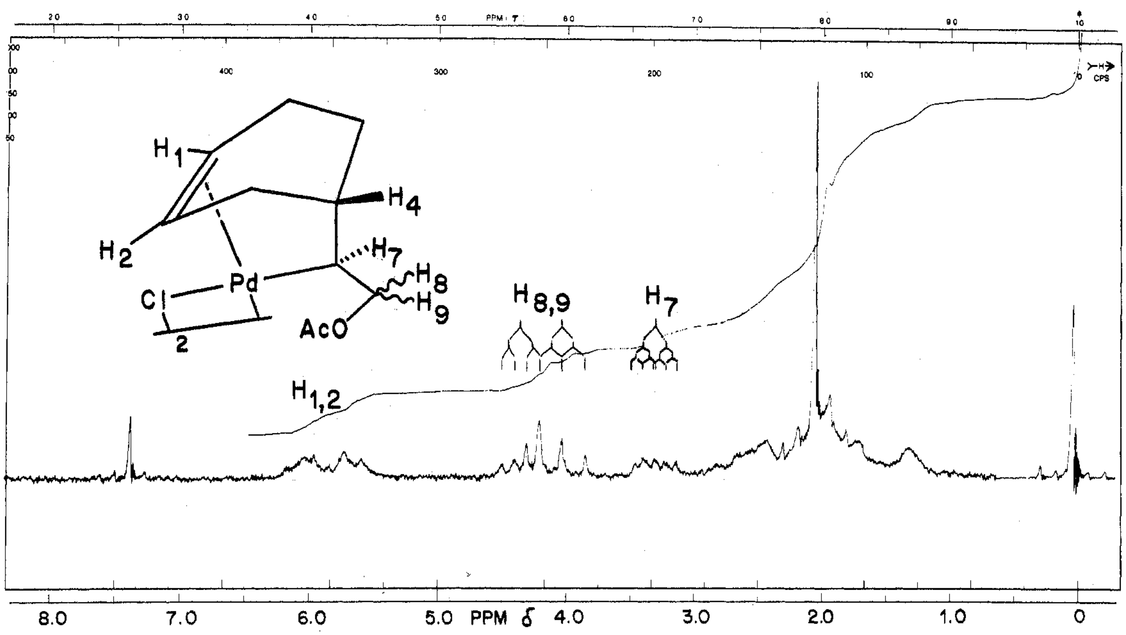
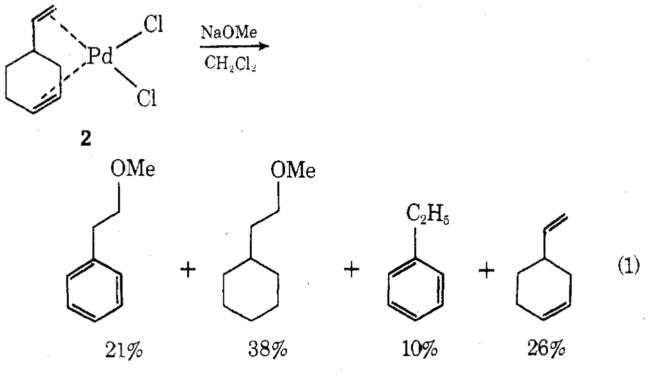


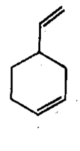
Figure 2. NMR spectrum (60 MHz) of complex 8 in $CDCl_3$ with Me_4Si as internal standard ($J_{4,7}$ and $J_{7,8}$ = 6, $J_{7,9}$ and $J_{8,9}$ = 11.5 Hz).

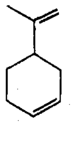
The 60-MHz NMR spectrum of 8 (Figure 2) shows the typical broad absorptions for the olefinic protons (δ 5.6–6.2 ppm), and a sharp acetoxy methyl group at δ 2.02 ppm. The methylene protons (H_8 and H_9) are magnetically nonequivalent since they are adjacent to a chiral center (C-7).[6] These give rise to two AB patterns at δ 4.35 and 4.0 ppm with a geminal coupling of 11.5 Hz. The complex pattern at δ 3.28 is assigned to H_7, which couples with H_8 and H_9 (J = 11.5 and 6.0 Hz) and H_4 (J = 6.0 Hz).

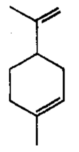
The instability of 8 when prepared in MeOH was thought to be due to a competition between acetate and methoxide ion. Attempts to prepare the methoxy analog of 8 by the reaction of 2 with $MeOH–Na_2CO_3$ failed; palladium metal and a sweet-smelling liquid (11 products by VPC) were isolated. A similar mixture was obtained from the reaction of 4-vinylcyclohexene with $PdCl_2$ or Na_2PdCl_4 in $MeOH–Na_2CO_3$. However, reaction of 2 with CH_2Cl_2–NaOMe gave four main products (eq 1) which were identified by VPC comparison with the pure compounds. The methyl ethers presumably result from nucleophilic attack on the olefins, and the aromatic products arise from disproportionation of the olefins.[7]

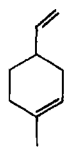


The addition of dienes 1 and 7 to solutions of palladium salts results in a discharge of the deep red color and precipitation of the diene complex. Under identical conditions, dipentene (10) fails to discharge the color and no precipitation occurs. Similarly, 1-methyl-4-vinylcyclohexane (11) behaves like dipentene and apparently fails to coordinate with the metal. It thus appears that the ring methyl substituent to 10 and 11 destabilizes the diene toward complex formation.


1


7

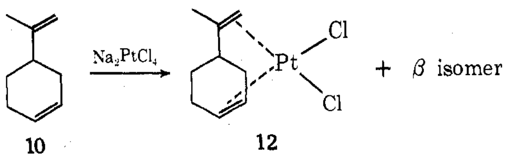

10


11

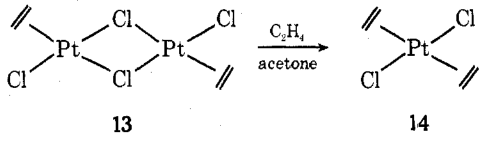
Discussion

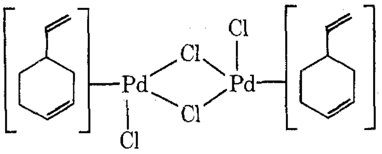
The foregoing evidence clearly indicates that the rearrangement of 4-vinylcyclohexene to 1,5-cyclooctadiene via a palladium complex did not occur; the nature of the brown, intermediate solid still remains to be determined.

Chatt and Wilkins[8] found that dipentene (10) forms two complexes with platinum. X-Ray crystallography revealed the more stable α isomer to be the normal 1,3-diene complex 12, but the structure of the β isomer remains unknown. Chatt proposed a structure in which Pt–Cl had added across one olefin bond. However, the insolubility of the complex argues against this since most σ, π complexes of this type are very soluble in the solute used.[9] The insolubility of 2 and 15 also prevent osmometric molecular weight determination.



Chatt and Wilkins also observed the formation of 14 from dimer 13 in the presence of excess ethylene and acetone.[10] In this reaction acetone functions to cleave the μ bridge in 13. We suggest that the brown complex is a di-



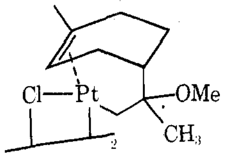


15

meric complex 15 analogous to 13 which is kinetically formed in nonpolar solvents. In polar solvents, the μ bridges are cleaved, resulting in the formation of the more thermodynamically stable gold-colored complex 2.

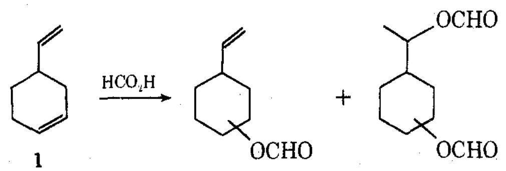
The NMR spectra of 2, 5, and 8 can be interpreted in light of current theory on the spectrum of palladium and platinum olefin complexes.[11,12] The olefinic protons are markedly deshielded in these complexes as is expected;[12] coordination of palladium results in a shift of electron density from the olefin to the metal, thereby reducing the electron density near the proton and causing a downfield shift. Palladium and platinum are unique in this respect, since upfield shifts are observed with all other uncharged metal complexes.[11] In addition to being deshielded, H_1 and H_2 in complexes 2, 5, and 8 are widely separated relative to the parent hydrocarbon ($\Delta\delta$ 0.8 ppm) owing to the unsymmetrical disposition of the olefin bond with respect to the palladium atom.[11]

Two interesting features of the acetate addition to diene complex 2 are the orientation and the selectivity of the addition. The anti-Markovnikov orientation of the product parallels that observed with other nucleophiles[13] as well as additions to other diene complexes (1,5 hexadiene[14] and 5-vinylbicyclo[2.2.2]oct-2-ene). However, addition of methoxide ion to the dipentene platinum complex gives the Markovnikov addition product 16.[15,16] In this case, the yield is very low (2.7%), and it could be that the anti-Markovnikov addition product is formed, but is unstable under the reaction conditions.



16

The selectivity does not parallel observations with other diene complexes (dipentene,[16] dicyclopentadiene,[16] 5-vinyl-2-norbornane[17]) in which nucleophilic additions to the complexes occur with the same selectivity as do ionic additions to the free dienes.[18] In the case of 4-vinylcyclohexene, nucleophilic additions to the complex occur at the acyclic double bond, but ionic additions to the free diene take place preferentially at the cyclohexene bond (eq 2).[19]



1 61% 27% (2)

Considerably more research is necessary to determine if there is any significance in this type of comparison.

The finding that 1 and 7 form palladium π complexes whereas 10 and 11 do not suggests that, at least with palladium, the complex can tolerate an alkyl group on the acyclic double bond, but not on the cyclohexenyl double bond. Although the electron-donating effect of a methyl group should tend to destabilize the complex,[20] the difference between 7 and 11 must be steric. In 7, there can be some rotation about the acyclic single bond which skews the double bonds, but puts the methyl group further away from the metal. In 11, the methyl group is constrained by the ring which leads to effectively a larger steric congestion.

In the case of the platinum dipentene complex, the greater stability of the platinum–olefin bond relative to that of palladium[21] is apparently able to overcome the steric destabilization.

Experimental Section

Melting points were taken on a Mel-Temp apparatus, and are uncorrected. Spectral measurements were made on the following instruments: NMR, Varian Associates Model A-60 and A-100; ir, Perkin-Elmer Model 237B grating spectrophotometer; VPC, Varian Associates Aerograph, Model 90-P, SE-30 column; CAT, Varian Model C-1024. Elemental analyses were performed by Schwarzkopf Microanalytical Lab, Woodside, N.Y. Bisbenzonitrilepalladium dichloride was prepared by the method of Kharasch.[22] All other chemicals were reagent grade materials.

General Procedure for the Reaction of Dienes with Palladium Salts. The palladium salt and the solvent were placed in an erlenmeyer flask, a serum cap was attached, and the flask was flushed with nitrogen. The diene was injected and the contents were stirred at room temperature until either a new solid formed, or a color change indicated completion of reaction. The contents were filtered, and the precipitate was washed with ligroin and dried in a desiccator. Additional solid could be obtained by diluting the solvent layer with ligroin and filtering as before.

Reaction of 4-Vinylcyclohexene with $(PhCN)_2PdCl_2$ in Benzene. The general procedure was followed using 0.192 g (0.5 mmol) of $(PhCN)_2PdCl_2$ and 0.5 ml of the diene in 10 ml of benzene. A dark brown precipitate formed immediately. Upon standing for 8 hr at room temperature, the solid turned bright yellow. This was isolated to give 0.099 g (70%) of gold-colored flakes (2), mp 132–136° dec. Anal. Calcd for $C_8H_{12}Cl_2Pd$ (285): C, 33.68; H, 4.21; Cl, 24.91. Found: C, 33.44; H, 4.12; Cl, 25.11 (Schwarzkopf B21756).

The procedure was repeated, but the brown solid was isolated immediately after precipitating. Three separate analyses on this solid gave inconsistent results, the chloride analysis being consistently high, mp 128–134° dec. This solid changed into the gold-colored flakes upon contact with polar solvents (acetone, $CHCl_3$, acetic acid, methanol).

In $CHCl_3$ or Acetone. The above procedure was repeated using chloroform and acetone as solvents. A bright golden solid was formed immediately upon contact of the diene with the palladium solution. These were isolated to give 92 and 78% yields of the same gold-colored complex (2), respectively.

Reaction of 4-Vinylcyclohexene with Na_2PdCl_4. Using the general procedure, 0.588 g (2.0 mmol) of the palladium salt was allowed to react with 1.0 ml of the diene in 20 ml of $CHCl_3$. After stirring for 1.5 hr, golden crystals had formed. These were isolated to give 0.544 g (94%) of a gold-colored solid (2), mp 129–134° dec (lit.[5] mp 128–130° dec). The NMR and ir spectra of this and the previously prepared compound were identical. Aside from the olefinic protons (see Figure 1), the aliphatic region appeared as a broad band at δ 1.8–3.4 ppm, ir (KBr) ν 1505 cm^{-1} (1c coordinated C=C).

Decomposition of Complex 2 with KCN. Each of the above complexes (complex 2) was stirred with a solution containing 5 ml of 1.5 *M* KCN and 5 ml of CCl_4. After 0.5 hr, the solids had dissolved, leaving a colorless liquid. Stirring was continued for an additional 0.5 hr, after which time the layers were separated. The organic layer was dried over $MgSO_4$ and the solvent was removed to leave a clear liquid which gave NMR and VPC retention data identical with those of 4-vinylcyclohexene.

Reaction of 2 with NaOAc. Complex 2 (0.298 g, 1.0 mmol), NaOAc (0.172 g, 2.0 mmol), and 10 ml of methanol were stirred in a Dry Ice–acetone bath for 0.5 hr. The pale yellow solution was allowed to warm, whereupon the solution turned gray. The solution was immediately filtered, and the precipitate was washed with ligroin and dried in a desiccator to give 0.244 g (79%) of 8 as a light gray solid: mp 95–103° dec; ir (KBr) ν 1736 (s, C=O), 1510 cm^{-1} (w, coordinated C=C).

Reaction of 4-Vinylcyclohexene with Na_2PdCl_4 in HOAc–

NaOAc. The general procedure was followed using 0.294 g (1.0 mmol) of Na_2PdCl_4, 0.164 g (2.0 mmol) of NaOAc, and 0.5 ml of the diene in 10 ml of HOAc. Within 5 min, a pale yellow solid formed. This was stirred for 0.5 hr and the solution was filtered. The solid was washed repeatedly with ligroin and water and dried in a desiccator to give 0.2377 g (73%) of **8** as a yellow solid: mp 103–105° dec; ir identical with that prepared above; NMR, see text. Anal. Calcd for $C_{20}H_{30}Cl_2O_4Pd_2$ (618.16): C, 38.86; H, 4.89; Cl, 11.47. Found: C, 38.99; H, 4.85; Cl, 11.81 (Hoffmann-La Roche 92735).

Hydrogenation of 8. The complex (0.162 g, 0.25 mmol) in 10 ml of THF was hydrogenated on a Paar apparatus for 0.5 hr at 20 psi. The solution was filtered, and the solvent was evaporated to give 0.042 g of a clear liquid. NMR, ir, and VPC data were identical with those of 2-cyclohexylethyl acetate (**9**) prepared from the commercially available alcohol.

Deuterio-3-cyclohexenecarboxaldehyde (3). The dithiane of 3-cyclohexenecarboxaldehyde was prepared in 94% yield according to Seebach;[23] analytical data were in accord with the proposed structure. The dithiane was deuterated by the method of Seebach[24] to afford the product in 91% yield as a clear liquid, bp 130° (4 mm); NMR integration indicated 99% deuterium incorporation.

The deuterated dithiane was hydrolyzed in 90% aqueous acetone according to the method of Seebach.[24] The deuterated aldehyde (**3**) was obtained as a clear liquid in 40% yield: bp 62° (30 mm); ir (CCl_4) ν 2045 (m, C–D), 1718 (s, C=O), 1650 cm^{-1} (w, C=C); NMR (CCl_4) δ 5.67 (2 H, s, CH=CH), 1.7–2.5 ppm (7 H, mound, ring H) and the absence of aldehyde H.

4-(α-Deuteriovinyl)cyclohexene (4). The method of Corey[25] was employed using 1.1 g (10.0 mmol) of aldehyde **3** and 10.0 mmol of methylenetriphenylphosphorane. The mixture was stirred for 15 min at room temperature, and the product was distilled. The fraction boiling below 40° (4 mm) was collected in a cold trap. This liquid was diluted with pentane, washed with water, and dried over $MgSO_4$. The clear liquid was passed through a short alumina column (Woelm neutral, activity I) using pentane as eluent. Evaporation of the solvent gave 0.24 g (23%) of diene **4**: ir (CCl_4) ν 1650 cm^{-1} (w, C=C) and absence of aldehyde C=O; NMR (CCl_4) δ 5.59 (2 H, s, CH=CH), 4.91 (2 H, mound, C=CH_2), and 1.05–2.5 ppm (7 H, mound, ring H).

4-(α-Deuteriovinyl)cyclohexenepalladium Dichloride (5). The deuterated diene (**4**) was added to a solution of 0.1 g of $(PhCN)_2PdCl_2$ in 2 ml of benzene. The dark brown solid which formed immediately was allowed to stand in the mother liquor for 8 hr, and then filtered. The dark gold-colored solid was washed with ligroin and dried in a desiccator to give 55.9 mg of **5**: mp 129–133° dec; ir (KBr) ν 1510 cm^{-1} (w, C=C); NMR ($CDCl_3$), see Figure 1.

4-Isopropenylcyclohexene (6). The procedure employed was identical with that used in the preparation of **4** starting from 12.4 g (0.1 mol) of 4-acetylcyclohexene (prepared according to literature report[26]). The crude product was passed through an alumina column (Woelm neutral, activity I) using pentane as eluent. After removing the solvent, 7.23 g (60%) of **6** was obtained as a clear liquid: bp 157° (760 mm) [lit.[27] bp 39–40° (10 mm)]; ir (CCl_4) ν 1643 cm^{-1} (w, C=C); NMR (CCl_4) δ 5.7 (2 H, s, CH=CH), 4.73 (2 H, s, C=CH_2), 1.8–2.4 (7 H, br mound, ring H), 1.7 ppm (3 H, s, C=CCH_3).

4-Isopropenylcyclohexenepalladium Dichloride (7). Using the general procedure, complex **7** was prepared in 62% yield from Na_2PdCl_4–$CHCl_3$, 82% yield from $(PhCN)_2PdCl_2$–$CHCl_3$, and 73% yield from $(PhCN)_2PdCl_2$–benzene. The dark, golden granules had identical melting behavior as well as ir and NMR spectra: mp 73–76° dec; ir (KBr) ν 1534 and 1515 cm^{-1} (w, coordinated C=C); NMR ($CDCl_3$), see text. Anal. Calcd for $C_9H_{14}Cl_2Pd$ (299): C, 36.12; H, 4.70; Cl, 23.7; Pd, 36.10.) Found: C, 35.65; H, 4.83; Cl, 23.74; Pd, 36.25 (Schwarzkopf B23617).

1-Methyl-4-vinylcyclohexene (11). The procedure employed for the preparation of **4** was followed, using 12.4 g (0.1 mol) of 4-methyl-3-cyclohexenecarboxaldehyde (prepared according to the literature[26]). The crude product was passed through an alumina column (Woelm neutral, activity I) using pentane as eluent. Evaporation of the solvent gave 5.98 g (49%) of **13** as a clear liquid: bp 152° (760 mm) [lit.[28] bp 87–90° (100 mm)]; ir (CCl_4) ν 1640 cm^{-1} (w, C=C) and the absence of aldehyde C=O; NMR (CCl_4) δ 5.8 (1 H, ABC pattern, CH=CH_2, $J_{1,3}$ = 17, $J_{2,3}$ = 10, $J_{3,4}$ = 5.8 Hz), 4.88 [1 H, m, CH=CH_2 (H_2)], 4.95 [1 H, m, CH=CH_2 (H_3)], 1.6–2.1 (7 H, mound, ring H), 1.66 ppm (3 H, br s, C=CCH_3).

Reaction of 2 with NaOMe. The general procedure was followed using 0.285 g (1.0 mmol) of complex **2** and 0.1 g (2.5 mmol) of NaOMe in 10 ml of CH_2Cl_2. After 0.5 hr, the contents had blackened. The mixture was filtered, and the solvent was reduced. VPC of the liquid (10% SE-30,110° column temperature) indicated the presence of four main products, and unidentified products with less than 3 min retention (eq 1). The four main products were identified by VPC comparison with pure compounds.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also thank Hoffmann-La Roche, Inc., Nutley, N.J., for partial support of this work.

Registry No.—**1**, 100-40-3; **2**, 41660-18-8; **3**, 56454-09-2; **4**, 56454-10-5; **5**, 56468-31-6; **6**, 26325-89-3; **7**, 56468-32-7; **8**, 56468-33-8; **11**, 17699-86-4; $(PhCN)_2PdCl_2$, 14220-64-5; $NaPdCl_4$, 13820-53-6; 4-acetylcyclohexene, 7353-76-6.

References and Notes

(1) (a) Board of Studies in Chemistry, University of California, Santa Cruz, Calif. 95064. (b) P. M. Maitlis, "The Organic Chemistry of Palladium", Vol. 1, Academic Press, New York, N.Y., 1971.
(2) J. F. Young, R. D. Gillard, and G. Wilkinson, *J. Chem. Soc.*, 5176 (1964).
(3) H. Frye, F. Kuljian, and J. Viebrock, *Inorg. Nucl. Chem. Lett.*, **2**, 119 (1966).
(4) (a) E. Kuljian and H. Frye, *Z. Naturforsch. B*, **20**, 204 (1965); (b) H. Frye and D. Chinn, *Ibid.*, **5**, 613 (1969).
(5) G. Paiaro, A. De Renzi, and R. Palumbo, *Chem. Commun.*, 1150 (1967).
(6) L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy", Pergamon Press, Elmsford, N.Y., 1959, p 116.
(7) F. J. Karol and W. L. Carrick, U.S. Patent 3,287,427; *Chem. Abstr.*, **66**, 115359d (1967).
(8) J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 2622 (1952).
(9) W. T. Wipke and G. L. Goeke, *J. Am. Chem. Soc.*, **96**, 4244 (1974).
(10) J. Chatt and A. A. Williams, *J. Chem. Soc.*, 3061 (1951).
(11) M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Adv. Organomet. Chem.*, **3**, 1–179 (1965).
(12) W. Partenheimer, Ph.D. Thesis, University of Iowa, 1968, p 211.
(13) R. Palumbo, A. DeRenzi, A. Panunzi, and G. Paiato, *J. Am. Chem. Soc.*, **91**, 3874 (1969).
(14) M. Graziani, G. Carturan, and R. E. Ros, *Chim. Ind. (Milan)*, **55**, 775 (1973).
(15) Clearly the orientation of addition is a result of many factors besides degree of substitution at each end of the olefin, e.g., see ref 9.
(16) J. K. Stille and R. A. Morgan, *J. Am. Chem. Soc.*, **88**, 5135 (1966).
(17) W. T. Wipke and G. L. Goeke, *J. Am. Chem. Soc.*, **96**, 4244 (1974).
(18) S. J. Cristol, W. K. Seifert, D. W. Johnson, and J. B. Jurale, *J. Am. Chem. Soc.*, **84**, 3918 (1962); G. T. Youngblood, C. D. Trivette, Jr., and P. Wilder, *J. Org. Chem.*, **23**, 684 (1958); E. E. Royals, *J. Am. Chem. Soc.*, **71**, 2568 (1949); K. Suga and S. Watanabe, *Nippon Kagaku Zasshi*, **81**, 1139 (1960); *Chem. Abstr.*, **56**, 507*b* (1962).
(19) R. C. Kudor, U.S. Patent 2,764,610; *Chem. Abstr.*, **51**, 4420*y* (1957).
(20) R. G. Denning, F. R. Hartley, and L. M. Venanzi, *J. Chem. Soc. A*, 324, 328 (1967).
(21) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 705 (1959).
(22) M. S. Kharasch, R. C. Seyler and F. R. Mayo, *J. Am. Chem. Soc.*, **60**, 882 (1938).
(23) D. Seebach, *Synthesis*, **1**, 17 (1969).
(24) D. Seebach, B. W. Erickson, and G. Singh, *J. Org. Chem.*, **31**, 4303 (1966).
(25) R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).
(26) K. Alder and W. Vogt, *Justus Liebigs Ann. Chem.*, **564**, 109 (1949).
(27) P. Frantisek, J. Miroslav, and J. Kovar, *Chem. Listy*, **45**, 300 (1951).
(28) A. A. Petrov and N. P. Sopov, *Zh. Obshch. Khim.*, **27**, 1795 (1957).