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REACTIONS OF BICYCLIC CYCLOPROPANES AND BICYCLIC CYCLOBUTANES WITH DICHLOROBIS(BENZONITRILE)PALLADIUM(II)

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Summary

Exo- and *endo*-9-methylbicyclo[6.1.0]non-4-enes react with dichlorobis(benzonitrile)palladium(II) to produce initially the isomeric dimeric (chlorine bridged) π-complexes, $(PdCl_2 \cdot C_{10}H_{16})_2$. The π-complexes rearrange within minutes in solution at room temperature to produce stereospecifically the chlorine bridged dimeric trihapto-σ,π-cyclooctenyl complexes which result from chloropalladation of the external cycopropane carbon—carbon bond, with chlorine bound at the carbon bound to methyl. The chloropalladations also occur during several hours at 75°C in the solid state. The σ,π-cyclooctenyls react with cyanide ion to produce quantitatively 9-methyl-*trans*-bicyclo[6.1.0]non-4-ene, which hydrocarbon was also independently synthesized. The *trans*-fusion in the product of cyanide displacement implies an inversion at carbon along the reaction pathway. The relationship of this chemistry to cyclopropane oxymercuration is discussed. The cyclobutane containing hydrocarbon bicyclo[6.2.0]dec-4-ene was incorporated in a π-complex similar to those above. The cyclobutane moiety was found to be inert to chloropalladation under mild to moderate conditions.

Introduction

In previous work from this laboratory we have demonstrated the versatility of organopalladium intermediates in the facile cleavage of cyclopropane carbon—carbon [1,2] and aziridine carbon—nitrogen bonds [3], and in the facile formation of carbon—carbon bonds on treatment of palladium chloroalkenyls with cyanide ion. Thus, bicyclo[6.1.0]non-4-ene, I, reacts readily with dichlorobis(benzonitrile)palladium(II), II, to give the σ,π-chelate, III, as in eq. 1. Reaction of III with cyanide then gives a quantitative yield of *trans*-bicyclo-

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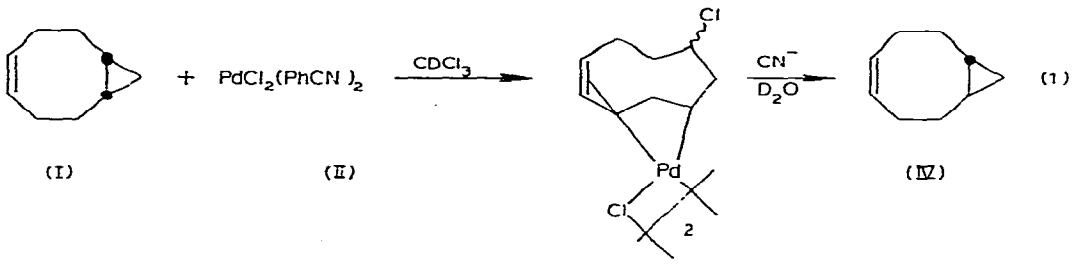
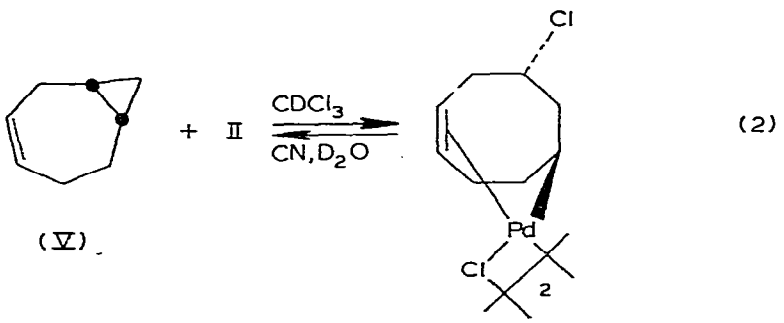
[6.1.0]non-4-ene, IV [1].



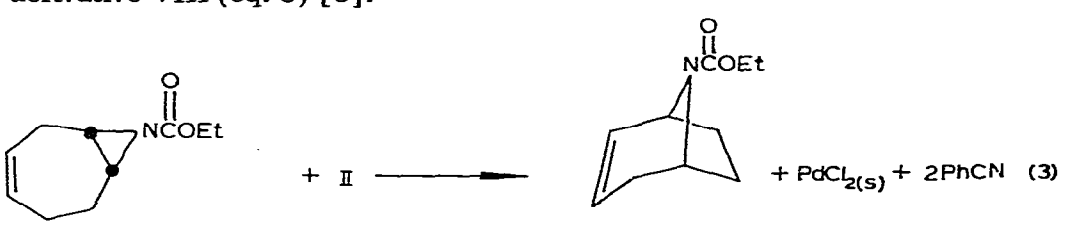
(I) (II) (III) (IV)

Similarly, reaction of bicyclo[5.1.0]non-3-ene, V, with II results in quantitative conversion to σ,π-chelate VI, which reacts with cyanide to reform starting V (eq. 2) [2]. The aziridine analogue of V, namely compound VII, was found to



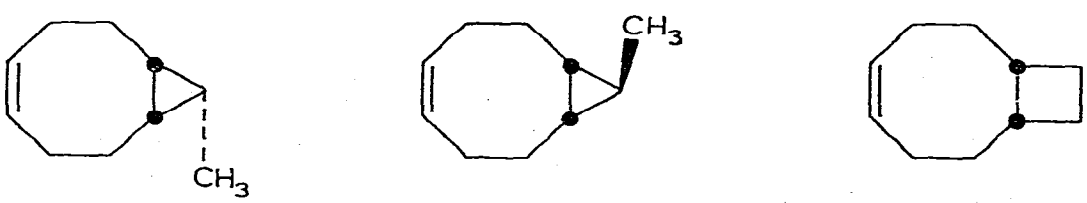
(V) (VI)

react both stoichiometrically and catalytically with II to form the tropane derivative VIII (eq. 3) [3].



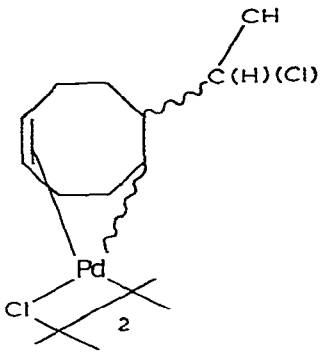
(VII) (VIII)

In the present communication we report the results of our further studies of reaction of II with three hydrocarbons: *endo*-9-methylbicyclo[6.1.0]non-4-ene, IX; *exo*-9-methylbicyclo[6.1.0]non-4-ene, X; and *cis*-bicyclo[6.2.0]dec-4-ene, XI.



(IX) (X) (XI)

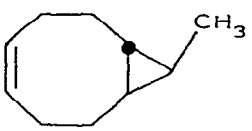
In contrast to the earlier work with I, we find that chloropalladation of IX and X proceeds with stereospecific cleavage of the exocyclic cyclopropane carbon—carbon bond to give intermediates of general formula XII. Intermediates XII, in which EN and EX refer only to the stereochemistry of the starting hydrocar-



(XII (EN) from IX ;

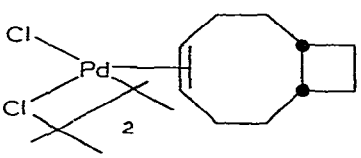
XII (EX) from X)

bon, react with cyanide to produce quantitatively the new hydrocarbon 9-methyl-*trans*-bicyclo[6.1.0]non-4-ene, XII. The relative stereochemistries of Pd and the α-chloroethyl groups in XII (EN) and XII (EX) are not as yet established (vide infra).



(XII)

Hydrocarbon XI reacts readily with II to form a π-complex XIV. However, XIV is surprisingly inert to further reaction such as cyclobutane ring opening via chloropalladation.



(XIV)

Experimental

^{1}H NMR spectra were obtained at 90 MHz (Varian EM390), ^{13}C NMR spectra were obtained at 22.639 MHz (Bruker WH90). Infrared spectra were obtained using a Perkin-Elmer Model 283 instrument. Dichlorobis(benzonitrile)-palladium(II) was prepared by the Kharasch procedure [4]. Microanalysis was performed by C.F. Geiger, Ontario, CA; or Chemalytics, Inc., Tempe, AZ.

Preparation of epimeric 9-methylbicyclo[6.1.0]non-4-enes [5]

cis,cis-1,5-Cyclooctadiene (159 g, 1.47 mol) was added to a solution of 72.6 g (0.588 mol) diethylzinc in 250 ml hexane (under nitrogen). Ethylidene iodide (138 g, 0.490 mol) was added dropwise to the hexane solution over a period of 3.5 h. The resulting solution was stirred for 22 h and was quenched with 12 ml 95% ethanol. The reaction mixture was washed with dilute hydrochloric acid, with water, and with dilute HCO_3^- solution, and was dried over anhydrous $MgSO_4$. Atmospheric pressure distillation up to 140°C removed low boiling fractions. The resdue was vacuum distilled (25 Torr) using a short path Vigreux column, and the total 66—118°C fraction was collected. The 66—118°C fraction was separated by vacuum distillation (25 Torr) using a Teflon spinning band column. Altogether 17.2 g *endo*-bicyclo[6.1.0]non-4-ene (b.pt. 82°C, 25 Torr), and 5.4 g *exo*-bicyclo[6.1.0]non-4-ene (b.pt. 73°C, 25 Torr) was collected, for an overall yield of 34% based on ethylidene iodide. The *endo* and *exo* epimers were estimated to be 99% and 96% pure (determined by gas chromatography).

exo-9-Methylbicyclo[6.1.0]non-4-ene: IR (neat) 1660 cm^{-1} (med, C=C stretch), 725 cm^{-1} (strong, *cis* double bond); ^1H NMR (CCl_4), δ 5.7—5.3 (m, 2 H, olefin), 2.3—1.0 (m, 8 H), 0.95 (d, 3 H, J = 6.0 Hz, CH_3), 0.6—0.3 (m, 2 H, cyclopropyl), 0.3 to —0.1 ppm (sextet, 1 H, J = 6.0 Hz, cyclopropyl H *gem* to CH_3). ^{13}C NMR ($CDCl_3$, ppm referenced to TMS): 130.4 (2 C), 29.6 (2 C), 27.4 (2 C), 25.4 (2 C), 20.7 (1 C), 19.1 ppm (1 C). Anal. Found: C, 87.76; H, 11.94. Calc'd for $C_{10}H_{16}$: C, 88.16; H, 11.84%. Mass spectrum: parent ion at *m/e* 136.

endo-9-Methylbicyclo[6.1.0]non-4-ene: IR (neat) 1660 cm^{-1} (med, C=C stretch), 730 cm^{-1} (strong, *cis* double bond), ^1H NMR (CCl_4), δ 5.7—5.2 (m, 2 H, olefin), 2.5—1.1 (m, 8 H), 0.86 (d, 3 H, $J \approx 2$ Hz, CH_3), 0.82—0.6 ppm, (m, 3 H, cyclopropyl hydrogens). ^{13}C NMR ($CDCl_3$): 129.5 (2 C), 27.7 (2 C), 23.4 (2 C), 18.0 (2 C), 11.7 (1 C), 8.33 ppm (1 C). Anal. Found: C, 87.65; H, 11.87. Calc'd as above. Mass spectrum: parent ion at *m/e* 136.

Preparation of dichloro-di-μ-chlorobis{4,5-η(endo-9-methylbicyclo[6.1.0]non-4-ene}dipalladium(II), XV

endo-9-Methylbicyclo[6.1.0]non-4-ene, IX, (0.301 g, 2.21 mmol) was placed in a 50 ml flask and was cooled to —10°C in an ice/acetone bath. Dichlorobis-(benzonitrile)palladium(II) (0.761 g, 1.98 mmol) was dissolved in 2 ml $CDCl_3$ and was filtered through cotton into the stirred and cooled olefin. The cotton was rinsed with 1 ml $CDCl_3$, which was added to the reaction mixture. There was immediate precipitation of a gold-brown powder. The powder was promptly filtered on a medium porosity glass frit, and was washed first with 20 ml chilled water (—10°C) and then with 20 ml chilled pantane (—10°C). The yield was 0.55 g (88%).

IR (NaCl pellet): 1512 cm^{-1} (coordinated olefin); (Nujol mull): 355 cm^{-1} (Pd—Cl_t), 302 and 270 cm^{-1} (Pd—Cl_{br}). ^1H NMR ($CDCl_3$) δ 6.20 (m, 2 H, coordinated olefinic hydrogen), 2.7—1.0 (m, 8 H), 0.82 (broad singlet, CH_3). Anal. Found: C, 38.34; H, 5.46; Cl, 21.62. Calc'd for $C_{20}H_{32}Cl_4Pd_2$: C, 38.31; H, 5.14; Cl, 22.61%. The gold powder decomposes at 145°C.

The preparation of dichloro-di-μ-chloro-bis{4,5-η-(exo-9-methylbicyclo-

[6.1.0]non-4-ene}dipalladium(II), XVI, proceeded analogously starting from *exo*-9-methylbicyclo[6.1.0]non-4-ene, X. IR (NaCl pellet): 1510 cm^{-1}; (Nujol): 360 cm^{-1}, 298 cm^{-1}, and 273 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.17 (m, 2 H), 2.7—0.1 ppm (m, remaining H [incl. 0.9 ppm (3 H, d, J = 6.0 Hz, CH_3]). Anal. Found: Pd: 33.04. Calc'd for $C_{20}H_{32}Cl_4Pd_2$: Pd, 33.93%. The gold powder decomposes at 125°C.

Preparation of di-μ-chlorobis{1,4,5-η-[8-(α-chloroethyl)cyclooctenyl}dipalladium(II)

A. Complex XII EX from exo-9-methylbicyclo[6.1.0]non-4-ene, X. Olefin X (0.500 g, 3.67 mmol) was dissolved in 5 ml CH_2Cl_2. Dichlorobis(benzonitrile)-palladium(II) (1.27 g, 3.30 mmol) in 10 ml CH_2Cl_2 was filtered into the olefin solution through a cotton plug. After stirring for two minutes, an orange brown powder was precipitated by addition of 50 ml pentane. The powder was filtered and washed with two 10 ml portions of ether and two 10 ml portions of pentane. The 665 mg product so obtained was placed in a 10 × 50 mm Soxhlet thimble and CH_2Cl_2 (room temperature) was dripped through the thimble until the extract was clear (about 150 ml). This treatment removed a brown impurity presumed to be $PdCl_2$. The CH_2Cl_2 solution was taken to dryness with the rotary evaporator. The resultant red-orange powder was heated in vacuo (0.5 mmHg) over refluxing $CHCl_3$ for 18 h to remove traces of benzonitrile, followed by a second extraction in a 10 × 50 mm thimble with 150 ml CH_2Cl_2 to remove traces of the brown impurity. On evaporating the second CH_2Cl_2 extract golden-yellow flakes of XII EX were obtained (0.53 g, 39%).

IR (NaCl) 1476 cm^{-1} (coordinated olefin); (Nujol) 324 cm^{-1} (Pd—Cl_{br}). ^1H NMR ($CDCl_3$) δ 6.2—5.8 (1 H, "quartet", J = 7 Hz, coordinated olefinic hydrogen), 5.7—5.3 (1 H, m, coordinated olefinic hydrogen), 4.15—3.75 (1 H, quintuplet, J = 6.1 Hz, Cl—C(CH_3)*H*), 3.72—3.55 (1 H, m, Pd—C—*H*), 2.6—0.7 ppm (m, 12 H, incl. 1.45 ppm [d, J = 6.1 Hz, Cl—C(*C*H_3)H]). Anal. Found: C, 38.63; H, 5.11; Cl, 22.35; Pd, 34.16. Calc'd for $C_{20}H_{32}Cl_4Pd_2$: C, 38.31; H, 5.14; Cl, 22.61; Pd, 33.93%. Mol. Wt. Calc'd 627.1. Found: 610 (toluene, 37°C).

B. Complex XII EN from endo-9-methylbicyclo[6.1.0]non-4-ene, IX. The procedure was exactly analogous to that using the *exo* epimer. The same quantities of starting material gave 620 mg of product (59%).

IR (NaCl) 1468 cm^{-1}; (Nujol) 324 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.2—5.7 (1 H, "quartet", J ~6.5 Hz), 5.75—5.35 (1 H, m), 4.2—3.8 (2 H, m, Pd—C—*H* and Cl—C(CH_3)*H*), 2.8—0.8 ppm (m, 12 H, incl. 1.55 ppm [d, J = 6.2 Hz, Cl—*C*(CH_3)H]). Anal. Found: Pd, 34.02%. Calc'd as above. Mol. Wt. 616 (toluene, 37°C).

Preparation of cis,trans-1,5-cyclooctadiene

The procedure of Deyrup and Betkouski was followed [6]. In a typical experiment, 6.75 g (0.0624 mol) *cis,cis*-1,5-cyclooctadiene, 6.75 g (0.0682 mol) CuCl, and 675 ml pentane were irradiated for 24 h at 2537 Å using a Rayonet apparatus. After work-up of the solid product, we obtained a solution of 200 mg *cis,trans*-1,5-cyclooctadiene in 60 ml pentane (determined using *cis,cis*-1,5-COD in pentane as a reference standard; a 6′ × 1/4″ Apiezon L on Chromosorb W column operating at 70°C easily separates *cis,cis*- and *cis,trans*-

1,5-cyclooctadiene). The pentane solution of our final product *cis,trans* diene showed only trace *cis,cis* diene present. Rapid concentration of the 60 ml pentane solution of the *cis,trans* diene allowed acquisition of the ^{1}H NMR. Immediately after the NMR experiment, the solution was diluted to 40 ml and was stored in the freezer.

^{1}H NMR: δ 5.75 (m, 2 H, olefin), 5.60 (m, 2 H, olefin), 2.6—2.0 ppm (m, 8 H). Irradiation at 2.15 ppm (high power) collapses the two olefinic multiplets to singlets centered at 5.75 and 5.60 ppm. The spin decoupling result agrees exactly with the same experiment conducted at 60 MHz by Cope and co-workers [7].

Preparation of 9-methyl-trans-bicyclo[6.1.0]non-4-ene, XIII

Ethylidene iodide (200 μl) was added to 40 ml of pentane containing 200 mg, *cis,trans*-1,5-cyclooctadiene. The system was stirred under nitrogen and 200 μl diethylzinc was added by syringe through a septum. After 24 h stirring, the reaction was quenched with 400 μl ethanol, and was worked up in a manner similar to the *cis* epimers above (through the $MgSO_4$ drying). A 9.3 *M* pentane solution was obtained. This pentane solution was analyzed by GC (6′ × 1/4″ Apiezon L on Chromosorb W) and was found to contain 65 mg XIII (26% yield), a trace of *cis,trans*-1,5-cyclooctadiene, about 10 mg *cis,cis*-1,5-cyclooctadiene, and no detectable IX or X. The pentane solution was microdistilled to less than 1 ml and the spectral sample of product XIII was collected from this 1 ml after separation on the GC (Apiezon column). The ^{1}H NMR of the spectral sample is identical in all respects to the ^{1}H NMR spectrum of the product from cyanation of either complex XII EN or XII EX, as described below. Also, compound XIII from any of the sources always has identical GC retention time.

IR (neat between plates) 1650 (weak, C=C stretch), 720 cm^{-1} (strong, *cis* double bond). Mass spectrum: parent ion at *m/e* 136. ^{1}H NMR ($CDCl_3$): δ 5.8—5.5 (m, 2 H, olefin); 2.4 to —0.1 ppm (m, 14 H [incl. 1.0 ppm "singlet", 3 H, methyl]). ^{13}C NMR ($CDCl_3$): δ 131.1, 130.9, 29.9, 28.2, 27.9, 27.1, 25.3, 23.8, 20.3, 13.8 ppm.

Reaction of complex XII EN with CN$^-$

Complex XII EN (300 mg) was dissolved in 3 ml CH_2Cl_2 and was shaken vigorously for 30 sec with 10 ml 1 *M* KCN in D_2O. The CH_2Cl_2 layer was filtered through a cotton plug and was evaporated to a small quantity of pale yellow oil. Gas chromatographic analysis of the oil showed that only trace quantities of volatile products other than XIII were present. The analytical and the NMR samples were collected manually from the chromatograph. ^{1}H NMR ($CDCl_3$): identical in all respects to that of XIII prepared from *cis,trans*-cycloocta-1,5-diene and essentially identical to the ^{1}H NMR obtained prior to gas chromatographic separation. Anal. Found: C, 87.92, H, 12.21. Calc'd for $C_{10}H_{16}$: C, 88.16; H, 11.84%.

Various other experiments both with XII EN and XII EX reacting with cyanide indicated essentially quantitative (90—100%) conversion of the σ,π-chelates to XIII (yields based on NMR and GC internal standards).

Preparation of cis-bicyclo[6.2.0]dec-4-ene, XI

cis-Bicyclo[6.2.0]deca-4,9-diene [8] (0.516 g, 3.85 mmol) and 0.53 g 5% Pd/C catalyst in 10 ml $CDCl_3$ were placed in a 25 ml Erlenmeyer flask. The flask was filled with hydrogen gas and was shaken vigorously by hand. Hydrogen was added at 10 min intervals and the progress of reaction was monitored by ^1H NMR and gas chromatography. After 35 min, the catalyst was filtered. Part of the $CDCl_3$ solution was set aside and part concentrated for manual collection of a mass spectral sample of the product from the gas chromatograph. IR (neat) 1650 cm^{-1} (med, C=C stretch), 725 cm^{-1} (*cis* double bond). ^1H NMR ($CDCl_3$): δ 5.8—5.4 (m, 2 H, olefin), 3.0—1.2 ppm (m, 14 H). Mass spectrum: parent ion at *m/e* 136.

Preparation of dichloro-di-μ-chlorobis(cis-bicyclo[6.2.0]dec-4-ene)dipalladium(II), XIV

Dichlorobis(benzonitrile)palladium(II) (0.756 g, 1.97 mmol) was dissolved in 15 ml CH_2Cl_2 and was filtered through a cotton plug into the ~8 ml of the $CDCl_3$ solution of XI which had been set aside above (estimated by GC to contain ~0.29 g, 2.1 mmol XI). The solution was stirred for 5 min, followed by addition of 50 ml pentane to induce precipitation. The orange-brown powder was filtered and was washed three times each with 5 ml portions first of ether, then of pentane. The product was dried at 0.3 Torr for 12 h over boiling chloroform (to remove any benzonitrile present), and was then extracted for one hour with CH_2Cl_2 in a micro Soxhlet apparatus. The final product was obtained by evaporation of the CH_2Cl_2 to dryness. The yield was 0.129 g (60%). IR ($CDCl_3$) 1518 cm^{-1} (coordinated olefin), 328 cm^{-1} (broad, Pd—Cl). ^1H NMR ($CDCl_3$) δ 6.5—5.9 (m, 2 H, coordinated olfenic hydrogen, 3.1—1.1 ppm (broad multiplets, 14 H). Anal. Found: C, 38.01; H, 5.25; Cl, 22.31, Pd, 33.94. Calc'd for $C_{20}H_{32}Cl_4Pd_2$: C, 38.31; H, 5.14; Cl, 22.61%. Mol. Wt. Calc'd: 627.1. Found: 608 (toluene, 37°C).

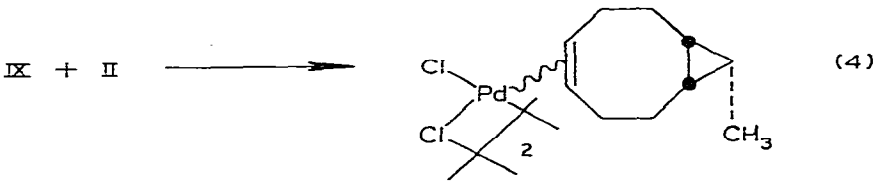
Results

Structural assignments for IX and X follow from the ^1H NMR results. Thus in *exo* epimer X the *endo*-9-hydrogen is anomalously shielded by the two vicinal carbon—carbon bonds and is found at ~0.3 to —0.1 ppm [9]. The *endo*-9-hydrogen is vicinally coupled to *exo*-9-methyl (J = 6.0 Hz). In the *endo* epimer IX, the three methyl hydrogens and the three rather similar cyclopropane hydrogens are quite close in chemical shift and the high field absorption characteristic of X is absent.

Hydrocarbon XIII (9-methyl-*trans*-bicyclo[6.1.0]non-4-ene) was synthesized by selective methylcarbenoid attack on the *trans* double bond of *cis,trans*-1,5-cyclooctadiene [10]. The ^1H NMR of XIII shows the expected olefinic, methyl, and cyclopropyl resonances. The ^{13}C NMR consists of 10 resolved nearly equally intense carbon signals, and the infrared spectrum of XIII indicates the presence of the *cis* double bond in the molecule. Hydrocarbon XIII as synthesized is identical in all respects to that obtained from XII EN or XII EX as described.

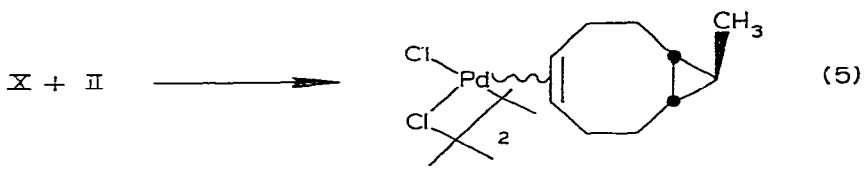
Reaction of II with IX or X must be conducted over short times (minutes)

and at low temperature (≤0°C) in order to isolate olefin π-complexes XV and XVI. The NMR spectra of XV and XVI must be obtained in less than 90 sec at



(4)

(XV)



(5)

(XVI)

room temperature, or significant interference from rearrangement products XII is observed. The characteristic ~1 ppm low-field shift [1—3] of the olefinic hydrogens is observed on coordination to form either XV or XVI. In addition the IR results in the double bond and Pd—Cl regions are fully supportive of the assigned structures. Finally, reaction of solid XV or XVI with CN^-/D_2O followed by addition of $CDCl_3$ led to the observation of only IX or X, respectively, by ^1H NMR.

π-Complexes XV and XVI rearrange rapidly to σ,π-chelate complexes XII EN and XII EX in $CDCl_3$ solution at room temperature. The rearrangement is readily followed by ^1H NMR and the half-completion times for approximately tenth molar solutions are 7 min and 3.5 min for XII EN and XII EX, respectively. The solution kinetics were not studied in detail. The XV → XII EN and XVI → XII EX rearrangements are very clean both at room temperature and at elevated temperatures. Thus the ^1H NMR spectra of the π-complexes change smoothly over a period of 20—30 min into spectra nearly identical to those of the isolated, analytically pure XII EN and XII EX. If the rearrangement experiment is extended to longer times (days) or higher temperatures (50—60°C), both XII EN and XII EX rearrange further to the same final product complex, which is currently believed to be π-allylic in nature.

A number of experiments were conducted on solid samples of π-dimers XV or XVI. At elevated temperatures (70—85°C) the solids rearranged to XII EN or XII EX over periods of several hours. In a typical experiment, ca. 30 mg XVI was placed in each of two NMR tubes. The tubes were capped and were placed in a 75°C bath for 5 h. Each sample darkened noticeably during the heating period. After heating, one sample was rapidly dissolved in $CDCl_3$ followed by immediate treatment with CN^-/D_2O (all within 15 sec). The ^1H NMR of the $CDCl_3$ layer was virtually identical to pure XIII. The other sample was dissolved in $CDCl_3$ and the ^1H NMR was run in less than 60 sec. That ^1H NMR was identical to XII EX. Both experiments imply solid state rearrangement of XVI →

XII EX. Similar results were obtained with XV → XII EN in the solid state.

The σ,π-complexes XII EN and XII EX can be isolated in analytically pure form. Both the molecular weight measurements and the far IR results confirm the chlorine-bridged dimeric formulations. Coordination of the cyclooctenyl olefinic moiety is indicated by both ^{1}H NMR and IR results. The palladium—carbon sigma bond is indicated by the ^{1}H NMR area one resonance near δ 3.8 ppm [11,12]. The $\geq$C(H)—C(H)(CH_3)(Cl) moiety which results from cyclopropane cleavage is clearly indicated in XII EX by the 0.50 ppm shift to low field of the methyl resonance (compared to X), and by the coupled pentuplet-doublet resonances of the α-chloroethyl group. In complex XII EN the downfield shift of methyl (~0.7 ppm) is also observed, and the resonances assigned to Pd—C—*H* and Cl—C*H*(CH_3) overlap so that spin—spin coupling is not observed for the latter. For XII EN in the presence of a several equivalent excess of pyridine, however, the Pd—C—*H* resonance is found at δ 3.5 ppm, and the expected Cl—C*H*(CH_3) pentuplet is totally resolved at δ 3.85 ppm. Finally, the diastereomeric relationship of XII EN and XII EX is shown both in the ^{1}H NMR spectra (δ 4.0 ppm region) and in the IR spectra, where there are numerous subtle differences in the fingerprint region.

Solutions of pure XII EN and XII EX react readily with aqueous cyanide ion to give quantitative yields of the *trans*-fused cyclopropane XIII (XIII was synthesized independently from *cis-trans*-cyclooctа-1,3-diene and ethylidene iodide/diethylzinc — See Experimental). Thus reaction of approximately tenth molar solutions of either XII EN or XII EX in $CDCl_3$ with excess cyanide in D_2O shows essentially complete conversion to XIII (the yield of 90—100% was determined by NMR integration with added internal standard CH_2Br_2, the aqueous layer presumably contains $Pd(CN)_4^{2-}$). Gas chromatographic analysis confirmed that XIII is the only volatile product of the cyanation reaction. On "titration" of a 0.2 molar solution of XII EN in $CDCl_3$ with 1 *M* KCN in D_2O, it was found that only two equivalents of cyanide are required for the quantitative liberation of XIII (in this case a white precipitate of $Pd(CN)_2$ is observed; the precipitate disappears on addition of two more equivalents of cyanide).

The cyclobutane-containing complex XIV was readily prepared from II and XI. The complex is quite stable, as is characteristic of higher molecular weight simple olefin complexes with $PdCl_2$. The characterization of the complex as a chlorine-bridged dimeric metal-coordinated olefin follows readily from the data presented. Complex XIV was unchanged on heating either the solid complex or a $CDCl_3$ solution of the complex at 50—60° C for three days. Under those conditions the ^{1}H NMR spectrum showed no change during the heating time. On reaction with cyanide ion, complex XIV readily liberates hydrocarbon XI, whose ^{1}H NMR spectrum is identical to starting XI.

Discussion

The lability of the cyclopropane ring in π-complexes XV and XVI was expected on the basis of our earlier work with bicyclo[6.1.0]non-4-ene [1]. We were, however, surprised that the chloropalladation reaction proceeds such that the cyclopropane ring cleaves externally at C—methyl rather than internally to form the 9-membered ring. Evidently the methyl group "stabilizes charge" on

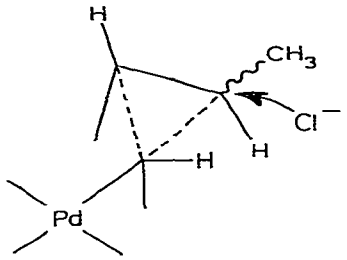
the cyclopropane carbon atom, activating that carbon toward nucleophilic attack by chloride ion. We have no indication in either XV or XVI that internal cleavage competes with external cleavage of the cyclopropane rings, as we observe only products from the external cleavage path. The sensitivity of the reaction pathway to substituent observed here has certainly been observed as well in oxymercuration of cyclopropane rings, where the nucleophile preferentially attacks the carbon whose substituents best stabilize positive charge [13]. Mass spectral fragmentation of cyclopropane rings has also been found to proceed such that positive charge accumulates on the most substituted carbon [14].

The chloropalladation reactions reported here proceed stereospecifically, as shown by the clearly different spectral characteristics of XII EN and XII EX. The most marked spectral differences are found near δ 4.0 ppm in the ^{1}H NMR spectrum. The Pd—C—*H* resonance for XII EX is centered at about 3.6 ppm, that for XII EN is found at δ 3.93 ppm, and each is a broad doublet with $J \sim 7$ Hz [15] DePuy [13a] has pointed out the potential importance of stereospecific ring openings of cyclopropane systems, where open chain products are formed which could have three asymmetric centers (as in the present case) in a controlled relationship to one another.

Quantitative recovery of *trans*-fused cyclopropane XIII from cyanide treatment of either XII EN or XII EX has some precedent in our earlier work [1] where we obtained *trans*-bicyclo[6.1.0]non-4-ene from a labile chloropalladation product of *cis*-bicyclo[6.1.0]non-4-ene. In the present case, epimerization at carbon bound to palladium is indicated, either in the electrophilic attack on the cyclopropane ring, or in the cyanide-induced carbon—carbon bond formation to form XIII. If the palladium electrophile cleaves the cyclopropane with retention at Pd—*C*, then the inversion would occur during carbon—carbon bond formation at the cyanide step. If on the other hand, the palladium electrophile attacks and inverts at Pd—C, then the second step must proceed with retention at that carbon. Both inversion and retention at electrophilically attacked carbon have been observed in oxymercuration of cyclopropanes [13,16]; however, no such precedents are available in the organopalladium literature. Obviously, it would be of immense benefit now to know the relative stereochemistries at Pd—C and $>$CH—C(H)(Cl)(CH_3) in either XII EN or XII EX. All attempts to date to crystallize for X-ray analysis XII EN, XII EX, or derivatives of either have failed, and we have been unable to extract the needed stereochemical information from the available ^{1}H NMR data.

One is now tempted to propose that the most likely reaction pathway along the way to XIII would involve "corner-palladation" of the cyclopropane ring, with chlorine attack at the activated carbon, as shown in XVII. In this scheme, the product stereochemistry at Pd—C is determined by the site of nucleophilic attack, and attack at —C—CH_3 leads to an inverted carbon at —Pd—*C*. A very similar scheme has been put forward by DePuy [13a] in his discussion of cyclopropane oxymercuration reactions. It is worth noting here that this same scheme accomodates our earlier [1] results as well. The finally delineated chloropalladation mechanism will also have to accomodate the fact that these reactions also proceed cleanly in the solid state, as described in the Experimental section.

Finally, we were interested in generalizing our studies to cyclobutane rings,



(XII (EN) from IX;

XII (EX) from X)

where there is about as much total ring strain as in cyclopropane rings [17]. However, as we have mentioned above, the π-complex XIV, whose hydrocarbon moiety is structurally analogous to the highly reactive I, V, IX, and X, is inert to rearrangement via chloropalladation of the cyclobutane rings. In view of the ring strain believed to be present in hydrocarbon XI, this inertness must have a kinetic origin. Wiberg, et al. [18] have discussed acetolysis rates in various cyclobutane and cyclopropane hydrocarbons. The millionfold slower electrophilic cleavages of cyclobutane rings were ascribed to poor overlap of the cyclobutane HOMO with incoming electrophile. This conclusion later received support in the ab initio study of Pakkanen and Whitten [19], who found that gas phase protonation of cyclobutane is quite favorable (highly exothermic) but much less so than for cycloprane protonation. Our results confirm earlier observations on cyclopropane/cyclobutane relative rates of electrophilic ring opening. In our case, the relatively large Pd^{II} electrophile acceptor orbitals should overlap better with the cyclobutane HOMO; however, hydrocarbon XI is at least 10^3—10^4 less reactive than any of the cyclopropane substrates which we have studied.

Conclusions

We have shown that cyclopropane chloropalladation is much like oxymercuration in that the course of the reaction is strongly influenced by substituents. The chloropalladations reported here have been found to be stereospecific, suggesting the possible utility of this type of reaction in controlled generation of asymmetric centers. The utility of the cyanide-induced dechloropalladation reaction is again demonstrated in the facile preparation of 9-methyl-*trans*-bicyclo[6.1.0]non-4-ene, XI, from the palladium α-chloroethylcyclooctenyls. The formation of XI from XII EN or XII EX implies novel stereochemical change in either the electrophilic attack on IX or X or the cyanide attack on XII EN or XII EX. That stereochemistry is under current and continuing scrutiny.

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