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PALLADIUM(II) CATALYZED REARRANGEMENT OF BICYCLO[6.1.0]-NON-4-ENE TO *cis,cis*-1,5-CYCLONONADIENE

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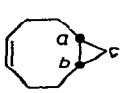
SUMMARY

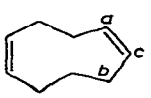
$PdCl_2(PhCN)_2$ reacts with bicyclo[6.1.0]non-4-ene, (I), in non-polar solvents to produce dichloro-*cis,cis*-1,5-cyclononadienepalladium(II) as the final product. The reaction involves cyclopropyl C–C and C–H bond cleavages in (I) to produce the isomeric diene. The reaction proceeds by *cis* addition of Pd–Cl to a strained C–C bond, followed by a stereospecific 1,2 hydrogen migration and Pd–Cl eliminination. PMR and chemical evidence is presented in support of the Pd–Cl addition. The reaction reported is synthetically useful for the preparation of both *cis,cis*-1,5-cyclononadiene and *trans*-bicyclo[6.1.0]non-4-ene, the latter being obtained on quenching the reaction mixture at short times.

INTRODUCTION

In contrast to the widespread current activity involving metal complex promoted reactions of highly strained hydrocarbons[1a–h], there has been only one report of a metal catalyzed isomerization of an unconjugated cyclopropyl derivative having a single cyclopropane ring as the only significant source of strain in the molecule: namely the cyclopropane to propylene conversion, catalyzed by Zeise's dimer[2]*. We report here the related facile Pd^{II} catalyzed conversion of the relatively unstrained



(I)



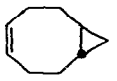
(II)

and thermally stable *cis*-bicyclo[6.1.0]non-4-ene, (I), to the isomeric *cis,cis*-1,5-cyclononadiene, (II), in high yield. We find that the catalysis by Pd^{II} [as $PdCl_2(RCN)_2$] is a stepwise reaction involving *cis* addition of Pd–Cl to the (*a–b*) bond in (I) followed by a 1,2 hydrogen migration and Pd–Cl elimination to give (II). Pd–Cl addition to monocyclopropyl systems is unprecedented, but such addition could be

* Tsuji and co-workers report[32] observing a "small amount" of propylene from reaction of cyclopropane and $PdCl_2$ at 50°.

involved in olefinic and/or more highly strained cyclopropyl derivatives; however, direct evidence for such addition is lacking in these latter cases[3-5].

The reactions reported here not only contribute to a better understanding of Pd^{II}–cyclopropane chemistry, but also represent the most convenient preparative routes to (II) and to *trans*-bicyclo[6.1.0]non-4-ene, (III), which may be isolated in good yield by quenching the (I)/Pd^{II} reaction using cyanide ion.



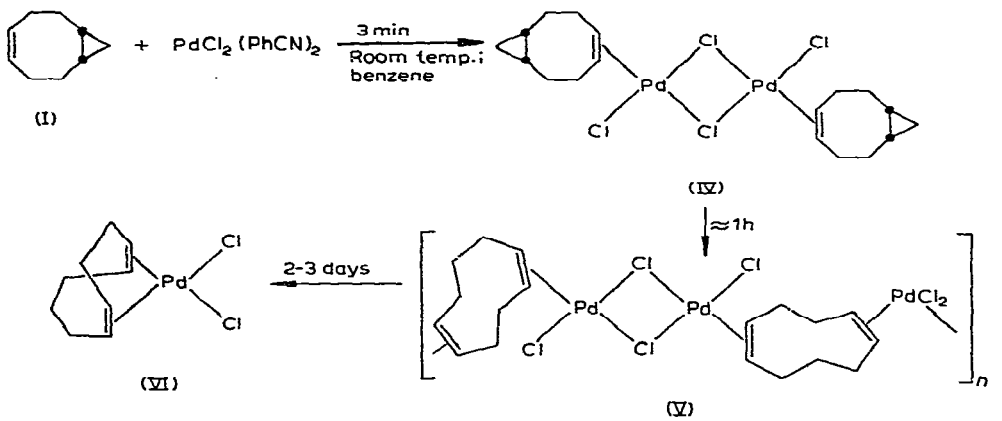
(III)

RESULTS AND DISCUSSION

A. Isolation and characterization of products in the reaction of (I) with $PdCl_2(PhCN)_2$

Solutions of $PdCl_2(PhCN)_2$ in benzene, chloroform, or dichloromethane* react immediately on addition of (I). We have isolated and characterized several products as outlined in Scheme 1, the details of which will now be described.

SCHEME 1



(I) (IV) (V) (VI)

Reaction of $\geqslant 0.08\ M$ solutions of (I) and $PdCl_2(PhCN)_2$ in benzene leads to immediate formation of a yellow powder, (IV), which must be isolated within 3 min. The material has empirical formula $PdCl_2C_9H_{14}$ by elemental analysis and we infer that it is a chlorine-bridged dimer with olefinically coordinated (I) for the following reasons: (1) (IV) liberates only (I) on treatment with pyridine, DMSO, or aqueous cyanide ion; (2) the IR of (IV) shows no ν(C=C) at 1600–1650 cm^{-1} (characteristic[19] of cyclic, uncoordinated olefin) but does show a band at 1505 cm^{-1} expected for C=C coordinated to Pd^{II} [7]; in addition the IR of (IV) has cyclopropane bands at 3060, 1030 and 1010 cm^{-1}, all similar to (I) and expected for *cis*-1,2 disubstituted cyclopropane derivatives[8]; finally, the IR of (IV) has Pd–Cl bands characteristic[9a,b] of

* In such solutions, the predominant Pd^{II} species is dimeric $[PdCl_2(PhCN)]_2$, formed by PhCN dissociation (see refs. 6a–c).

trans-$[PdCl_2L]_2$ at 345 cm^{-1} (Pd–Cl terminal), as well as 290 and 260 cm^{-1} (Pd–Cl bridge). The *trans* isomer is favored on the basis of IR results, and on the basis of X-ray[10a,b] and dipole moment data[11] for similar $(PdCl_2 \cdot L)_2$ species. In solution, (IV) may equilibrate with the *cis* isomer, but it is expected that the *trans* form will predominate in the non-polar solvents used here. Solution molecular weight studies failed with (IV) because of poor solubility and because the complex rapidly decomposes in solution. PMR studies (below) support the structure proposed for (IV).

If (IV) is stirred with benzene, or if the reaction of (I) with $PdCl_2(PhCN)_2$ is allowed to proceed for about an hour at room temperature without isolation of (IV), an extremely insoluble yellow-orange powder, (V), is formed. Isolated (V) has empirical formula $Pd_3Cl_6C_{18}H_{28}$ by elemental analysis. The IR of (V) shows the following: (1) the cyclopropane bands are absent; (2) there is no absorption at 1600–1650 cm^{-1}, but there is a strong band at 1505 cm^{-1}, indicative of coordinated olefin; (3) there are vibrations characteristic[9ab] of terminal Pd–Cl from a chlorine bridged polymer and/or a *cis*-disubstituted $PdCl_2L_2$ species (345 and 315 cm^{-1}). Treatment of (V) with various nucleophiles liberates a hydrocarbon different from (I), which hydrocarbon we have shown to be (II) by comparison of its spectroscopic properties with an authentic sample[12a]. We propose the structure for (V) shown in Scheme 1. The polymeric structure is suggested by the stoichiometry, by the extreme insolubility of (V), by the absence of uncoordinated olefin, and by the low frequency Pd–Cl vibrations. Finally, (II) itself reacts with $PdCl_2(PhCN)_2$ to give immediate formation of (V)*.

Regardless of initial concentrations, reaction of (I) with $PdCl_2(PhCN)_2$ in benzene, chloroform, or dichloromethane yields yellow, highly crystalline (VI) if the reaction is allowed to proceed for 2–3 days at room temperature [or for a few hours if excess (I) is used]. (VI) is $[PdCl_2C_9H_{14}]$ by elemental analysis and molecular weight, and the hydrocarbon moiety is coordinated (II) on the basis of the following: (1) (VI) liberates only (II) on treatment with nucleophiles; (2) the IR shows no cyclopropyl bands, no uncoordinated olefin, and a strong band indicative of coordinated diene[13a–d] at 1515 cm^{-1}; in addition Pd–Cl bands characteristic[13d–f] of monomeric *cis*-MCl_2-(diene), M = Pd^{II} or Pt^{II}, are present at 325 and 293 cm^{-1}; (3) (VI) may be prepared directly from (II) and $PdCl_2(PhCN)_2$ if the reaction is allowed to proceed past the formation of (V); (4) the PMR of (VI) in $CDCl_3$ shows a broad 4 H multiplet at δ 6.60 and a 10 H multiplet from 2.9 to 1.5 ppm. The deshielding ($\delta \approx 1.1$ ppm) of the olefinic resonance is similar to that observed[14] for $PdCl_2$(cyclooctadiene). Thus the final product in the reaction, (VI), has the monomeric structure shown in Scheme 1.

The reaction of (I) with $PdBr_2(PhCN)_2$ was also carried out. Here we isolated only $PdBr_2 \cdot$ (II), an orange-red, highly crystalline material. The usual characterization indicates clearly that $PdBr_2 \cdot$(II) is isostructural with (VI). The reaction of (I) with $PdCl_2(RCN)_2$, R = cyclopropyl or isobutyl, proceeds exactly as with R = phenyl, as far as we could determine.

Reaction of (I) with $PtCl_2(PhCN)_2$ in refluxing benzene or with Zeise's salt

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* It has been reported by Nagendrappa and Devaprabhakara[12b] that (II) reacts with $PdCl_2(PhCN)_2$ to give $[PdCl_2 \cdot (II)]_n$ whose properties are similar to our (V), $[Pd_3Cl_6 \cdot (II)_2]_n$. We however, found that following their procedure only (V) forms immediately, and only on standing for several days does (V) convert to (VI), which has the 1/1 stoichiometry claimed[12b].

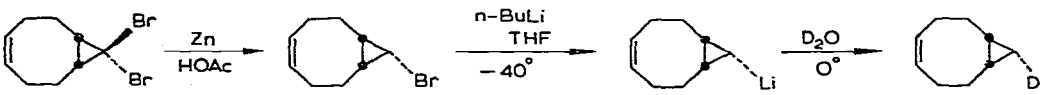
in ethanol at elevated temperature did not lead to rearrangement while reaction of (I) with bis(ethylene)RhIAcac refluxing in benzene leads to (II) in good yield at higher temperatures. These results will be reported elsewhere, along with related results using Ag^{I}.

B. Mechanistic study of the reaction of (I) with Pd^{II}

The simplest pathway for the (I)→(II) arrangement involves cleavage of the (*a*–*b*) bond of (I) and a 1,2 hydrogen migration from carbon *c* to either *a* or *b*. The final result is formation of a *cis*-disubstituted olefin from a *cis*-disubstituted cyclopropane. The reaction is catalytic: we have converted over a one-hundred-fold excess of (I) to (II) in high yield. In view of the unusual features of the reaction—particularly the fact that the cyclopropane is not additionally strained or conjugated, yet rearranges to olefin under mild conditions—we decided to study the mechanism in detail.

In order to determine whether or not the cyclopropyl hydrogen migrates stereospecifically, we prepared *endo*-9-deuterio-bicyclo[6.1.0]non-4-ene, (VII), by the route outlined in Scheme 2.

SCHEME 2

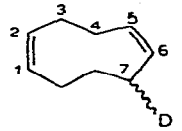


98%

(VII)

Since the highest field PMR signal in (I) has been shown to arise solely from the *endo*-H of the cyclopropyl group[15], we were able to show by PMR that (VII) was 86% deuterated at the *endo* position. Mass spectral examination of (VII) indicated 84% overall deuteration. This indicates that the product is about 85% (VII) and 15% (I) (which ratio we assume throughout).

Reaction of the 85/15 (VII)/(I) mixture with $PdCl_2(PhCN)_2$ gave only *one* deuterated, rearranged hydrocarbon product, which we believe to be 7-deuterio-*cis*, *cis*-1,5-cyclononadiene, (VIII). (VIII) arises from stereospecific 1,2 *endo*-D migration



(VIII)

from (VII). Thus the isolated (VIII)/(II) mixture gave the PMR integral ratio 0.43 for the olefinic/aliphatic areas, compared to the theoretical ratio of 0.44 for exclusive *endo*-D or H migration in the (VIII)/(I) mixture. Randomization of the label would have given an integral ratio of 0.37, while retention of the label in the vinylic position would lead to a ratio of 0.31. Also, the relative area of the olefinic/unique methylene resonances in the (VIII)/(II) mixture is almost exactly 2/1, proving that the label is in an *allylic* position. We cannot be certain that we have 7-D as opposed to 3-D [see (VIII)]; however, the 7-D formulation requires only a 1,2 shift, while a route to the 3-D isomer which would not require randomization is difficult to imagine. Further, the IR

of isolated (VIII)/(II) shows only a single C–D band at 2170 cm^{-1} confirming the absence of vinylic C–D [the cyclopropyl C–D stretch in (VII) is a single peak at 2260 cm^{-1}; we would expect the non-observed vinylic C–D at $\approx$2235 cm^{-1}, since the cyclopropyl C–H stretch is about 60 cm^{-1} to higher wave number than the olefinic C–H in (II)]. Finally, the mass spectrum of the (VIII)/(II) mixture showed that it is 85/15 $C_9H_{13}D/C_9H_{14}$, proving that none of the D label is lost in the reaction. Thus we are led to the conclusion that only the *endo*-H(D) undergoes a 1,2 shift on reaction of (I)/(VII) with Pd^{II}.

The presence of a large concentration of reactive intermediate in the reaction of (I) with Pd^{II} was implied both by quenching experiments and by PMR time studies. We found that quenching the reaction mixture with aqueous cyanide liberates 3 hydrocarbons, (I), (II), and (III), whose relative amounts are time-dependent. Thus, during a typical reaction (0.025 *M* in both reactants in benzene or CH_2Cl_2), the isolated amount of (I) shows a first order decrease with time, (II) increases, and (III) first increases, then decreases. In this experiment, the concentration of (III) maximized at 18 min. (III) was isolated by GLC and was characterized spectroscopically and by

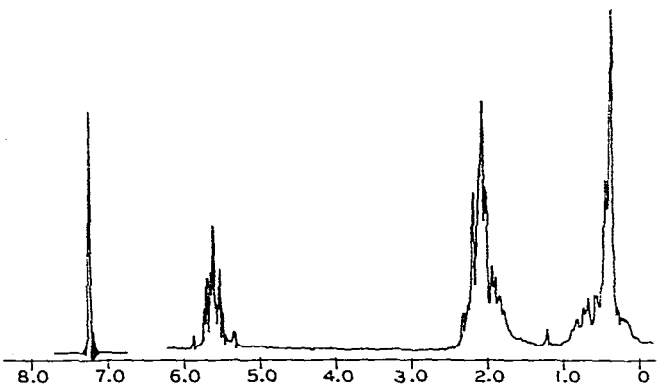


Fig. 1. PMR Spectrum of (III), *trans*-bicyclo[6.1.0]non-4-ene, in $CDCl_3$. The peak at δ 7.24 ppm is residual $CHCl_3$.

elemental analysis. The elemental analysis and the mass spectrum indicate the molecular formula C_9H_{14}. The PMR spectrum of (III) (Fig. 1) in consistent with the assigned structure: *trans*-bicyclo[6.1.0]non-4-ene. Thus, the olefinic absorption is a complex AA′ multiplet having a center of symmetry and integrating for 2 H's; the other 12 H's are found upfield in two multiplets integrating for 6 and 6 H's each. The highest field multiplet is assigned to 4 cyclopropyl hydrogens and 2 hydrogens adjacent to the cyclopropyl, the latter so situated that they experience a remote cyclopropyl shielding effect[16a–g] (Fig. 2). The IR of (III) is very similar to that of (I), as expected. (III) has

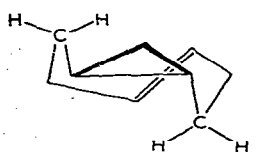


Fig. 2.

been prepared by a different route, and our PMR data are in agreement with those reported*.

The appearance of (III) on treatment of the reaction mixtures with aqueous cyanide implies a relatively large concentration of reactive intermediate in which the (*a*–*b*) bond of (I) is broken, which intermediate has the ability to reform the (*a*–*b*) bond in the *trans*-fused manner on treatment with CN^- [(I) itself is stable to aqueous cyanide]. It is worth noting that parallel quenching experiments with other nucleophiles (pyridine, DMSO, I^-) gave only traces of (III) at the same times that CN^- produced large amounts of (III). Apparently the reaction of CN^- with the intermediate is remarkably specific in its ability to produce (III). We comment on this below.

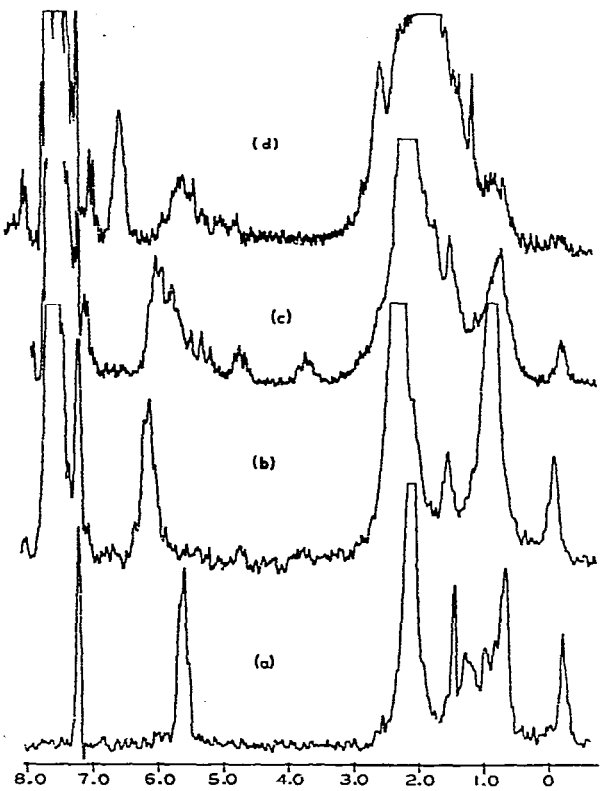


Fig. 3. Time dependence of the PMR spectrum of 0.05 *M* $PdCl_2(PhCN)_2$ and 0.1 *M* (I) in $CDCl_3$. (a) Spectrum of (I) prior to addition of $PdCl_2(PhCN)_2$; (b) Spectrum immediately after mixing ($\approx$1.5 min); (c) 9 min; (d) 60 h.

PMR studies of the reaction of $PdCl_2(PhCN)_2$ with (I) were quite informative, and we describe here a typical experiment on a reaction with initial concentrations of 0.05 *M* in each component in chloroform-*d*. The spectra are shown as a function of time in Fig. 3. The spectrum obtained immediately after mixing (b) shows the expected[14] downfield shift of the olefinic resonance on coordination to Pd^{II} and also shows that the cyclopropyl group is intact. Spectrum (b) thus corresponds to (IV). After 9

* We thank Prof. Wiberg for providing spectral data for (III), see ref. 17.

min, spectrum (c) is obtained. Here two new features are clearly visible: equal area multiplets at δ 4.8 and 3.8 ppm, which we assign to an intermediate Pd^{II} complex, (IX). These multiplets increase and decrease in intensity with approximately the same time-dependence as the increase and decrease in yield of (III) on quenching the reaction with cyanide, and we believe that the cyanide reacts with (IX) to liberate (III). One also sees in spectrum (c) the formation of free (II) [the multiplet centered at δ 5.5 ppm is characteristic of (II)], corresponding to formation of (V) with liberation of (II) (precipitate formation occurs in the NMR tube at this time). In spectrum (d). at 60 h, the olefinic resonance of (VI) is apparent at δ 6.60 ppm, along with low resolution olefinic absorption due to (II) at δ 5.1–6.0 ppm (the poor resolution arises from precipitate in tne NMR tube). The PMR spectrum of isolated (VI) is shown in Fig. 4.

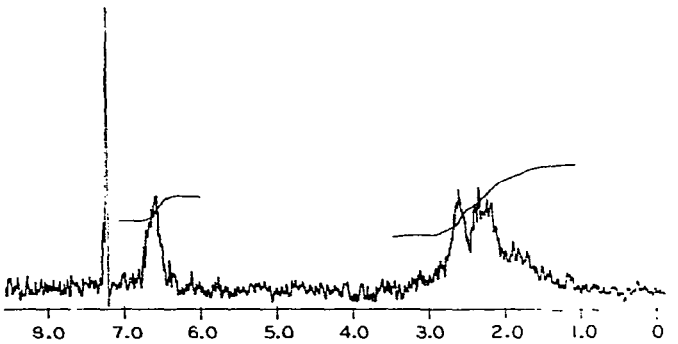
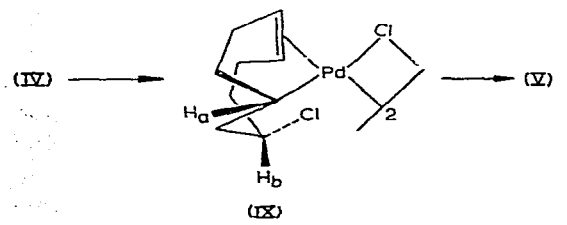


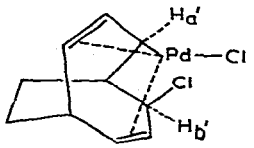
Fig. 4. PMR Spectrum of (VI), dichloro-*cis,cis*-1,5-cyclononadienepalladium(II), in $CDCl_3$. The peak at δ7.24 ppm is residual $CHCl_3$.

What is the nature of the reactive intermediate, (IX), in this system, and how does it arise? The cyanide quenching experiments suggest that the (*a–b*) bond of (I) is cleaved in (IX) while the PMR shows rather deshielded, equal area multiplets which are assigned to (IX). The results suggest that the first complex formed, (IV), decomposes to (IX), and we believe that the crucial step is a *cis*-Pd–Cl addition to the (*a–b*) bond of the cyclopropyl group, giving (IX), as shown in Scheme 3:

SCHEME 3

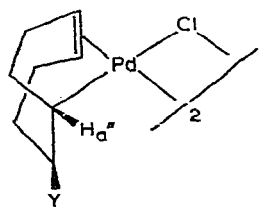


The partial PMR spectrum of (IX) is consistent with the proposed structure. We assign the δ 3.8 ppm multiplet to H_a and the δ 4.8 ppm multiplet to H_b, mainly on the basis of results from model compounds. The best model system is (X), reported by Vedejs in his study of the rearrangement of bullvalene by $PdCl_2(PhCN)_2$[18].



(X)

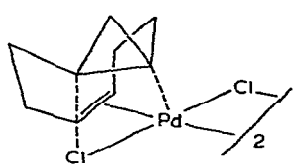
In (X), peaks at δ 4.21 ($H_{a'}$) and 5.18 ppm ($H_{b'}$) correspond to those assigned to H_a and H_b in (IX). The resonances in (X) are understandably about δ 0.4 ppm to lower field than are those in (IX), because in (X) the $H_{a'}$ and $H_{b'}$ are allylic. In general, one expects R–CHCl–R to appear in the range δ 5.2[18] to 3.6 ppm[19]. It is more difficult to estimate chemical shifts for Pd–CHR_2. In compounds of the type (XI) the hydrogen α to Pd ($H_{a''}$) is found between δ 4.2[18] and 2.7 ppm[20] and our assignment is in this range. It



(XI)

is indeed noteworthy that the structure proposed for (IX) is the same basic structure found in known stable compounds of type (XI) with a hydrocarbon chelate both π and σ bonded to Pd.

In order to understand the formation of (IX), we make the following observations. The (IV) → (IX) conversion probably involves a transition state similar to (XII), in which the coordinated olefin lies *in* the Pd coordination plane. In contrast to this,



(XII)

the most stable coordinated olefin geometry in solution is expected to have the olefin *perpendicular* to the coordination plane, on the basis of X-ray results for crystalline metal–olefin complexes[10a–f], observed barriers to olefin rotation (for Rh^I and Pt^{II} complexes) measured by PMR[21–23] and molecular orbital calculations[24]. In addition, it has been shown by PMR that the perpendicular olefin orientation is the most stable in dissolved complexes of the type PtCl(Acac)(olefin)[21b]. If indeed some fraction of the metal–olefin bond energy is lost in (XII) (due to poorer overall in-plane bonding), the now relatively ligand-deficient palladium may be electrophilic enough to attack and cleave the cyclopropyl group. The fact that the hydrocarbon is "chelated" in (XII) probably also assists the C–C cleavage. This rather specific transition state

geometry helps us understand why Pd–Cl does not cleave or add to other monocyclopropyl systems[3] under mild conditions.

The formation of (II) from (IX) involves chloride abstraction, hydrogen migration, and formation of the new double bond. Since the hydrogen shift has been shown to occur stereospecifically (only the *endo* hydrogen migrates), we sought a structural feature in (IX) which could account for the stereochemical result. The transformation of (XII) to (IX) involves, in our view, 90° rotation of the coordinated olefin, returning to the expected stable perpendicular orientation. When this is accomplished, the carbon-bound chlorine is found to "occupy" the 5th coordination position of Pd^{II}, at least in the sense that models suggest a very close Pd...Cl–C approach. At the same time, the original *endo* hydrogen occupies a *trans* configuration with respect to the carbon-bound chlorine. The chloride abstraction by Pd^{II} can thus be assisted by a back-side attack of what was the *endo*-H originally, simultaneous with the formation of the new double bond (see Fig. 5). In this way the unique stereo-

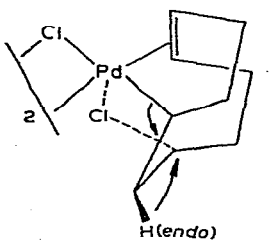


Fig. 5.

specificity may be visualized. In support of the proposed Pd...Cl–C interaction, we observe that the chemical shift of H_b in (IX) (δ 4.8 ppm) is at the low-field end of the usual range, consistent with the presence of a bridging (electron deficient) chlorine.

The appearance of (III) on reaction of (IX) with cyanide may also be understood on the basis of the assigned structure for (IX). We show in Fig. 6 the likely initial

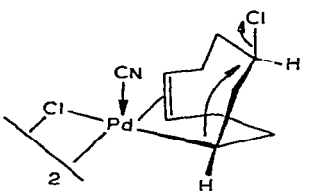


Fig. 6.

product of cyanide attack on (IX). We suggest that addition of one or more CN^- to (IX) will result in the displacement of the Pd–C σ bond, and that the developing carbanionic center nucleophilically displaces neighboring chlorine. The expected inversion at the CHCl carbon yields the *trans*-fused (III). The facts that *aqueous* cyanide is used and that we observe no chlorocyclononene in the quenched products argue against the appearance of a metal-free carbanion. Weaker nucleophiles (pyridine, DMSO, I^-) are apparently incapable of causing the Pd–C bond rupture in the same manner as cyanide.

After the rearrangement step, the precipitation of (V) with liberation of an equivalent of (II) is no doubt the result of the extreme insolubility of (V). In the absence of (II), (V) slowly converts to (VI), but in the presence of (II), solid (V) converts

to (VI) more rapidly. The most interesting feature of this step of the reaction is its extreme slowness, compared for example with the instantaneous formation of monomeric [$PdCl_2$(cyclooctadiene)] from $PdCl_2(C_6H_5CN)_2$ and cyclooctadiene.

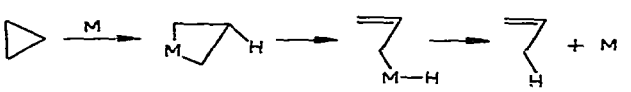
CONCLUSIONS

The crucial feature of the reaction studied here is *cis* addition of Pd–Cl to a strained carbon–carbon σ bond. Addition of the elements of Pd–Cl to unsaturated substrates (allenes[25], olefins[26], acetylenes[27,28]) is a general organopalladium reaction, and has been implicated in a number of catalytic reactions[26,27]. It is well known that the strained C–C bonds in cyclopropanes exhibit "olefinic" behavior in much of their chemistry[29], *i.e.*, transmission of conjugation effects, so by analogy with olefinic and acetylenic systems, we should expect Pd–Cl addition to cyclopropyl under certain conditions. It does not appear, however, that Pd–Cl addition to cyclopropanes is a general reaction, in view of the failure[3] of *cis*- and *trans*-1,2-dimethylcyclopropane to react with $PdCl_2(PhCN)_2$. We have pointed out the special features of our system: enhanced electrophilicity of Pd^{II} in the transition state due to olefin rotation, and inclusion of the cyclopropyl in a chelate ring in the transition state, both of which could promote Pd–Cl addition. Other reactions which could but have not been shown to involve Pd–Cl addition to σ bonds include: (1) Pd^{II} catalyzed rearrangement of bicyclobutane derivatives to diolefins[1h,30a–c]; (2) reaction of $PdCl_2L_2$ with vinylcyclopropanes[4,5]; (3) reaction of $PdCl_2L_2$ with dicyclopropyl derivatives (spiropentane and dicyclopropyl methane)[3]; (4) rearrangement of cubanes with chloropalladium species[1d,31]; and (5) chlorocarbonylation of cyclopropanes catalyzed by $PdCl_2$[32]. In none of these cases has Pd–Cl addition to the strained σ bond been postulated or demonstrated; our results suggest that such a possibility is a real one.

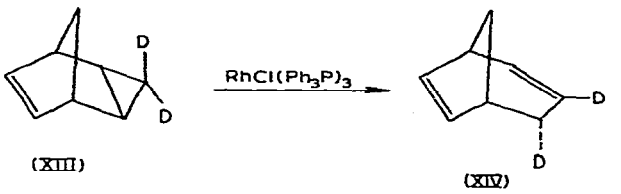
The rearrangement of (I) to (II) is a "cyclopropyl to propylene" isomerization, other examples of which have been reported. The rearrangement of cyclopropane itself to propylene, catalyzed by $[PtCl_2(CH_2{=}CH_2)]_2$ or $H[PtCl_3(CH_2{=}CH_2)]$ has been reported by Brown[2], but mechanistic details are unavailable.

Another mechanism for "cyclopropyl to propylene" isomerization has been proposed by Katz and Cerefice[1a] and by Powell and McQuillan[41]; this involves oxidative addition to the strained C–C bond, and metal assisted hydrogen migration.

SCHEME 4

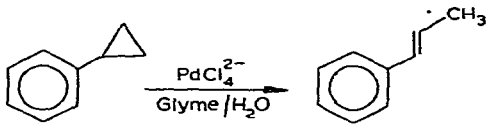


The mechanistic proposal in Scheme 4 has been particularly attractive for metal catalysts (M) able to undergo oxidative addition with cyclopropyl substrates (Rh^{I} [1a,41], Pd^{0} [42]). In the case of (XIII) rearranging to (XIV), it has been suggested that the migrating D was originally *exo*, and this was taken as evidence[1a] in support of Scheme 4. We observe that in the (I) → (II) rearrangement reported here, the *endo-H migrates*, as would be expected on the basis of the rather different mechanism proposed. Indeed we consider that *endo*-H migration rules out Scheme 4 for the Pd^{II} catalysis of (I) → (II), and this is not surprising in view of the expected inaccessibility of Pd^{IV} in the presence of hydrocarbon ligands.



(XIII) (XIV)

The isomerization of phenylcyclopropane, (XV) to *trans*-propenylbenzene, (XVI), catalyzed by $PdCl_4^{2-}$ in glyme/water has been reported by Ouelette and Levin[33].



(XV) (XVI)

The (XV) → (XVI) rearrangement was found to compete with oxidation of (XV) to propiophenone under the same conditions. Ouelette and Levin[33] proposed a Pd–OH addition to cyclopropyl in (XV) (analogous to the Pd^{II} aqueous oxidation of ethylene) to account for the oxidation to propiophenone. The mechanism of the (XV) → (XVI) conversion was not detailed, although it was observed that (XVI) is produced only under conditions where formation of Pd–OH is suppressed [high ratios of (XV)/Pd^{II}]. On the basis of the present results, we suggest that (XVI) may arise in a two-step process: (1) formation of a "$Pd^{II}Cl_n$"–arene[43] complex, (XVII), which, by analogy with the known chemistry of Pd^{II}–vinylcyclopropane complexes[4,5], decomposes to (XVIII); (2) rearrangement of (XVIII) to a complex of *trans*-propenylbenzene, by a path analogous to that shown in Fig. 5.

(XVII) (XVIII)

The results reported in this paper and in the papers by Ouelette and Levin[33] suggest definite parallels in the mode of reaction of Pd–Cl and Pd–OH with olefins on the one hand and with cyclopropanes on the other. Many other synthetic applications of either *cis* or *trans* Pd–X addition to cyclopropyl are therefore anticipated.

EXPERIMENTAL SECTION

Microanalyses for C, H, and Cl were performed by C. F. Geiger, Ontario, California and Chemalytics, Inc., Tempe, Arizona. Pd was determined by ignition to constant weight and weighing the residue as Pd. Melting points are uncorrected. The IR spectra were obtained on a Perkin–Elmer Model 621 grating spectrophotometer. PMR spectra were obtained with Varian A-60, A-60D, or T-60 NMR spectrometers.

Chemical shifts (δ) are given in ppm relative to tetramethylsilane. Mass spectra were obtained using a Perkin–Elmer/Hitachi RMU-9D double focussing spectrometer. Molecular weights were measured with a Mechrolab Osmometer, Model 301A.

Gas-liquid chromatography (GLC) was done using an Aerograph Model 90P instrument with the following columns: (1) 6′ × 1/4″ $AgNO_3$ SE-30 on Chromosorb P; (2) 10′ × 1/4″ 30% SE-30 on Chromosorb W; (3) 5′ × 1/4″ 20% Carbowax on Chromosorb P; (4) 10′ × 1/4″ Apiezon L on Chromosorb W. Preparative GLC was accomplished with a Nester/Faust 850 Prepkromatic instrument using a 6′ × 1½″ 30% SE-30 on Chromosorb P column. Solvents were dried with molecular sieves or were distilled from $BaO(CDCl_3)$.

Cis,cis-1,5-cyclononadiene, (II)[12], *endo*-9-bromobicyclo[6.1.0]non-4-ene[34], dichloribis(benzonitrile)palladium(II)[35], and dichlorobis(benzonitrile)platinum(II)[35] were prepared by the literature methods. The PMR of (II) consists of a complex olefinic (4H) multiplet at δ 5.1–6.0 ppm, an 8H allylic multiplet at δ 1.7–2.2 ppm, and a 2H methylenic multiplet (for the unique methylene) at δ 1.25–1.75 ppm.

Bicyclo[6.1.0]non-4-ene, (I)

Using a reported modification[36] of the Simmons–Smith[37] reaction, we obtained (from cyclooctadiene, CH_2I_2, and Zn/Cu) a mixture containing 42% (I). This was purified by preparative GLC, n_D^{22} 1.495 (lit. n_D^{25} 1.493)[38]. (Found: C, 88.69; H, 11.24; C_9H_{14} calcd.: C, 88.48; H, 11.52%.) PMR [see Fig. 3(a)]: multiplet at δ 5.63 (2 H), multiplet at 2.17 (6 H), a broad multiplet from 1.6 to 0.5 ppm (5 H), and a multiplet at −0.20 ppm (1 H). The IR as a thin film exhibited the following bands, among others: 1620 w, 720 s, typical for a *cis*-olefin[39], 3060 m, 1020 m, characteristic of 1,2 disubstituted cyclopropanes[8].

endo-9-Deuteriobicyclo[6.1.0]non-4-ene, (VII)

Using a modification of the reported[40] preparation of carbanionoid cyclopropyl derivatives, 10 g (0.05 mole) of *endo*-9-bromobicyclo[6.1.0]non-4-ene[34] was added to 25 ml dry THF. n-Butyllithium (42 ml of 1.19 *M*) solution in hexane was added dropwise to the cooled (−40°) nitrogen flushed system. Addition was complete in 30 min. The flask was slowly warmed to 0° and stirred for 15 min. D_2O (3 ml) was added slowly with stirring. The organic layer was extracted with ether, washed with water until neutral, and dried over anhydrous $MgSO_4$. The solvent was evaporated and the product vacuum distilled. The fraction boiling at 74–75°/28 mmHg was collected (5.1 g, 80%). PMR: multiplet at δ 5.60 (2.0 H), multiplet at 2.09 (6 H), multiplet from 1.65 to 0.5 (5 H), and a residual *endo*-9(H) multiplet at −0.20 ppm (0.14 H), indicating 86% *endo* deuteration. The mass spectrum of the product indicated an 84/16 mixture of $C_9H_{13}D/C_9H_{14}$. The results indicate that the purified product is a mixture of ≈85% (VII) and ≈15% (I). IR: 2260 w, assigned to cyclopropyl C–D; 1020 w, from residual (I); 805–815 (m–s, presumed to be the cyclopropyl (CHD) "wag" shifted from 1020 cm^{-1}. With these exceptions, the IR is similar to that of (I).

Dichlorobis(isobutyronitrile)palladium(II)

Isobutyronitrile (5 ml) was added to a solution of 0.85 g $PdCl_2(PhCN)_2$ in 20 ml benzene. The solution immediately turned from dark red to yellow. After cooling to 5°, followed by the addition of 25 ml hexane to assist precipitation, the mixture was

filtered. The filtrate was treated with more hexane to obtain a second crop of crystals. The product was washed with hexane and vacuum dried for 1 h, 0.60 g were collected, m.p. 72–73° with decomposition. (Found: C, 30.01; H, 4.48; Cl, 22.51; Pd, 33.60. $PdCl_2C_8H_{14}N_2$ calcd.: C, 30.45; H, 4.36; Cl, 22.50; Pd, 33.78%.) IR: ν(C≡N), 2300 cm^{-1}.

Dichlorobis(cyclopropylnitrile)palladium(II)

The preparation is identical to that for the isobutyronitrile complex: 1.3 g $PdCl_2(PhCN)_2$ gave 0.8 g product, m.p. 100–105° with decomposition. (Found: Pd, 34,41. $PdCl_2C_8H_{10}N_2$ calcd.: Pd, 34.20%.) IR: ν(C≡N), 2290 cm^{-1}.

Dibromobis(benzonitrile)palladium(II)

Following the procedure used to prepare the chloro complex[35], 0.44 g $PdBr_2$ gave 0.51 g $PdBr_2(PhCN)_2$, m.p. 94–98° with decomposition. (Found: 22.65. $PdBr_2$-$C_{14}H_{10}N_2$ calcd.: Pd, 22.55%.)

Di-μ-chlorodichlorobis(bicyclo[6.1.0]non-4-ene)dipalladium(II), (IV)

$PdCl_2(PhCN)_2$ (0.45 g; 1.2 mmole) was added to 0.15 g (1.2 mmole) (I) in 15 ml benzene and was stirred while warming on a steam bath for 1/2 min. The solution was then cooled to 5° for 3 min and was filtered, washed with 2 ml benzene, 20 ml pentane, and vacuum dried for 2 h. Orange-yellow powder (0.14 g) was obtained, m.p. 109–110° with decomposition. (Found: C, 35.96; H, 4.51; Pd, 35.96. $PdCl_2C_9$-H_{14} calcd.: C, 36.10; H, 4.67; Pd, 35.54%.) PMR in $CDCl_3$ (Fig. 3b): multiplet at δ −0.10 (1 H), multiplet at 0.88 (5 H), multiplet at 2.4 (6 H) and a multiplet at 6.16 ppm (2 H).

[cis-cis-1,5-Cyclononadiene)$_2Pd_3Cl_6$]$_n$, (V)

The procedure and amounts of reactants are identical to the preparation of (IV), with the exception of reaction time. The reaction mixture was allowed to stand at room temperature for 1 h before filtering. Yellow powder (0.23 g) was collected, m.p. 144–146° with decomposition. (Found: C, 28.04; H, 4.10; Pd, 41.31. $Pd_3Cl_6C_{18}H_{28}$ calcd.: C, 27.85; H, 3.65; Pd, 41.12%.)

Dichloro-cis,cis-1,5-cyclononadienepalladium(II), (VI)

$PdCl_2(PhCN)_2$ (0.30 g; 0.78 mmole) was dissolved in 20 ml benzene, filtered immediately, and was then treated with 0.15 g (1.22 mmole) (I). The solution was allowed to stand overnight at room temperature. The resultant orange-yellow needles were filtered and washed with 10 ml pentane and vacuum dried for 2 h. 0.15 g (0.50 mmole, 64%) was collected, m.p. 159–163° with decomposition. (Found: C, 35.98; H, 4.73; Cl, 23.48. $PdCl_2C_9H_{14}$ calcd.: C, 36.10; H, 4.67; Cl, 23.68%.) The molecular weight in CH_2Cl_2 was 301 g/mole; calculated for $PdCl_2C_9H_{14}$ is 299.3 g/mole. The PMR recorded as a $CDCl_3$ solution (Fig. 4) exhibits a multiplet centered at δ 6.60 (4 H), and a broad multiplet from 2.9 to 1.5 ppm (10 H). The IR results are virtually identical to results we obtained with $PdCl_2$(cyclooctadiene).[ν(C=C) 1520, ν(Pd–Cl) 325 and 290 cm^{-1}], and the IR results for both compounds are in accord with expectations for the monomeric structure[13a–f].

Dibromo-cis,cis-1,5-cyclononadienepalladium(II)

$PdBr_2(PhCN)_2$ (0.24 g; 0.51 mmole) was added to 0.061 g (0.50 mmole) (I) in

15 ml benzene. The solution was stirred and allowed to stand overnight. The reddish-orange crystals were filtered, washed with pentane, and vacuum dried for 2 h, yielding 0.12 g (0.31 mmole, 61%) product, m.p. 150–152° with decomposition. Only (II) is evolved on treatment with nucleophilic reagents. The IR is identical to that of the chloride complex, (VI), between 4000 and 400 cm^{-1}. (Found: Pd, 27.31. $PdBr_2C_9H_{14}$ calcd.: Pd, 27.34%.)

Reaction of $PdCl_2(PhCN)_2$ with endo-9-D-bicyclo[6.1.0]non-4-ene: formation of 7-deuterio-cis,cis-1,5-cyclononadiene, (VIII)

A filtered solution of 0.38 g (1.0 mmole) $PdCl_2(PhCN)_2$ in 20 ml benzene was added to 0.125 g (1.0 mmole) and 85/15 (VII)/(I). This was allowed to stand in the dark for 18 h. The resulting precipitate was filtered and washed with hexane. Solid product (0.26 g) was collected, and this was treated with 5 ml saturated aqueous cyanide. The aqueous cyanide was then extracted with 1 ml benzene. The liberated hydrocarbons were purified by GLC using column #2. 100 mg (VIII)/(II) (80% yield) was collected. The mass spectrum of the mixture indicated an 85/15 ratio of $C_9H_{13}D/C_9H_{14}$ the same isotopic ratio as the starting (VII)/(I). The IR and PMR of the (VIII)/(II) mixture are nearly identical to pure (II). The IR has a weak band at 2170 cm^{-1}, assigned to aliphatic C–D. The PMR spectrum contains a multiplet at δ 1.25–1.75 (2 H), a multiplet at 1.7–2.2 (7.2 H) and a broad multiplet from 5.1 to 6.0 ppm (4 H). The olefinic/aliphatic integral ratio is 0.43.

PMR time Studies of the reaction of (I) with $PdX_2(PhCN)_2$

The time studies were done using a Varian T-60 or an HA-100 spectrometer (for maximum *S/N*). Spectra were recorded at 50 s sweep times using the highest possible non-saturating power level. Normally, spectra were recorded at 90 s intervals commencing immediately upon mixing. The results in Fig. 3 are typical of what we obtained in many other experiments. Other time studies were carried out for equimolar solutions of (I) and $PdCl_2(PhCN)_2$ under the following conditions: (1) 0.05 *M*, $CDCl_3$, 60 MHz; (2) 0.05 *M*, C_6D_6, 60 MHz; (3) 0.075 *M*, $CDCl_3$, 60 MHz; (4) 0.075 *M*, C_6D_6, 60 MHz; (5) 0.10 *M*, $CDCl_3$, 60 MHz; (6) 0.15 *M*, $CDCl_3$, 60 and 100 MHz; (7) 0.20 *M*, $CDCl_3$, 60 and 100 MHz. In each case studied the features in Fig. 3 were apparent. In particular the δ 3.8 and 4.8 ppm resonances always maximized in intensity in the narrow range 6–12 mins.

In one experiment with $[PdBr_2(PhCN)_2]$ (0.05 *M*, benzene, with 10% *v/v* PhCN, 60 MHz) the general features of Fig. 3 were observed, with the exception that no absorption appeared in the δ 2.9–5 ppm range, implying that any intermediate analogous to (IX) does not accumulate.

Catalytic conversion of (I) to (II)

To 1.924 g (16 mmole) of (I) in 2 ml of benzene was added 0.060 g (0.15 mmole) $PdCl_2(PhCN)_2$, and the solution was stirred at room temperature for 60 h. The mixture was treated with aqueous cyanide and the benzene layer was analyzed by GLC. The solution contained 86% (II) and 14% (I). (II) was collected by GLC using column (2) and was shown to be identical with an authentic sample of (II) by spectroscopic analysis.

Isolation and characterization of trans-bicyclo[6.1.0]non-4-ene, (III)

Dichlorobis(cyclopropylnitrile)palladium(II) (0.884 g; 3.6 mmole) and 0.370

g (3.0 mmole) (I) were stirred for 18 min in 145 ml CH_2Cl_2. After this period, the solution was extracted with 200 ml 1 *M* KCN, washed with water, and dried with anhydrous $MgSO_4$. The CH_2Cl_2 was removed, and the residue was separated by GLC using column 1 at 95° and 100 ml/min flow. We collected about 75 mg (III) in this experiment [20% yield based on (I)], but other experiments suggest that 50% yield may be approached by varying the conditions. The mass spectral molecular weight is 122 (C_9H_{14}). (Found: C, 88.82; H, 11.28. C_9H_{14} calcd.: C, 88.48; H, 11.52%.) IR (cm^{-1}): 3060 m, 3000 s, 2920 vs, 2855 s, 1690–1620 m(br), 1455 m, 1295 w, 1240 w, 1225 w, 1210 w, 1135 w, 1105 w, 1080 w, 1035 m, 1025 m, 1012 m, 979 w, 959 w, 920 w, 890 w, 863 s, 852 w(sh), 775 m, 721 s. The peaks at 3060, 1080, 1035 and 1025 cm^{-1} indicate cyclopropyl; the 3000, 1690–1620 and 721 cm^{-1} peaks indicate *cis* olefin; and the 2855 and 1455 cm^{-1} peaks indicate methylene. 60 MHz PMR (Fig. 1): olefinic AA′ multiplet at δ 5.88–5.35 (2 H); multiplet at 2.4–1.65 (6 H); multiplet at 0.98–0.05 ppm (6 H). The highest field multiplet is assigned to 4 cyclopropyl H's and 2 substituent H's remotely shielded by cyclopropyl (see Discussion). The 100 MHz PMR is similar. Decoupling of the δ 2.4–1.6 ppm multiplet causes collapse of the AA′ pattern to a singlet. In this preparation, cyclopropylnitrile was used because it is easily separated from the hydrocarbons using GLC.

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