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THE REACTION OF 1,2,3-TRIPHENYLCYCLOPROPENE WITH PALLADIUM(II) CHLORIDE. A NOVEL RING-OPENING REACTION IN THE CYCLOPROPENE SERIES

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Current interest in the preparation and properties of π-allyl complexes of various transition metals[1], including those recently derived from precursors bearing cyclopropyl substituents[2,3], prompts us to report the isolation and characterization of an unusual π-allylic complex obtained via reaction of the title hydrocarbon (I) with palladium(II) chloride. This is apparently the first established example of a metal-promoted ring opening reaction in the cyclopropene series.

Treatment of a solution of I in acetone, benzene, or ethanol—methylene chloride with dichlorobis(benzonitrile)palladium(II) at room temperature furnishes, in 80% yield, a highly stable, bright yellow complex II, m.p. 148—150° (dec). Combustion analysis corresponds to a product obtained by 1/1 reaction of I with the metal halide while molecular weight determination indicates a dimeric structure $(C_{21}H_{16}PdCl_2)_2$. The chemical and spectral properties cited below clearly support a ring-opened π-allylic structure for II.

In the infrared, II shows the complete absence of absorption characteristic of 1,2-disubstituted cyclopropenes (uncomplexed) in the region of 1800 cm^{-1} and the presence of a strong band at 565 cm^{-1} which may be attributed to deformation vibrations of an allyl carbon skeleton. The NMR spectrum (60 MHz) of the complex in $CDCl_3$ exhibits a sharp singlet at τ 4.80 (1H) and 2.82 (5H) in addition to broad featureless resonances at 2.10 (4H) and 2.47 (6H). The downfield shift of *ca.* 1.8 ppm for the one proton singlet at II relative to the corresponding lone ring proton of I is inconsistent with an unrearranged π-alkenyl palladium(II) structure, but is in reasonable agreement with a rearranged π-allylic structure. In the aromatic region the unresolved multiplets at τ 2.10 and 2.47 may be assigned respectively to the *ortho* and *meta—para* protons of terminal phenyl groups lying in the deshielding plane of a π-allylic nucleus while the sharp phenyl spike is attributed to the protons of a phenyl attached at the central allyl carbon which by virtue of their displacement out of the plane of delocalization appear upfield from the protons of the coplanar phenyl groups.

Complex II undergoes a number of reactions to form characteristic organometallic derivatives of π-allyl metal(II) halides[4,**]. Thus reaction of II with LiBr give the

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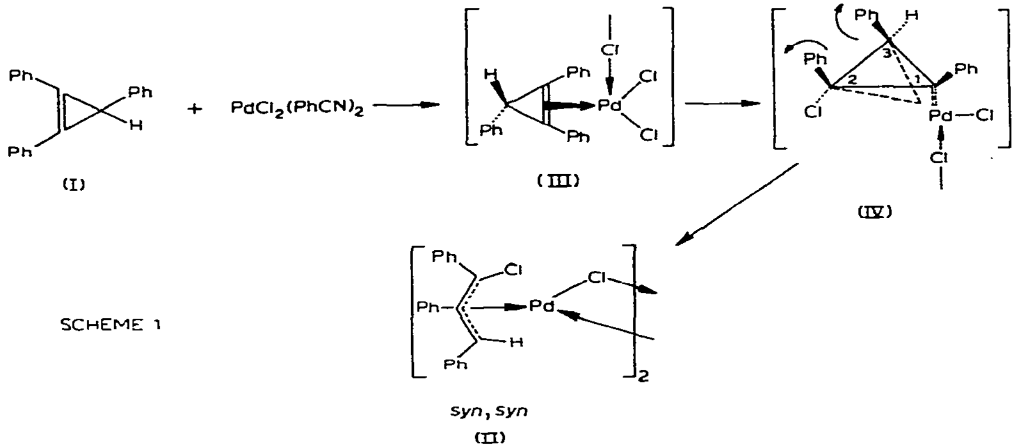
**Satisfactory elemental analyses were obtained for all new compounds.

metathesis product $(C_{21}H_{16}PdBrCl)_2$ while treatment with pyridine yields a mononuclear pyridine adduct $C_{26}H_{21}NPdCl_2$ which on heating above its melting point (130–135°) reverts back to dimer with evolution of the ligand. Thallium(I) acetylacetonate (Tl^{I}acac) reacts with II to yield the acetylacetonato derivative $(C_{21}H_{16}Cl)(acac)Pd^{II}$ characterized by NMR and mass spectral analysis. These chemical transformations confirm the chloro-bridged π-allylic nature of the complex and establish the presence of carbon-bound chlorine.



SCHEME 1

Catalytic and chemical reductions of II were carried out in an effort to determine the geometry of substituents about the allyl group. Catalytic reduction of II gave a mixture of 1,2,3-triphenylpropane and a chlorohydrocarbon identified by NMR, UV and mass spectral analysis as *cis*-1-chloro-1,2,3-triphenylpropene. Chemical reduction of the complex with $LiAlH_4$ gave only 1,2,3-triphenylpropane while decomposition of the complex in methanolic KOH solution[5] furnished *cis*-1,2,3-triphenylpropene characterized by NMR and UV[6] means as well as authentic sample comparison. The latter reaction has been found to be of general diagnostic value in structural investigations of π-allyl complexes of palladium[5].

On the basis of the above spectral and chemical evidence we tentatively assign the di-μ-chlorobis(π-1-chloro-*syn*,*syn*-1,2,3-triphenylallyl)dipalladium(II) structure to complex II (see Scheme 1). Final proof of configuration in this complex must await X-ray crystallographic analysis now under consideration.

The mode of formation of II presumably involves the unstable[7,★] π-complex III as the initial intermediate. Since addition reactions involving the double bond of I proceed via the less hindered side[8], the 3-phenyl substituent in II should lie *anti* to the bridged metallo halide moiety. A concerted process involving Pd→C transfer of a chloro group[3,4,9] is postulated to convert II to the σ-C–Pd bonded intermediate IV. Release of strain energy (*ca.* 27 kcal · mole^{-1}) in proceeding to this cyclopropyl complex from the more strained cyclopropenyl system in III apparently provides the requisite driving force for rearrangement. The net *cis* addition of the elements of $PdCl_2$ from the less hindered side

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[★] By analogy to failure of *cis*-stilbene to yield an isolable π-complex with palladium(II) chloride[7].

of I establishes the stereochemistry of all substituents in IV as depicted. The relative instability of a cyclopropyl σ-bonded palladium complex *versus* a π-allyl structure having multicentric bonding and the severe steric crowding of the bulky Cl and PdCl groups constitute factors for subsequent rearrangement of IV to II. Woodward–Hoffmann rules as applied to cyclopropyl systems[10] such as IV in which the phenyl groups on C_2 and C_3 lie *trans* to the PdCl group provide for disrotatory (outward) ring opening as indicated, yielding *syn,syn* geometry of the phenyl substituents.

The above conversion of I to II may be considered as a metal-promoted analog of the related acid-catalyzed ring opening reactions of alkyl- and aryl-cyclopropenes[11]. Further study of II and a general investigation of reactions involving other olefinic small ring compounds are in progress.

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