

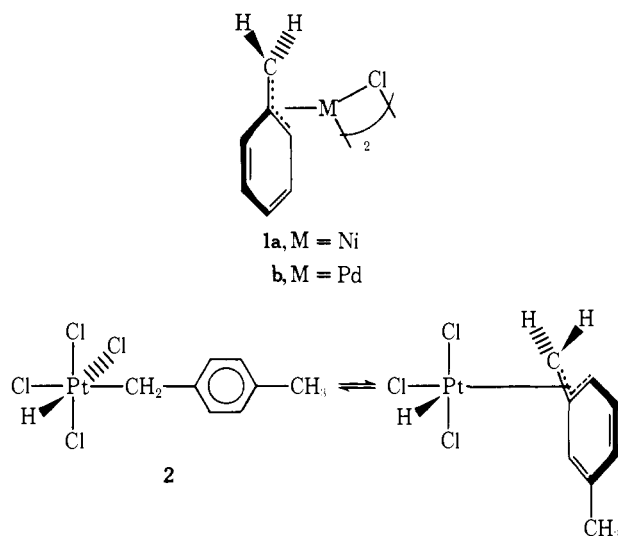
The Dynamic η^1 - and η^3 -Benzylbis(triethylphosphine)palladium(II) Cations. Mechanisms of Interconversion

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Abstract: The reaction of (*S*)-(-)-*trans*-chloro(η^1 - α -deuteriobenzyl)bis(triethylphosphine)palladium(II) (**6**) with sodium tetraphenylborate gives (*S*)-(+)-(η^3 - α -deuteriobenzyl)bis(triethylphosphine)palladium(II) tetraphenylborate (**7**), a π -benzylpalladium cation, that retains its optical activity in solution. Regeneration of σ -benzyl complex **6** from **7** with chloride gives a product with 94% net retention of configuration at the benzyl carbon. The analogous undeuterated η^3 complex (tetrafluoroborate) in chloroform shows ³¹P and ¹H NMR spectra characteristic of this π -benzyl species; however, in nitrile solvents at low temperatures, both the η^3 and the η^1 complexes can be observed. At elevated temperature, interconversion of the two takes place rapidly, displaying one ³¹P phosphine singlet and one ¹H benzyl singlet. These results are most consistent with a rearrangement mechanism involving rapid suprafacial shifts of the π -benzyl species, and an antarafacial rearrangement that proceeds through the σ -benzyl intermediate.

The π -benzyl ligand, possessing fluxional character, represents an unusual type of coordination to a transition metal. Although this type of bonding was first recognized only recently in the complex (η^3 -benzyl)-(η^5 -cyclopentadienyl)dicarbonylmolybdenum,² it represents an important type of intermediate in a number of organometallic transformations and catalytic reactions. π -Benzyl complexes of the platinum group are involved in a number of such reactions, either by implication or direct observation. Bis(1,2,3- η^3 -benzyl)di- μ -chloro-nickel(II) (**1a**) is probably an intermediate in the nickel carbonyl catalyzed coupling of the benzyl halides to bibenzyl and benzil.³ The palladium analogue (**1b**) is a reactive complex

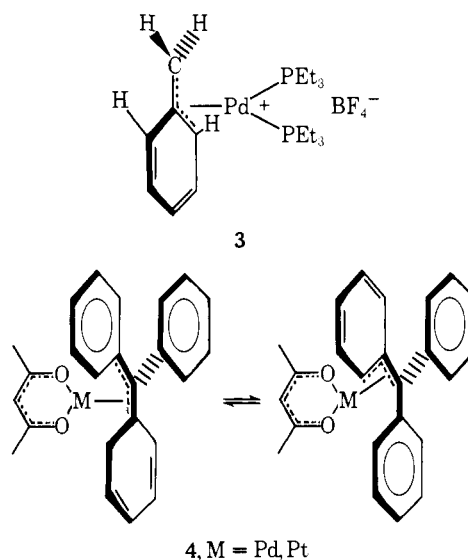


that can be carbonylated in methanol to give methyl phenylacetate, reacts with acetate to afford benzyl acetate, and catalyzes the benzylation of olefins.⁴ Hydrogen isotope exchange in the methyl groups of toluene and *p*-xylene, catalyzed by PtCl_4^{2-} in D_2O , probably takes place by oxidative addition of the methyl C-H bond (hydrocarbon activation) to form the hydridoplatinum(IV) complex (**2**) containing the benzylplatinum σ bond in equilibrium with the π -benzyl complex.⁵

The fluxional character of **1b** and a number of closely related π -benzyl complexes have been observed spectroscopically, but the mechanistic details of the transformations in the platinum-group complexes have not been elucidated. The ¹H temperature-dependent NMR spectrum of **3** shows a time-average equivalence of the two benzyl protons and the two

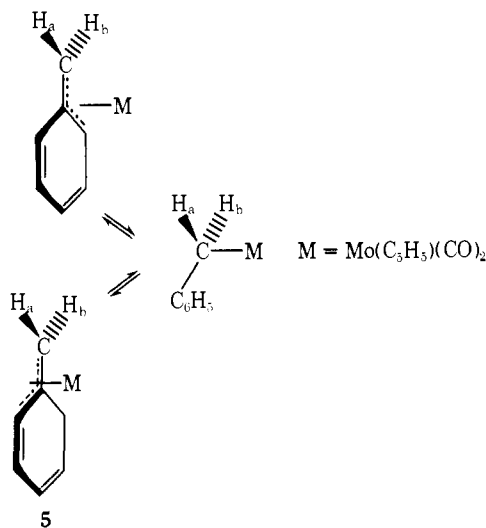
ortho protons of the π -benzyl ligand.⁶ At -83°C , the benzyl protons in the *o*-chloro derivative became nonequivalent as a result of the positioning of palladium at the two different edges. A similar behavior was observed in the ¹H temperature-dependent spectrum of the 3,4-dimethyl derivative of **1b**.⁴ Addition of excess triethylphosphine ultimately produced the ¹H spectrum characteristic of the σ -benzyl complex.

The ¹H and ¹³C NMR spectrum of complex **4** reveals the occurrence of three different types of fluxional isomerism.⁷ In addition to a suprafacial jump process analogous to that observed in **1b** and **3**, a propeller-like rotation occurs, making all



three phenyl groups equivalent. A third process involves the exchange of independent sites on the acetylacetonate ligand. In all three rearrangements, higher activation energies are required for the platinum complexes.

The structure⁸ and most of the mechanistic details of rearrangement⁹ of the fluxional complex (η^3 - $\text{C}_6\text{H}_5\text{CH}_2$)(η^5 - C_5H_5)(CO)₂Mo (**5**) have been elucidated. The x-ray structure revealed marked alteration in the carbon-carbon bond distance in the benzene ring, characteristic of a nonaromatic alternating single and double bond structure as a result of a frozen suprafacial rearrangement. In solution, the spectrum of this type of complex, particularly that of the 3,5-diisopropylbenzyl analogue, revealed that molybdenum has access to all four positions (edge and face combinations) for bonding to the

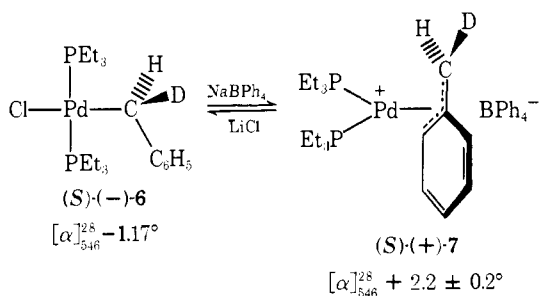


benzyl group, demonstrating that both suprafacial and antarafacial shifts were taking place. The mechanism proposed⁹ for the antarafacial shift included the generation of the short-lived (undetected) 16-electron σ -bonded benzyl intermediate that undergoes rapid 180° rotation of the phenyl ring to place molybdenum on the opposite face, and then reverts to the π -benzyl structure capable of rapid suprafacial jumps.

Results and Discussion

Although the formation of a σ -bonded benzyl intermediate is the most attractive mechanism for face to face rearrangement of the π -benzyl group bonded to transition metal, this type of σ intermediate has not been demonstrated in the fluxional system. Rearrangement through a σ -bonded intermediate requires that an asymmetric benzyl carbon retain its configuration during this process. Thus, the $\alpha \rightarrow \delta$ shift⁹ interchanging environmental edges would not interchange benzyl protons (H_a and H_b , 5).

The reaction of (*S*)-(-)-*trans*-chloro(η^1 - α -deuteriobenzyl)bis(triethylphosphine)palladium(II) (6) with sodium



tetraphenylborate gave (*S*)-(+)-(η^3 - α -deuteriobenzyl)-bis(triethylphosphine)palladium(II) tetraphenylborate (7), which was stable in solution, retaining its optical activity at ambient temperature for days. Reactions of the π -benzylpalladium cation (7) with excess lithium chloride regenerated the starting optically active σ -benzyl complex (6) with 94% net retention of configuration at the benzyl carbon (Table I).

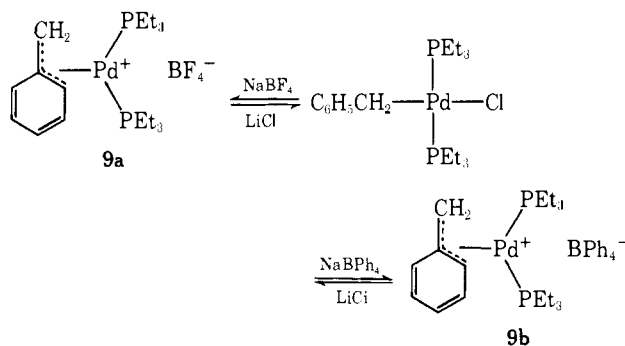
These results demonstrate that any face to face (antarafacial) rearrangement cannot take place by a 180° rotation of the π -benzyl group in complex 7. Either 7 does not undergo face to face rearrangement, or if it does, then the rearrangement proceeds through some intermediate that preserves the optical integrity of the benzyl carbon. Chirality retention at methylene has been observed in substituted π -allyl palladium complexes;¹⁰ however, an optically active ligand is used to demonstrate this phenomenon.

The optically inactive undeuterated complexes, (η^3 -benzyl)bis(triethylphosphine)palladium(II) tetrafluoroborate (9a)

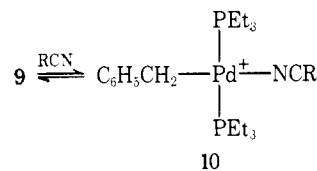
Table I. Specific Rotations^a of (*S*)-(-)-6 before NaBPh₄ Exchange (I) and after LiCl Quenching of (*S*)-(+)-7 (II)^d

λ , nm	I ^b	II ^c	Overall stereospecificity
589	-0.890 (4)	-0.84 (2)	94 ± 2.4%
578	-0.959 (4)	-0.89 (2)	92.8 ± 2.6%
546	-1.227 (4)	-1.17 (2)	95.4 ± 2%

^a Rotations measured at 28 °C in CH₂Cl₂, $l = 1$. Starting (*S*)-(-)-6 was synthesized from (*R*)-(-)- α -deuteriobenzyl chloride of ee 80.7 ± 4%. ^b c 0.447 g/mL. ^c c 0.1095 g/mL. ^d Estimated experimental error in parentheses.



and tetraphenylborate (9b), were prepared by the reaction of *trans*-chlorobenzylbis(triethylphosphine)palladium(II) (8) with sodium tetrafluoroborate and tetraphenylborate, respectively. Because the tetrafluoroborate salt (9a) was more stable in the solid state and in solution, NMR spectra of this complex were observed. The ³¹P NMR spectrum of 9a in deuteriochloroform at -20 °C showed two doublets centered at -18.865 and 26.816 ppm, $J_{31P-1H} = 82$ Hz, characteristic of the two different phosphorus ligands coupled to each other. This nonequivalence results from the inability of the benzyl group to undergo free rotation. When benzonitrile was added to the solution, a third absorption, a singlet at -4.61 ppm, characteristic of the σ -benzyl complex containing equivalent phosphines appeared. The ³¹P{¹H} temperature-dependent spectra of these complexes in a 3:1 mixture of butyronitrile and perdeuterioacetone (deuterium lock) is shown in Figure 1. This temperature-dependent behavior is clearly a result of equilibria between the π -benzyl cation (9) and the σ complex (10) in solution.



Rate constants were obtained for this equilibrium using from the ³¹P{¹H} spectra the approximate equation

$$k = T_2^{-1} \cdot \text{exchange} = \pi(W - W_B - W_0)$$

where W is the measured spectral line width at half-height, W_B is the broadening which had been added by digital smoothing, and W_0 is the line width in hertz in the frozen spectrum. To obtain the activation enthalpy and entropy, the data were fitted by

$$\ln(k/T) = \ln(k_B/hT) - \Delta H^\ddagger/RT + \Delta S^\ddagger/R$$

using standard weighted linear least squares. The weighting coefficients were proportional to $(k/T)^2$, consistent with the assumption that the experimental error in k is independent of the value of k . Five data points were used over the temperature

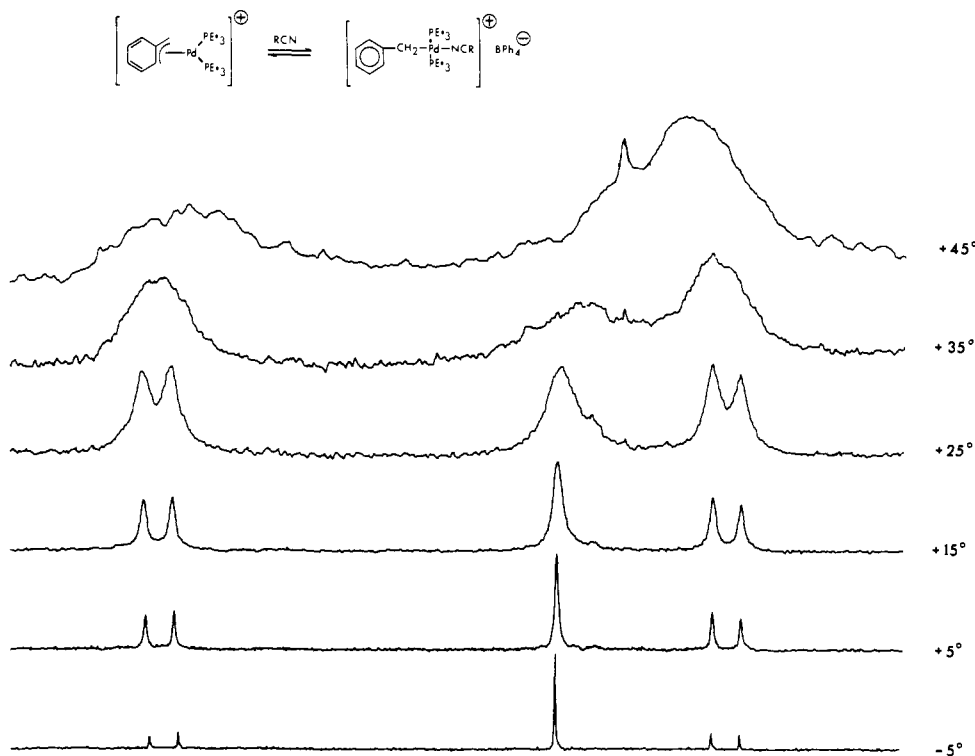


Figure 1. $^{31}\text{P}\{^1\text{H}\}$ NMR temperature-dependent spectrum of **9a** in nitrile solvents.

range 271.2–292.3 K, to give $\Delta H^\ddagger = 25.6 \pm 2.1$ kcal/mol; the errors ($\sim \pm 1$ kcal/mol deg) did not allow an estimate of ΔS^\ddagger . The indicated error for ΔH^\ddagger represents two standard deviations. This value for ΔH^\ddagger is slightly higher than those reported⁹ for the analogous molybdenum species, **5**, in which the σ -benzyl complex could not be observed. In the case of **5**, however, the two π -benzyl forms could be frozen. The energy barrier for the suprafacial jump in **5** is much higher than in the Pd system. Thus, two processes are being observed in the Pd system: an extremely fast suprafacial jump process, having very small ΔH^\ddagger , and intramolecular phosphine exchange through a σ complex, having a large ΔH^\ddagger .

The equilibria obtained at 253 K with various para-substituted benzonitriles and a plot of $\log K$ for the π -benzyl rearrangement with σ_p gave the linear free energy relationship with $\rho = +1.5$ (Figure 2). This large positive value of ρ is suggestive of considerable delocalization of the positive charge on palladium to the benzonitrile ligand. The nitrile carbon should be susceptible to nucleophilic attack, as has been observed in the platinum analogue.¹¹

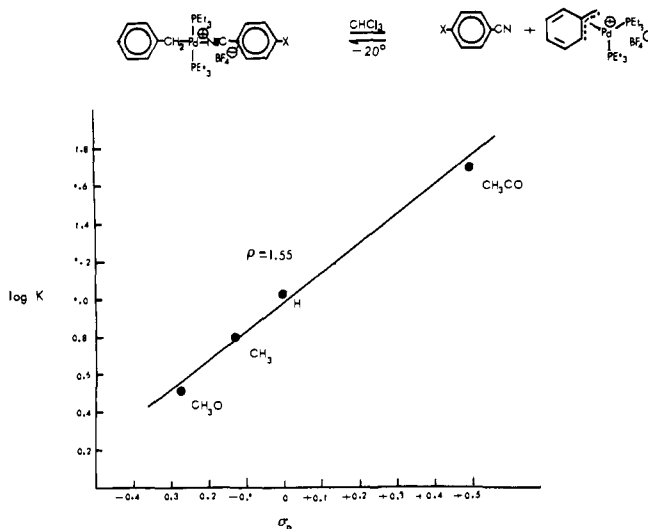
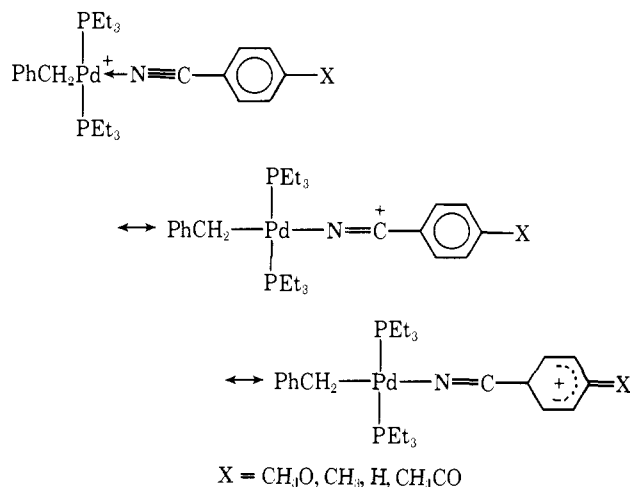


Figure 2. Hammett plot of π - σ equilibrium in the presence of para-substituted benzonitriles.

The ^1H NMR spectrum of **9a** at -20°C in deuteriochloroform was identical with that reported,⁶ and showed a doublet for the equivalent methylene protons. Coupling of the benzyl protons takes place only with the “trans” phosphine.¹¹ No significant changes in this spectrum were observed in raising the temperature, and no broadening of the doublet was observed down to -80°C in CD_2Cl_2 . In a noncoordinating solvent, therefore, the π -benzyl complex (**9**) predominates, and the two benzyl protons remain equivalent at low temperatures at least via rapid suprafacial rearrangement.

In the low-temperature ^1H NMR spectrum of **9a** in deuterioacetonitrile (Figure 3), six peaks were observed in the methylene region: (a) a sharp singlet due to water that moved upfield at higher temperatures, (b) a triplet from the symmetrical σ complex (**10**), and (c) the doublet of the π -benzyl species (**9**). Above room temperature, the doublet and triplet signals coalesced to a singlet.

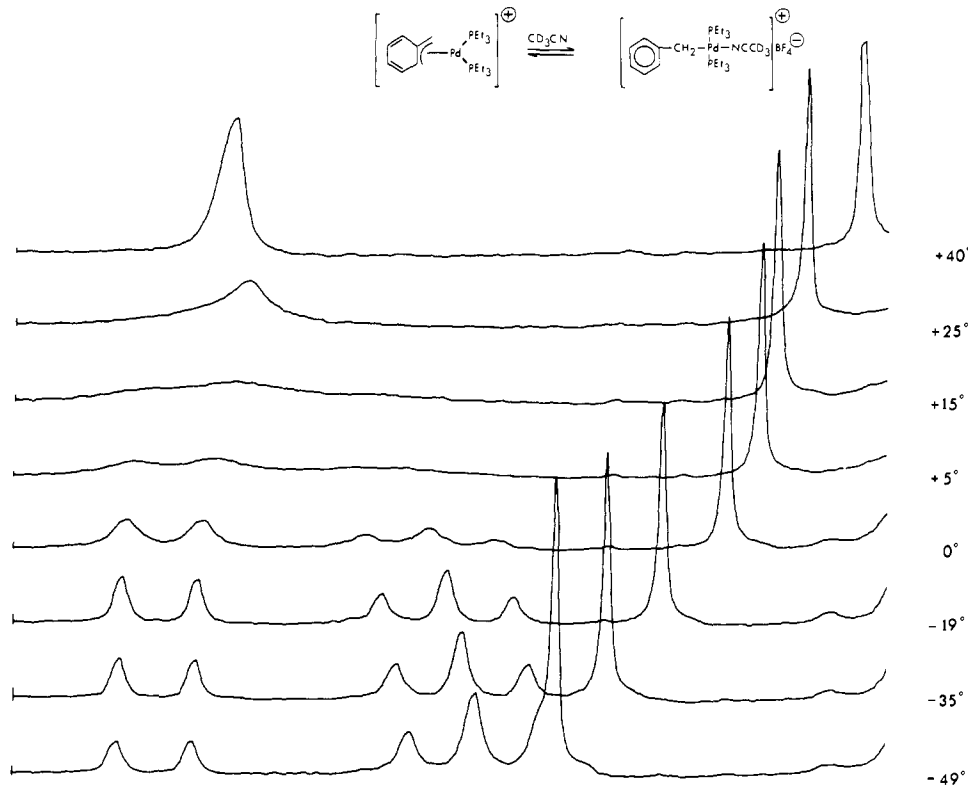


Figure 3. ^1H NMR temperature-dependent spectrum of **9a** in perdeuterioacetonitrile.

The rearrangements of the η^1 - and η^3 -benzylbis(triethylphosphine)palladium(II) cations that are consistent with these results are summarized in Figure 4. In a noncoordinating solvent, the relative energy of the σ -cation intermediate is apparently too high, and therefore present in too low a concentration to be detected. The presence of a coordinating nitrile solvent stabilized the σ -cation intermediate, allowing its detection. Above ambient temperature in the nitrile solutions, the two species rapidly equilibrate; however, under these conditions both the phosphorus and benzyl protons became equivalent. This mechanism, proposed earlier for the neutral molybdenum(II) complex (**5**)⁹ and requiring the intermediacy of the benzylpalladium σ -bonded complex for the antarafacial rearrangement, also dictates that the benzyl carbon maintain its stereochemical integrity. Thus an antarafacial rearrangement interchanges the ortho protons, H_1 and H_2 , relative to the benzyl protons H_a and H_b .

Experimental Section

All operations were conducted in Schlenk tubes under deoxygenated argon atmosphere.

η^3 -(α -Deuteriobenzyl)bis(triethylphosphine)palladium(II) Tetraphenylborate (7). To a stirred solution of (*S*)-(-)-chloro(α -deuteriobenzyl)bis(triethylphosphine)palladium(II) (**6**),¹³ 447 mg, 0.951 mmol, $[\alpha]^{28}_{\text{D}} -0.890 \pm 0.004^\circ$, CH_2Cl_2 , $l = 1$) in 15 mL of degassed anhydrous ethanol was added a solution of NaBPh_4 (651 mg, 1.902 mmol) in 6 mL of ethanol. Immediately a copious pale yellow precipitate was formed. After 15 min the precipitate was collected and washed well with ethanol and ether. The crude product was dried at 25°C (4 μm) for 2 h to give 566 mg (79%) of π -(α -deuteriobenzyl)bis(triethylphosphine)palladium(II) tetraphenylborate: ^1H NMR (CDCl_3) δ 7.55–6.75 (complex multiplet, 23 H, aromatic), 6.4 (m, 2 H, ortho hydrogens on π -benzyl ring), 2.6 (d, 1 H, $J = 8$ Hz, -CHD-), 2.2–0.35 (bm, 30 H, $\text{C}_2\text{H}_5\text{P}$); $[\alpha]^{28}_{546} +2.2 \pm 0.2^\circ$ (CHCl_3 , $l = 1$, c 161 mg/mL). An analytical sample was prepared by crystallization from acetonitrile. The pale yellow crystals were washed with ethanol and ether and dried under high vacuum, mp 91 – 92°C dec. Anal. Calcd for $\text{C}_{43}\text{H}_{57}\text{BP}_2\text{Pd}$: C, 68.51; H, 7.70; P, 8.24. Found: C, 67.65; H, 7.86; P, 8.73.

Reaction of η^3 -(α -Deuteriobenzyl)bis(triethylphosphine)palladium(II)

Tetraphenylborate (7a) with Lithium Chloride. Formation of Chloro-(α -deuteriobenzyl)bis(triethylphosphine)palladium(II) (6). To a vigorously stirred solution of 500 mg of LiCl (11.8 mmol) in 4 mL of methanol covered with a 20-mL layer of pentane was added in small portions 282 mg (0.374 mmol) of π -(α -deuteriobenzyl)bis(triethylphosphine)palladium(II) tetraphenylborate from the previous experiment. The resulting slurry was stirred for 10 min. The pentane layer was removed by means of a Pasteur pipet and the methanol layer was covered with another 20 mL of pentane. Stirring was continued for another 5 min. The procedure was repeated once more and the combined pentane extracts were dried over MgSO_4 . Concentration of the solvent in vacuo gave 211 mg of a pale yellow oil which solidified on standing. Recrystallization from pentane yielded 109.5 mg of pale yellow crystals of (*S*)-(-)-chloro(α -deuteriobenzyl)bis(triethylphosphine)palladium(II), mp 77 – 79°C . Rotations are given in Table I.

π -(Benzyl)bis(triethylphosphine)palladium(II) Tetrafluoroborate Monohydrate [($\text{C}_6\text{H}_5\text{CH}_2$) $\text{Pd}(\text{PEt}_3)_2$] $^+\text{[BF}_4\text{]}^- \cdot \text{H}_2\text{O}$ (9a). To a stirred solution of chlorobenzylbis(triethylphosphine)palladium(II) (**8**, 1.87 g, 3.99 mmol) in 25 mL of degassed absolute ethanol was added, under argon, a solution of NaBF_4 (3.078 g, 28.5 mmol) in 10 mL of water. After stirring for 1 h at 25°C the solution was kept overnight at 0°C . Large, colorless crystals separated. The yellow solution was decanted and the crystals were washed with 5 mL of EtOH . The combined liquids were lyophilized. The dry yellow solid was dissolved in 15 mL of acetonitrile and filtered. The filtrate was concentrated in vacuo to give the crude product as a yellow powder (1.758 g, 3.26 mmol, 82%). The complex was purified by recrystallization from 10 mL of dry, degassed THF followed by addition of 10 mL of ether. Pale-yellow microcrystals separated, mp 122 – 123°C dec.

Anal. Calcd for $\text{C}_{19}\text{H}_{39}\text{BF}_4\text{OP}_2\text{Pd}$: C, 42.36; H, 7.24. Found: C, 42.35; H, 6.92. The ^1H NMR spectrum in CDCl_3 was identical with the published spectrum.⁶

^{31}P NMR Spectra. Proton-decoupled ^{31}P pulse Fourier-transform NMR spectra were obtained on a Bruker HX90E instrument, modified by the addition of a Bruker SXP high-power rf pulse amplifier, a high-power decoupler amplifier, and a Nicolet B-NC 12 computer with a Nicolet Model 293 I/O controller for instrument control. Sampling pulses of 9.2 μs and 30° were used with a repetition time of 2 s; 4096-point free-induction decays (FIDs) were collected, with a spectrum width of 2000 Hz. Each FID was multiplied by a decaying exponential for smoothing purposes, and then padded with zeros to

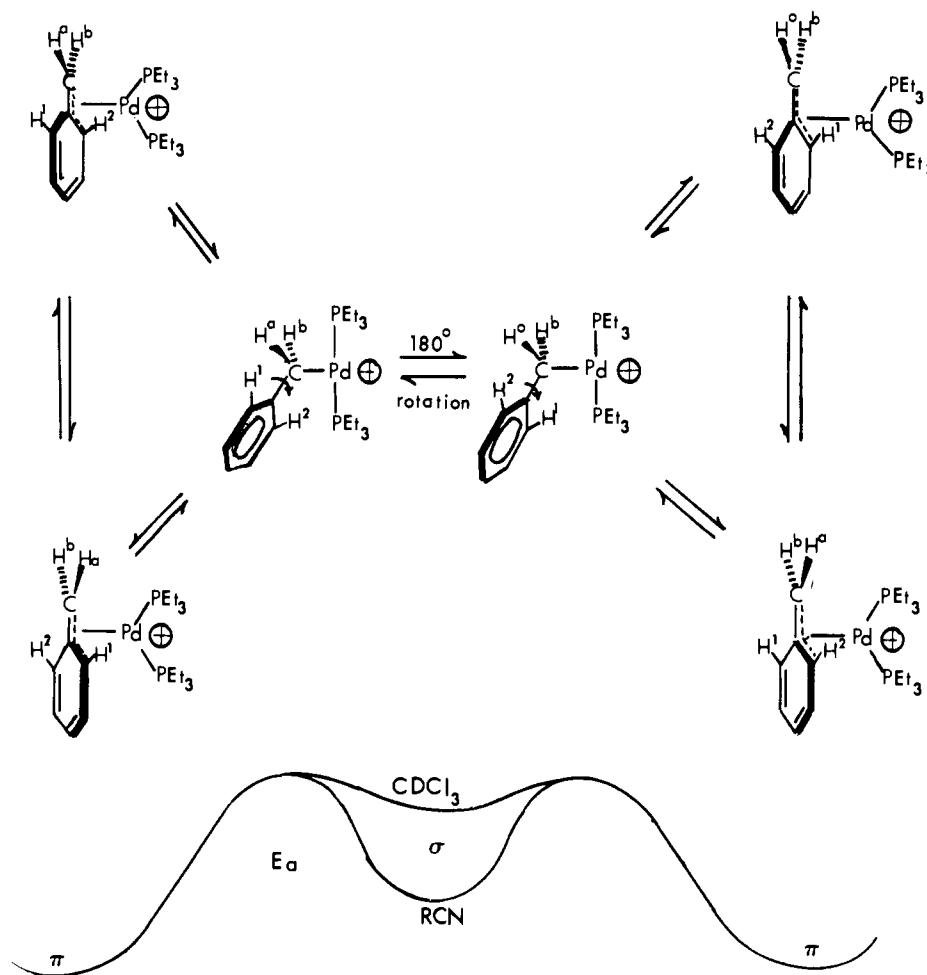


Figure 4. η^1 - and η^3 -benzylbis(triethylphosphine)palladium(II) cation rearrangements.

increase digital resolution of the frequency domain spectrum. The probe temperature controller was calibrated by means of a deuterium NMR thermometer, using the lock channel. The deuterium thermometer was calibrated by the methanol ^1H NMR thermometer, using van Geet's results.¹⁴ The deuterium NMR thermometer will be described elsewhere in greater detail. Absolute temperature errors are estimated to be about 1 K, and temperature differences are estimated to be accurate to approximately 0.5 K. The following rate constants (s^{-1}) were obtained (K in parentheses): 0.631 (271.2), 2.2 (276.4), 11 (281.7), 22.3 (287.05), 53.4 (292.3).

^1H NMR Spectra. Temperature-dependent ^1H spectra of η^3 -benzylbis(triethylphosphine)palladium(II) tetrafluoroborate monohydrate (**9a**) were taken on the same instrument in CD_3CN or CDCl_3 . Temperature readings were obtained from the MeOH calibrated temperature controller. The ^1H spectrum at -85°C was taken in CD_2Cl_2 .

Linear Free Energy Relationship. A solution of η^3 -benzylbis(triethylphosphine)palladium(II) tetrafluoroborate monohydrate (**9a**, 60 mg, 0.11 mmol) in 1.4 mL of CDCl_3 (0.078 M) was cooled to -20°C and the $^{31}\text{P}\{^1\text{H}\}$ spectrum was taken as described above. An AB spectrum was observed, in accordance with predominance of the π -benzyl form. Upon gradual addition of $\text{C}_6\text{H}_5\text{CN}$ a singlet signal appeared; its intensity was proportional to the amount of the benzonitrile added. The singlet signal in the $^{31}\text{P}\{^1\text{H}\}$ spectrum was assigned to the σ -benzyl form. The equilibrium constant K was calculated from the relative area of the σ and π forms according to the equation $K_{-20^\circ\text{C}} = ([\text{C}_6\text{H}_5\text{CN}][\pi]) / [\sigma]$ (Figure 4).

The concentrations of the σ and π forms were calculated from their relative area in the $^{31}\text{P}\{^1\text{H}\}$ spectrum, and the total palladium(II) concentration, corrected for volume change brought about by the added benzonitrile. Since high concentrations of $\text{C}_6\text{H}_5\text{CN}$ were used (1.89 or 1.354 M) relative to the total Pd(II) concentration, the decrease in concentration of free $\text{C}_6\text{H}_5\text{CN}$ due to coordination to Pd(II) was neglected. For the above two $[\text{C}_6\text{H}_5\text{CN}]$ concentrations were

Table II. Data for Figure 2

X	σ_p	$K_{-20^\circ\text{C}}$	Log K
CH_3O	-0.27	3.3	0.51
CH_3	-0.7	6.3	0.79
H	0	10.85 ^a	1.03
COCH_3	+0.5	48	1.68

^a Recalculated for $\text{C}_6\text{H}_5\text{CN}$ concentration of 1.77 M at -20°C .

obtained the following $K_{-20^\circ\text{C}}$: $K_{1.89}^{-20} = 11.73$; $K_{1.354}^{-20} = 11.77$. The experiment was repeated with the following benzonitriles, all at 1.83 M: $p\text{-CH}_3\text{C}_6\text{H}_4\text{CN}$, $p\text{-CH}_3\text{OC}_6\text{H}_4\text{CN}$, and $p\text{-CH}_3\text{COC}_6\text{H}_4\text{CN}$ (Table II). Plotting σ_p vs. K gave a straight line (Figure 2); its slope yielded a ρ value of 1.55, using the equation $\log K - \log K_0 = \sigma_p\rho$.

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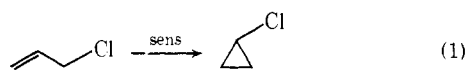
Photochemical Transformations. 20. Intermediates in the Sensitized Photorearrangements of the α - and γ -Methylallyl Chlorides¹

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Abstract: The acetone-sensitized photorearrangements of α - and *cis*- and *trans*- γ -methylallyl chlorides to each other and to *cis*- and *trans*-2-chloro-1-methylcyclopropane have been studied. Quenching with piperylene of the cyclopropyl chloride formation indicates that excitation transfer from triplet acetone to the allylic chlorides occurs at a rate approximately 1/100 that of transfer to piperylene, and gives a species with a quenchable lifetime of 2–3 ns which leads to the rearrangement–cyclization. Quenching of the triplet-sensitized rearrangements of *trans*-crotyl chloride to the *cis* isomer and to the allylic isomer gives similar excitation transfer rate constants with a quenchable lifetime of about 10 ns for the *cis* isomer production, and with a negative “lifetime” for the α isomer formation. These results are not consistent with the idea that a single quenchable intermediate leads to all of the products. The data are consistent with the idea that there are two (or more) excited-state intermediates, one of which (differing from each allylic isomer) leads to the cyclopropanes. The second intermediate may be postulated to interconnect the three allylic isomers, with its decay ratio in the absence of quencher different from its decay ratio when it interacts with quencher.

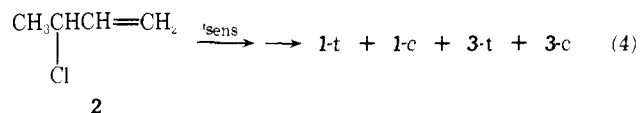
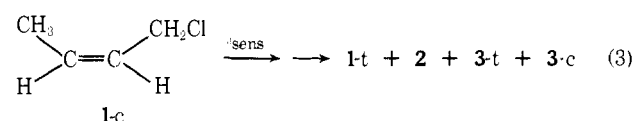
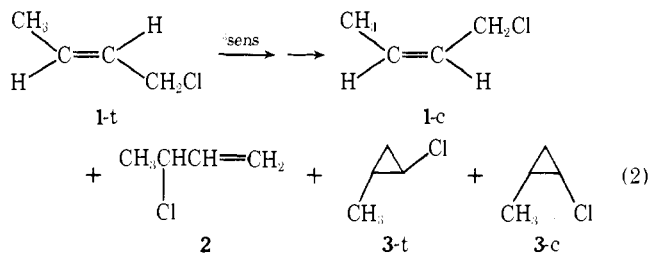
The α -methylallyl chloride– γ -methylallyl (crotyl) chloride system was the first one in which the photosensitized rearrangement of allylic halides to cyclopropyl halides was observed.² The general reaction (eq 1) may be described formally



as a [1,2]-sigmatropic rearrangement, accompanied (or followed) by ring closure, similar to the di- π -methane rearrangement.³ It occurs in competition with allylic ([1,3]-sigmatropic) rearrangement and with *cis*–*trans* isomerization, in systems where these processes can be observed. The general nature of the photorearrangement–cyclization, as well as of the other photoprocesses, has been demonstrated by extension to a wide range of acyclic and cyclic allylic halides,^{2,4} with notable exceptions for the photorearrangement–cyclizations when certain substituents are in the β position.⁵

The α -methylallyl–crotyl system is a useful one for studying details of these photoprocesses, as they all may be observed simultaneously. Thus each of the allylic chloride isomers—*trans*-crotyl (1-t), *cis*-crotyl (1-c), and α -methylallyl (2)—gives four products on photosensitization. These are *cis*- and *trans*-2-chloro-1-methylcyclopropane (3-c and 3-t), as well as those two of the three allylic chlorides (1-c, 1-t, and 2) not used as starting materials (see eq 2, 3, and 4).

It is of obvious interest to learn whether all of the products arise from the same or from different excited state progenitor(s). It has already been reported^{4b} that 1-t and 1-c show considerable and different selectivities in their transformations to 3-t and 3-c, so that it was clear that 1-t and 1-c (and presumably 2) give different intermediates, but the question of how many product-determining excited-state intermediates are derived from each allylic chloride remained. The work described in this paper is an attempt to address that question.



As our previous work^{2,4,6} had implicated the intermediacy of triplet species in such photoreactions, we decided to initiate studies of quenching by species of low triplet energy. The Stern–Volmer⁷ treatment (a plot of ϕ_0/ϕ_q vs. [Q]) demonstrates the intervention of long-lived species (generally triplet sensitizers and/or triplet substrates) in reactants excited by direct light absorption. However, as has been noted,^{4e,6,8} easily interpretable results do not readily obtain with triplet sensitization. Thus, when the reacting substrate is not the light-absorbing species—that is, when a sensitizer is used—quenching of both excited-state sensitizer and excited-state reactant may occur. A further complication is that the fraction of excitation transferred from sensitizer to reactant and to quencher will vary with the ratio of reactant to quencher. These factors result in expressions^{4e,6,8} for ϕ_0/ϕ_q which are quadratic in [Q], and which depend on reactant concentration as well,