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KINETICS AND MECHANISM OF THE PALLADIUM (II) PROMOTED RING OPENING OF TRI- AND TETRASUBSTITUTED CYCLOPROPENES

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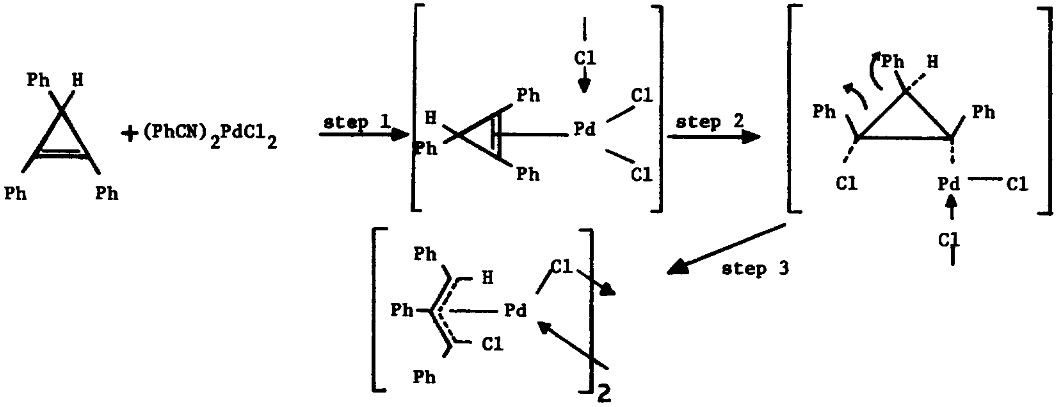
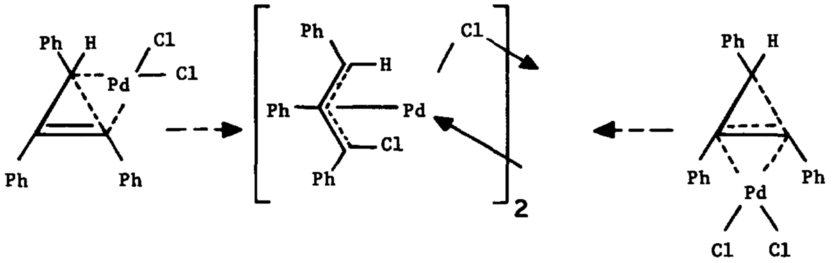
An example of an interesting and potentially general method for preparing pi-allyl palladium chloride complexes from reaction of cyclopropenes with palladium (II) chloride was recently reported. In the specific case cited[2], 1,2,3-triphenylcyclopropene (1) was converted to di-μ-chlorobis(π-1-chloro-syn,syn-1,2,3-triphenylallyl)palladium(II) in 80% isolated yield. Evidence for the initially proposed mechanism (Scheme I) rested primarily on product structure confirmation and analogy to related addition reactions of 1. The results, however, were not inconsistent with a process involving palladium (II) promoted sigma-bond cleavage in conjunction with or in the absence of coordination with the cyclopropenyl pi-bond (Scheme II). We now wish to report additional findings which serve to further delineate the scope and mechanism of this reaction.

SCHEME I



SCHEME II

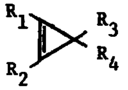


Reaction of tri- and tetrasubstituted cyclopropenes 1-7 with $(PhCN)_2PdCl_2$ in benzene proceeds with quantitative conversion (nmr) of olefin to the corresponding pi-allyl palladium (II) chloride complex(es).[3] The data obtained from integration of peaks which were singularly attributable to starting material or products allowed determination of competitive rates of pi-allyl complex formation in the same series (Table I). The k_{rel} values, determined by use of a competitive second-order kinetics equation[4], were invariant over 30-80% reaction and a wide range of initial reactant concentrations.

Since the para-substituents in cyclopropenes 1-4 should have little, if any, steric effect on either of the potential metal coordination sites (pi or sigma bond)[5], sigma-bond cleavage in the rate determining step would experience a polar 3-substituent effect at least comparable in magnitude and direction to the analogous 1-substituent effect. This is clearly not the case ($k_2 > k_3 \approx k_1$) and would strongly suggest that sigma-bond cleavage is not occuring in the rate determining step. The absence of any rate change in comparing olefins 1 and 3 when contrasted to the substituent effects found in the solvolysis[6] of 1-aryl ($\rho^+ = -4.31$) and 2-aryl ($\rho = -1.75$) cyclopropyl tosylates would also seem to rule out step 3 of the pi-attack mechanism as a rate determining step.

Further analysis of the relative rates for olefins 1,2, and 4 gives a reasonable σ_p^+-rho correlation with rho = -0.50. This value is identical to that reported by Powell[7] for palladium (II) pi-complex formation in a series of para-substituted styrenes. In addition, comparison of the relative rates of pi-allyl complex formation for olefins 1, 2, and 4 with the relative rates of epoxidation[8] ($k_H = 1.00$, $k_{CH_3} = 2.29$, $k_{OCH_3} = 4.87$) and bromination[9] ($k_H = 1.00$, $k_{CH_3} = 9.10$, $k_{OCH_3} = 2395$) for a series of analogously substituted <u>trans</u>-stilbenes would seem to indicate that pi-allyl complex formation and epoxidation have similar rate-structure requirements. On the other hand, bromination proceeds through a highly unsymmetrical transition state and therefore has a much greater sensitivity to substituent changes.

TABLE I. Relative Rate Constants for the Reaction of $(PhCN)_2PdCl_2$ with Tri- and Tetrasubstituted Cyclopropenes in Benzene at 25°.

	R_1	R_2	R_3	R_4		k_{rel} [a]	
1,	Ph	Ph	Ph	H		3.46 ± 0.04	(2)
2,	*p*-Tolyl	Ph	Ph	H		4.88 ± 0.20	(2)
3,	Ph	Ph	*p*-Tolyl	H		3.43 ± 0.12	(4)
4,	*p*-Anisyl	Ph	Ph	H		8.88 ± 0.43	(3)[b]
5,	Ph	Ph	CH_3	CH_3		(1.00)	
6,	Ph	CH_3	CH_3	CH_3		3.21 ± 0.42	(4)[c]
7,	CH_3	CH_3	CH_3	CH_3		3.33 ± 0.26	(3)[d]

[a] Unless otherwise specified, all olefins were run competitively against olefin 5 (initial olefin concentrations 0.05-0.10 *M*, initial $(PhCN)_2PdCl_2$ concentration 0.05-0.10 *M*). Errors are standard deviation of independent runs with the indicated degrees of freedom. [b] This value represents an average obtained from competitive runs between olefins 4 and 5 (k_4/k_5 = 8.445) and 4 and 3 (k_4/k_3 = 2.717, $k_4/k_3 \times k_3/k_5$ = 9.305). [c] Run against olefin 1 (k_6/k_1 = 0.926, $k_6/k_1 \times k_1/k_5$ = 3.208). [d] Run against olefin 1 (k_7/k_1 = 0.961, $k_7/k_1 \times k_1/k_5$ = 3.329).

Analysis of the above would appear to be similar to that recently reported for the kinetics of hydroboration[10] of a series of para-substituted styrenes. In that case, initial pi-complex formation was proposed as a possible slow step of the reaction sequence, although the possibility that the subsequent step, addition of the elements of H_2B-H across the double bond, might occur with comparable velocity could not be eliminated. While the analogous possibility (Scheme I: $k_{step\ 1} = k_{step\ 2}$) exists in our case, partial resolution of the problem can be found in comparison of k_{rel} of pi-complex formation for olefins 5, 6, and tetramethylcyclopropene. While experimental determination of k_{rel} for tetramethylcyclopropene presents problems, a value can be approximated from k_{rel} for olefin 7. In the absence of a large 3-substituent polar effect, substitution of a 3-phenyl for a 3-methyl substituent could slow pi-allyl complex formation by a factor $\geq$ 2, assuming $k_{syn\ to\ methyl} > k_{syn\ to\ phenyl}$.[11] Based on k_{rel} for 7 and using the statistical correction factor, the k_{rel} expected for tetramethylcyclopropene would be 6.66. With this value the k_{rel} for pi-allyl complex formation in the series **5**, **6**, and tetramethylcyclopropene is in good agreement with the k_{rel} found for peracid oxidation of the identical series of cyclopropenes or an analogous series of acyclic olefins.[11] The results again strongly implicate symmetrical pi-complex formation as the rate determining step.

The increase in relative rates of pi-allyl complex formation correlates, for olefins **1**, **3**, and **4**, with decrease in ionization potential (IP) (HOMO), while the results for **5**, **6**, and **7** show that this is not a general rule (IP_{5} = 7.49 eV, IP_{6} = 7.86 eV, IP_{7} = 8.30 eV)[12]. Apparently, unfavorable steric effects override favorable electronic effects in controlling the rate of olefin-Pd(II) complex formation. This is consistent with results reported for palladium(II) pi-complex formation in a series of acyclic olefins.[5]

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