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A GENERAL SYNTHESIS OF π-ALLYL PALLADIUM CHLORIDE DIMERS FROM CYCLOALKENES AND ALKYLIDENECYCLOALKANES

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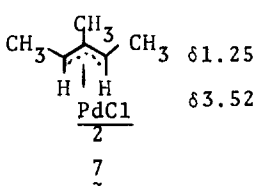
The formation of π-allyl palladium chloride dimers from olefins has been a capricious reaction.[2-6] Conversion of cycloalkenes and alkylidenecycloalkanes to their π-allyl palladium derivatives has been specially troublesome and, among them, the six-membered ring derivatives have been the most difficult.[3-5] The utility of our approach for allylic alkylation depends crucially on the ability to perform this reaction in high yield.[7] In this communication, we want to report a general procedure for this conversion.

Table 1 outlines the olefins employed. The active palladating solution is prepared by heating a solution of palladium chloride, sodium chloride, sodium acetate, and cupric chloride in acetic acid at 90-95°, cooling to 60°, and then introducing the olefin. In each case, the complex was completely characterized by spectral and analytical methods. The proton nmr allows unambiguous positional assignment as depicted (see Table 2). The assignment of the syn configuration for 4 arises by comparison of its nmr spectral parameters (see Table 2) to those of 7,[6c] 8,[8] and 9.[8]



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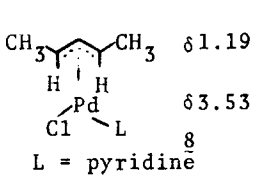
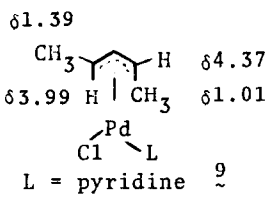


8

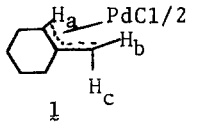
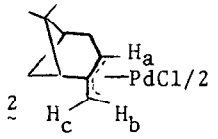
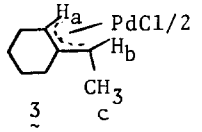
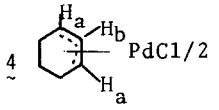
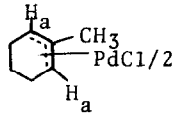
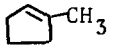
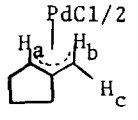
L = pyridine



9

L = pyridine

Table 1. Preparation of π-Allyl Palladium Complexes[a]

Entry	Olefin	Complex	% Yield	M.P.
1		 1	92	131-138° (dec)
2	β-pinene	 2	60	161-168° (dec)
3		 3	57	123-129° (dec)
4		 4	100	92-95° (dec)[b]
5		 5	86	88-90° (dec)[c]
6		 6	66	129-132° (dec)

a) All compounds had satisfactory spectral properties. All new compounds had satisfactory elemental analyses.
b) Lit.[3b] mp 90-95°. c) Lit.[3b] mp 87-89°.

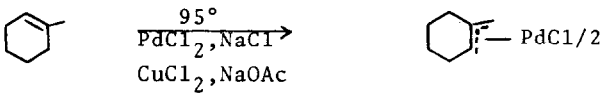
Table 2. Partial NMR Parameters

	Complex					
Proton	1	2	3	4	5	6
a	4.14 (s)[a]	3.69 (s)[a]	3.88(s)[a]	5.25(m)	4.84 (m)	4.20(s)[a]
b	2.60 (s)	2.97 (s)[a]	3.42(q,6Hz)	5.53t(6.5Hz)		3.09(s)
c	3.60 (s)	4.1(m)				3.97(s)
CH_3			1.14(d,6Hz)		2.08	

a) unresolved fine splitting

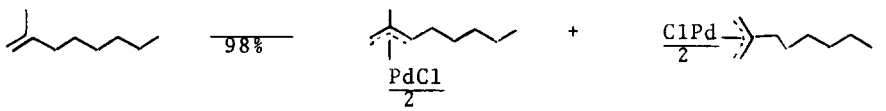
Most noteworthy is the regiospecificity of the reaction. Whereas 1-methylcyclohexane gives only the endocyclic isomer 5, 1-methylcyclopentene gives only the exocyclic isomer 6. Ethylidenecyclohexane (Table 1, entry 3) gives only the Markownikoff type product--the endocyclic isomer.

Temperature control is crucial for these cyclic cases. Forming the complex from 1-methylcyclohexane at 95° rather than 60° produces only a low yield



20 hr	15%
66 hr	5%

of 1 which decreases with time. None of the isomeric product 5 (which is the exclusive product at the lower temperature) is detectable. Both products appear to be the result of kinetic control since attempted isomerization of 5 to 1 failed. The lability of the complexes to the reaction conditions appears restricted to the cyclic cases since 2-methyl-1-octene was converted quantitatively to its π-allyl palladium complexes even after 3 days at 95°.



3 : 4

A typical procedure follows. Sodium acetate (24.0 g, 0.293 mol), sodium chloride (16.8 g, 0.288 mol), cupric chloride (18.4 g, 0.137 mol), and palladium chloride (4.0 g, 0.0226 mol) are stirred 2 hr at 95° in 250 ml of glacial acetic acid and 5 ml of acetic anhydride. The solution is cooled to 60° and 5.0 g (0.052 mol) of methylenecyclohexane in 15 ml of acetic acid is

added in one portion. The solution is kept at 60° for 24 hr, cooled to room temperature, and filtered. After an aqueous work-up and extraction with benzene, the crude yellow oil is purified by chromatography on silica gel with chloroform as eluting solvent. Addition of hexane to the purified yellow oil induces crystallization to give 4.94 g (92%) of pure yellow crystals.

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9. 1-Methylcyclohexene has been reported to give 5 at one time, but 1 at a later date. See ref. 2 and 3b.