

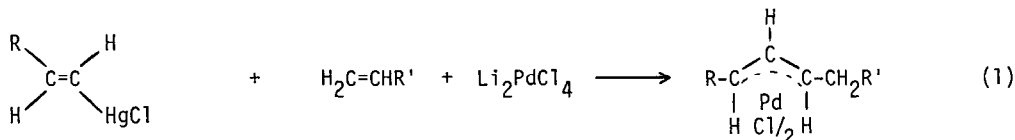
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SYNTHESIS OF  $\pi$ -ALLYL- AND ALKYL-PALLADIUM COMPOUNDS  
VIA VINYL-PALLADIATION OF CYCLIC OLEFINS

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Summary: Vinylmercurials react with  $\text{Li}_2\text{PdCl}_4$  and monocyclic olefins to produce  $\pi$ -allylpalladium compounds or 1,4-dienes if triethylamine is added. Bicyclic olefins afford stable alkylpalladium compounds useful in the synthesis of functionally substituted bicyclic alkanes.

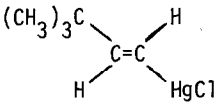

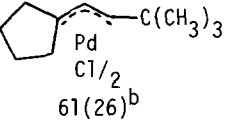
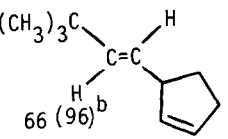

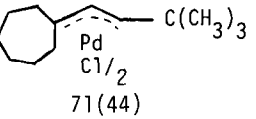
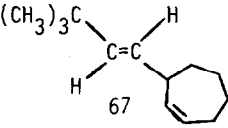

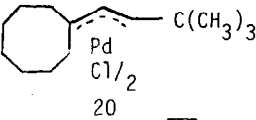
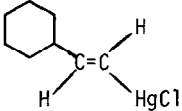

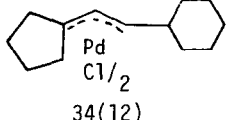
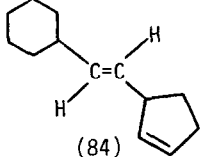
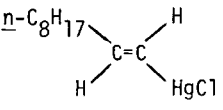
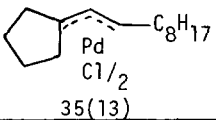
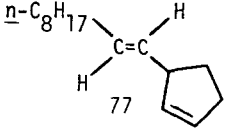
Organopalladium compounds, especially  $\pi$ -allylpalladium compounds, have recently found widespread application in organic synthesis.<sup>1</sup> Not long ago we reported a useful new regio-specific route to  $\pi$ -allylpalladium compounds by reaction of vinylmercurials,  $\text{Li}_2\text{PdCl}_4$  and acyclic olefins (eq. 1).<sup>2</sup> Our original mechanism involved vinylpalladium formation; cis



addition to the olefin; cis, beta elimination of palladium and the allylic hydrogen to form a  $\pi$  complex; and finally collapse of the  $\pi$ -complex to a sigma allylpalladium species which then rearranges to the more stable  $\pi$ -allylpalladium product.<sup>2</sup> Since the initial organopalladium adduct derived from simple monocyclic olefins cannot undergo an analogous cis, beta elimination, we were quite surprised to find that these olefins also afford reasonable yields of  $\pi$ -allylpalladium compounds in this reaction as shown in Table 1.

To account for the formation of  $\pi$ -allylpalladium compounds in this reaction, we need to modify our original mechanism. Initial vinylpalladium formation and subsequent cis addition to the cyclic olefin presumably occurs as suggested earlier. Judging from the yields, it appears that the ease of vinylpalladium addition to cyclic olefins decreases in the following order: cycloheptene  $\approx$  cyclopentene > cyclooctene > cyclohexene. In order for the required palladium rearrangement to occur, either a trans palladium-allylic hydrogen elimination is required (which we consider unlikely and for which there seems to be no literature precedent) or cis elimination of a remote beta hydrogen must occur, followed by palladium hydride readdition to the opposite side of the ring. Subsequent cis palladium hydride elimination and readdition then generates the  $\pi$ -allylpalladium compounds observed. We prefer this latter explanation (Scheme 1).

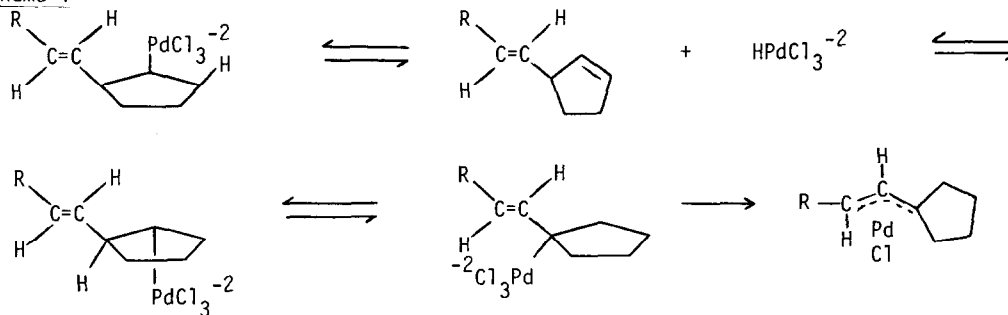
Table 1. Synthesis of  $\pi$ -Allylpalladium Compounds and 1,4-Dienes

Vinylmercuric Chloride	Olefin (5-10 equiv)	$\pi$ -Allylpalladium Compound <sup>a</sup>	1,4-Diene <sup>a</sup>
		 61(26) <sup>b</sup>	 66 (96) <sup>b</sup>
		 71(44)	 67
		 20	
		 34(12)	 (84)
		 35(13)	 77

<sup>a</sup> Correct elemental analyses and spectral data were obtained for all new compounds.

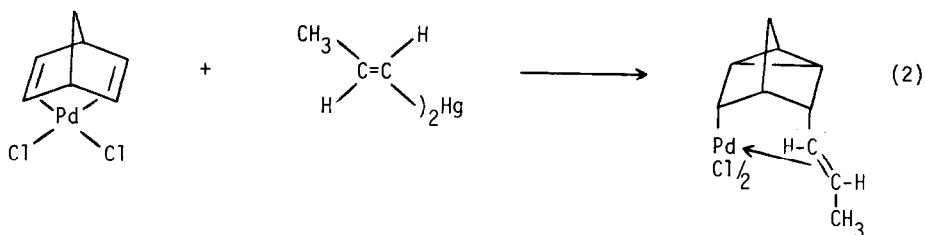
<sup>b</sup> Isolated yield after column chromatography (recrystallized yield of  $\pi$ -allylpalladium compound or gas chromatographic yield of 1,4-diene). Yields based on vinylmercurial or palladium chloride used in equivalent amounts.

Scheme 1

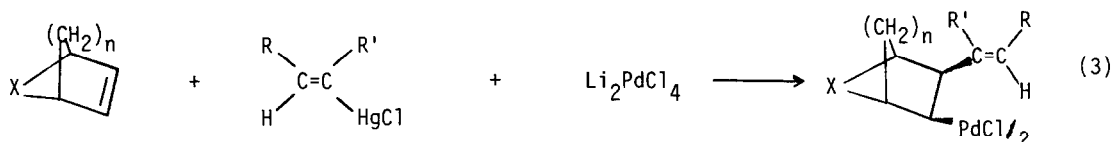


Consistent with this mechanism is the observation that 1,4-dienes often accompany these reactions. In fact, the addition of triethylamine eliminates  $\pi$ -allylpalladium formation and produces 1,4-dienes as the major product (Table 1). This route to 1,4-dienes via vinylmercurials provides a useful alternative to our earlier approach using  $Li_2PdCl_4$  and allylic halides.<sup>3</sup>

While the addition of  $\pi$ -allyl<sup>4</sup> and arylpalladium<sup>5</sup> compounds to bicyclic olefins, has received considerable attention, there appears to be only one example of the vinylpalladation of a bicyclic olefin (eq. 2).<sup>6</sup> We have observed that the reaction of vinylmercuric chlorides,



$\text{Li}_2\text{PdCl}_4$  and bicyclic olefins affords stable, cis-exo, alkylpalladium adducts (eq. 3) (Table 2). These compounds are bright yellow, air stable solids with characteristic



decomposition temperatures. Their unusual stability is no doubt a result of two factors. First of all, they do not possess a beta hydrogen cis to palladium to eliminate and, secondly,  $\pi$ -coordination by the neighboring double bond is available to stabilize the palladium moiety. As indicated in Table 2, less strained bicyclic olefins such as bicyclo[2.2.2]oct-2-ene and bicyclo[3.2.1]oct-6-en-3-one also give adducts, but the yields are lower.

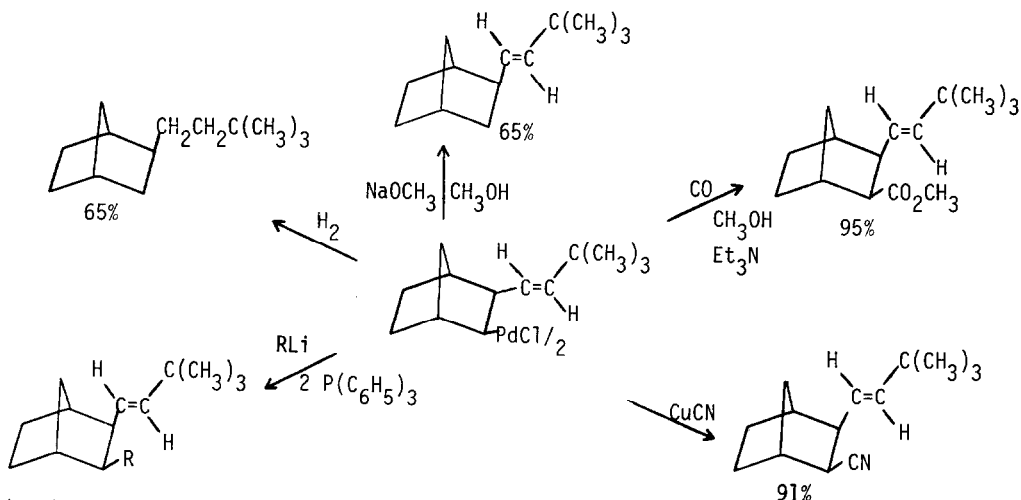
Table 2. Vinylpalladation of Bicyclic Olefins

X	n	R	R'	% Yield Organopalladium Product <sup>a</sup>
-CH <sub>2</sub> CH <sub>2</sub> -	1	H	H	63(46)
		Cl	H	77(40)
		(CH <sub>3</sub> ) <sub>3</sub> C	H	89(45)
		(CH <sub>3</sub> ) <sub>3</sub> C	CH <sub>3</sub>	88(58)
		(CH <sub>3</sub> ) <sub>3</sub> C	H	45(15) <sup>b</sup>
EtO <sub>2</sub> CN-     O -CH <sub>2</sub> CCH <sub>2</sub> -    O	2	(CH <sub>3</sub> ) <sub>3</sub> C	H	16(10) <sup>b</sup>
			H	15(8)

<sup>a</sup> Crude yield (recrystallized yield). Correct elemental analyses and spectral data were obtained for all new compounds.

<sup>b</sup> 1.1 Equivalents of the bicyclic olefin was employed; other yields were obtained using 10 equivalents of bicyclic olefin.

With the ready availability of these organopalladium compounds, we have briefly examined their chemistry. Scheme 2 indicates the synthetic versatility of these intermediates. With Scheme 2



R = CH<sub>3</sub> (83%); CH=CH<sub>2</sub> (34%);  
C≡CH (54%); C<sub>6</sub>H<sub>5</sub> (24%).

the strict retention of exo stereochemistry observed in all palladium substitution reactions, these reactions nicely complement the Diels-Alder approach to these bicyclic systems. We have also found these reactions valuable for the synthesis of prostaglandin endoperoxide analogs, work we will report on shortly.

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