

Ketovinylation of Alkyl Palladium Complexes

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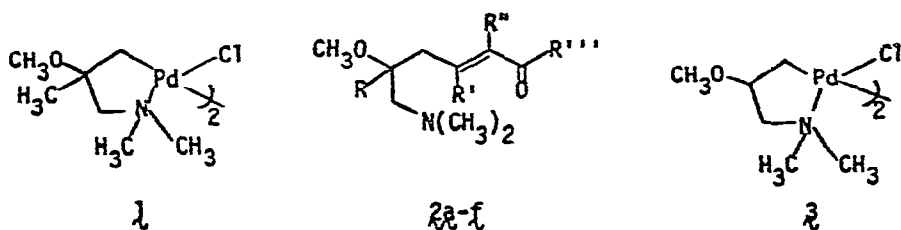
SUMMARY: Stable chelated alkyl palladium II complexes di- μ -chloro-bis(2-methoxy-2-methyl-3-N,N-dimethylaminopropyl)dipalladium (1) and di- μ -chloro-bis(2-methoxy-3-N,N-dimethylaminopropyl)dipalladium (3) react with simple vinyl ketones to produce, in high yield, adducts derived by olefin insertion into the carbon-palladium σ bond.

Stable alkyl palladium complexes containing chelating amino functionality have been known for some time.³ Despite their ready availability and possible potential as intermediates in organic synthesis, only their reaction with carbon monoxide has been studied.⁴ We wish to report the initial results of our studies designed to further explore the chemistry of such complexes.

The insertion of olefins, particularly vinyl ketones and esters, into aryl palladium complexes, generated *in situ* from palladium chloride and aryl mercurials, to give styrene derivatives, has been studied in detail.⁵ Aryl palladium complexes containing chelating *ortho* benzylic amines add to vinyl ketones to give high yields of β -phenyl enones.⁶ It has recently been reported that vinyl mercurials undergo a similar reaction with vinyl ketones in the presence of lithium tetrachloropalladate to provide π -allylic complexes.⁷ Few examples of olefin insertion into alkyl palladium complexes have been observed,⁸ presumably due to the lability of these complexes with respect to β -elimination.

We have found that alkyl palladium complexes stabilized by chelating amino functionality react with vinyl ketones to give adducts derived by olefin insertion into the palladium-carbon σ bond. Thus, treatment of di- μ -chloro-bis(2-methoxy-2-methyl-3-N,N-di-methylaminopropyl)dipalladium (1)³ with methyl vinyl ketone (8 equiv)

in refluxing benzene containing excess triethylamine⁶ for 5 hr leads to the product of enone $2a-f$ ($R'=R''=H$, $R'R'''=CH_3$); bp $95^\circ/1mm$; ir ($CHCl_3$) 6.00μ ; nmr ($CDCl_3$) 1.13 (s, 3) 2.24 (s, 3), 2.30 (s, 8), 2.50 (d, 2, $J=7Hz$), 3.21 (s, 3) 6.12 (d, 1, $J=17H$ 6.88 (m, 1); in 86% isolated yield. That this reaction is applicable to other vinyl ketones as well as the analogous di- μ -chloro-bis(2-methoxy-3-N,N-dimethylamino-



propyl)dipalladium (3)³ is illustrated by the results listed in the Table. Isolation and purification of enones $2a-f$ is hampered by their sensitivity to acid and their thermal instability,⁹ factors which at least partially account for lowered yields in some cases. Furthermore, low molecular weights and water solubility of the β -alkoxy amino ligands serve to prevent analysis of the fate of these fragment other than enone insertion.

Similarity to the previously described⁶ insertion of enones by stable σ -aryl palladium complexes containing chelating amino functionality may be observed. However, although enone addition to σ -aryl complexes is accelerated in the presence of acetic acid, no recognizable enone addition products from σ -alkyl complexes can be isolated under these conditions. Indeed, enone $2a$ is itself converted to a number of products upon dissolution in acetic acid; neither 1 nor 3 is stable to these conditions.

Attempted addition of 1 or 3 to enones containing either α - or β -substituent has proved fruitless; neither 3-pentene-2-one nor 3-phenyl-3-butene-2-one lead to adducts upon treatment with 1 or 3 in refluxing toluene or benzene. Cyclopentene and cyclohexenone also fail to give addition products. Other electron deficient olefins are less satisfactory than vinyl ketones: ethyl acrylate reacts with 1 or 3 to produce an adduct in $\sim 15\%$ yield; use of acrylonitrile does not lead to an isolable adduct. Neither 1 nor 3 is inert to these conditions in the absence

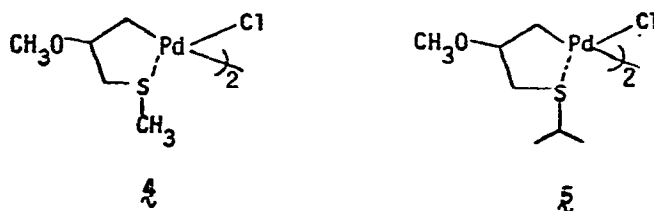
Table

Palladium Complex	Enone	R	Adduct ^a			% Yield ^b
			R'	R''	R'''	
1	Methyl vinyl ketone	2a;CH ₃	H	H	CH ₃	86
1	Ethyl vinyl ketone	2b;CH ₃	H	H	C ₂ H ₅	60
1	n-Hexyl vinyl ketone	2c;CH ₃	H	H	C ₆ H ₁₃	25 ^c
1	3-Pentene-2-one	2d;CH ₃	CH ₃	H	CH ₃	0
2	Methyl vinyl ketone	2e;H	H	H	CH ₃	70
2	Ethyl vinyl ketone	2f;H	H	H	C ₂ H ₅	50

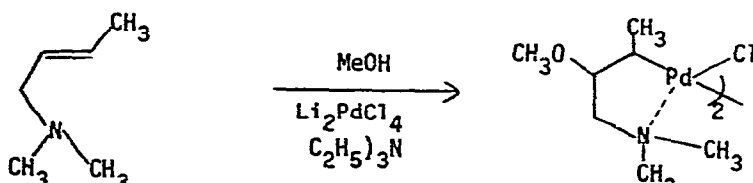
(a) Structures consistent with ir, nmr, and mass spectra. All new compounds give correct analytical data. Only trans-adducts have been isolated, cis adducts have not been detected. (b) Based on palladium complex. (c) Toluene, triethylamine, reflux 3 hr; 0.9 mol equiv enone.

of enone: Decomposition of 1 requires 3 hr in refluxing toluene (very slow decomposition in refluxing benzene); decomposition of 2 requires ca. 15 hr in refluxing benzene, 45 min in refluxing toluene.

Surprisingly, neither of the complexes 4 or 5, derived from allylic sulfides,¹⁰ adds to enones. Either 4 or 5 gives rise to a plethora of unidentified products (no detectable enone addition product) upon treatment with methyl vinyl ketone in refluxing benzene or toluene. Although both 4 and 5 are moderately stable in acetic acid solution, neither produces an adduct with methyl vinyl ketone within 24 hr



In an effort to extend the ketovinylation reaction to complexes bearing carbon substituents at C-3, we decided to prepare complex 6. Surprisingly, the procedure



of Cope, et. al.³ (which gave rise to complexes 1, 2, 4, and 5 in excellent yield when applied to 1-dimethylamino-trans-2-butene, gave 6 in only ca. 10% yield, also with many other unidentified products. We have not been able to study ketovinylation of 6 due to this difficulty.

Thus, it appears that further study of ketovinylation of σ -alkyl palladium complexes must await the development of new methodology for the preparation of the complexes. We are currently exploring the introduction of nucleophiles other than methanol into complexes similar to 1 and 2. Applications of these processes to the synthesis of natural products will be the subject of future communication.

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References and Notes

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2. David Ross Predoctoral Fellow, 1975-1977.
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4. D. Medema, R. van Helden, and C. F. Köhll, Inorg. Chim. Acta, **3**, 255 (1969).
5. See, for example, I. Moritani and Y. Fujiwara, Synthesis, 524 (1973).
6. R. A. Holton, Tetrahedron Lett., 355 (1977).
7. R. C. Larock and M. A. Mitchell, J. Amer. Chem. Soc., **98**, 6718 (1976).
8. Heck has reported the reaction of methyl mercuric chloride, tetramethyltin, and tetramethyl lead with styrene and methyl acrylate in the presence of lith tetrachloropalladate to give low yields of insertion products: R. F. Heck, ibid., **90**, 5518 (1968).
9. For example, attempts to prepare the hydrochloride, methiodide, or bisulfite addition compound of enone 2a all resulted in immediate decomposition. Best purification results were obtained via bulb-to-bulb vacuum distillation.
10. Prepared by the method of Y. Takahashi, A. Tokuda, S. Sakai, and Y. Ishii, J. Organometal. Chem., **35**, 415 (1972).