Preparation of π-Allylic Palladium Complexes from Tin(II) Chloride, Allylic Halides, and Palladium Salts

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π-ALLYLIC palladium complexes have been prepared by reaction of olefins,[1] unsaturated alcohols,[2] or allylic halides[3] with suitable palladium salts and solvents. Dent, Long, and Wilkinson[4] reported an interesting preparative method in which carbon monoxide was introduced into a methanolic solution of allylic halides and sodium chloropalladite.

In the course of our study on palladium–tin complexes, tin(II) chloride was found to be an effective reagent for the preparation of π-allylic palladium complexes from allylic halides and palladium salts in quantitative yield.

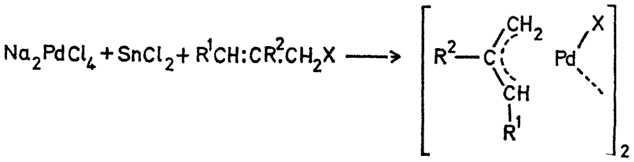
Tin(II) chloride (anhydrous, 2·8 mmoles) was added to the solution of sodium chloropalladite, previously prepared from palladium chloride (2·8 mmoles) and sodium chloride (5·6 mmoles) in methanol (25 ml.). The brownish solution immediately became dark red, and then allyl chloride (0·8 ml.) was added with stirring during ½ hr. The reaction took place smoothly and the solution became orange-yellow, a slight precipitate being formed. The reaction mixture was poured into water and then extracted with chloroform. After evaporation of the solvent under

TABLE

	Product	Allylic halide	m.p. (°c)[a]	Yield (%)
(I)	$R^1 = R^2 = H$ $X = Cl$	Allyl chloride	130·6 (decomp.) (130—131)	90
(II)	$R^1 = R^2 = H$ $X = Br$	Allyl bromide	145 (decomp.) (>135)	98
(III)	$R^1 = H$, $R^2 = Me$ $X = Cl$	Methallyl chloride	167—168 (166—168)	77
(IV)	$R^1 = Me$, $R^2 = H$ $X = Cl$	Crotyl chloride	136—137 (136—137)	93
(V)	$R^1 = Ph$, $R^2 = H$ $X = Br$	Cinnamyl bromide	195 (decomp.) (—)	81

[a] Values in parentheses show m.p. reported in the literature.

reduced pressure, a yellow complex (I) was obtained in 90% yield. The structure was consistent with the i.r. and n.m.r. spectra and elemental analysis. Other π-allylic complexes (II)—(V) were prepared similarly. Cramer and his co-workers[5] suggested the five-co-ordinate complex, $[Pt(SnCl_3)_5]$, as an active intermediate of the catalytic system Pt^{II}–Sn^{II} for olefin hydrogenation.



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[1] R. Hüttel and H. Christ, *Chem. Ber.*, 1963, **96**, 3101.
[2] J. Smidt and W. Hafner, *Angew. Chem.*, 1969, **71**, 284.
[3] R. Hüttel and J. Kratzer, *Angew. Chem.*, 1959, **71**, 456.
[4] W. T. Dent, R. Long, and A. J. Wilkinson, *J. Chem. Soc.*, 1964, 1585.
[5] R. D. Cramer, E. L. Jenner, R. V. Lindsey, jun., and U. G. Stolberg, *J. Amer. Chem. Soc.*, 1963, **85**, 1691.