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π-ALLYLIC COMPLEXES FROM ALLENE

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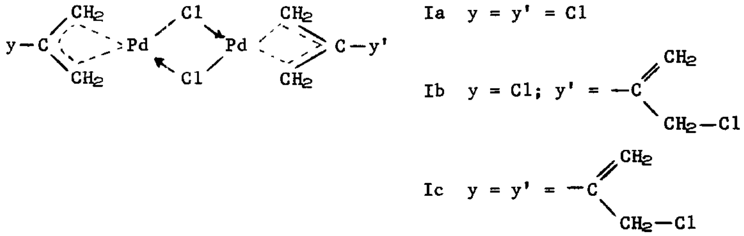
The preparation of π-allylic palladium complex compounds has been reported using allyl alcohols (1a,b), allyl halides (1c,d,e), and conjugated dienes (1f). We now wish to report that novel π-allylic palladium complexes may be made directly from allene. When allene is bubbled into a benzene solution of dichloro bis-benzonitrile palladium (II) (2) a rapid reaction occurs and di-μ-chloro-di-π-(β-chloroallyl) dipalladium (II) /Ia/ (3) is isolated (80% yield).



Ia y = y' = Cl

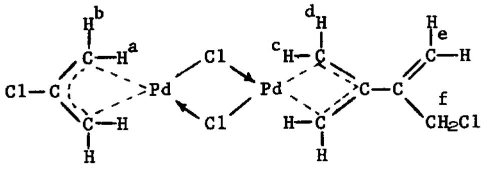
Ib y = Cl; y' = $-C(=CH_2)CH_2-Cl$

Ic y = y' = $-C(=CH_2)CH_2-Cl$

When an inverse method of addition is used (i.e. dichloro bisbenzonitrile palladium (II) introduced as a solid to allene in benzene), the major product (94.6% yield) is di-μ-chloro-π-(β-chloroallyl)-π'-(β-(3-chloro-1-propen-2-yl)-allyl) dipalladium (II) /Ib/. Some Ia is also formed. When allene is bubbled into a benzonitrile solution of dichloro bisbenzonitrile palladium (II), the product in 78.5% yield is di-μ-chloro-di-π-(β-(3-chloro-1-propen-2-yl)-allyl)-dipalladium (II) /Ic/. Satisfactory elemental analyses (C, H, Cl, residue) have been obtained for all compounds reported. The NMR data supporting the assigned structures are presented in Table I.

TABLE I

Proton NMR Data



Compound	Solvent	H_a	H_b	H_c	H_d	H_e	H_f
Ia	A	-4.57		--	--	--	--
	B	-3.27(1)	-4.22(1)	--	--	--	--
Ib	A	-4.56(2)		-3.78(2)		-6.03 -6.21(1)	-4.85(1)
	C	-2.30(2)	-3.79(v)	-2.41 -2.46(2)	-3.79(v)	-4.87 -5.04(2)	-3.79(v)
	B	-3.18(2)	-4.12(v)	-2.75(2)	-4.10 or -4.15(v)	-5.30 -5.48(2)	-4.15 or -4.10 (v)
Ic	A	--	--	-4.07(2)		-6.04 -6.21(1)	-4.86(1)
$[C_3H_5PdCl]_2$				β-Hydrogen			
	A	-4.37(4)		-6.30(1) (pentet)			
	C	-2.41(2)(w)	-3.57(2)(x)	-4.62(1) (heptet)			
	B	-2.96(2)(y)	-4.01(2)(z)	-5.37(1) (heptet)			

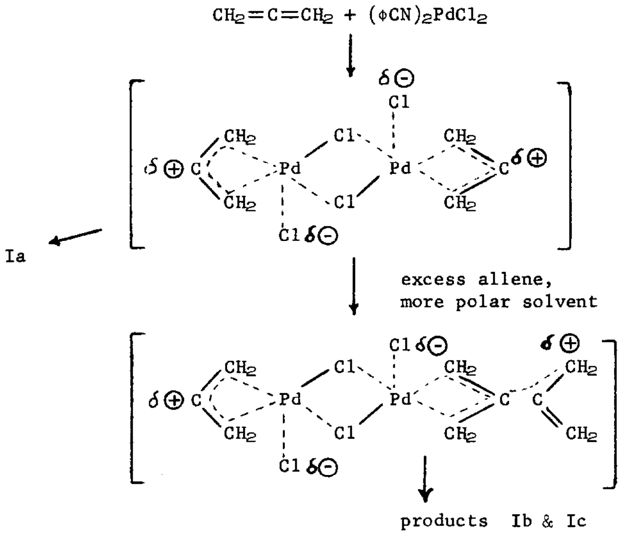
Notes to table:

NMR data is presented as ppm relative to a tetramethyl silane standard. Relative peak intensities in parentheses. Varian Associates A-60 instrument. Solvents: A, dimethyl sulfoxide; B, benzonitrile; C, benzene.

(v) peaks unresolved; total relative intensity, 6.
(w) doublet, J = 12 cps
(x) doublet, J = 7.5 cps
(y) doublet, J = 12 cps
(z) doublet, J = 7 cps

The bonding change ($\pi \rightarrow \sigma$) observed in dimethyl sulfoxide solution has been previously reported and discussed.(3)

It is possible that the reaction proceeds as outlined below, with the polarity of the solvent and the relative amounts of allene and dichloro bisbenzonitrile palladium (II) acting as determining factors in the product formation.



Further details of this work, as well as data on other allene reactions, will be published later.

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