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π-ALLYLIC COMPLEXES FROM ALLENE[1]

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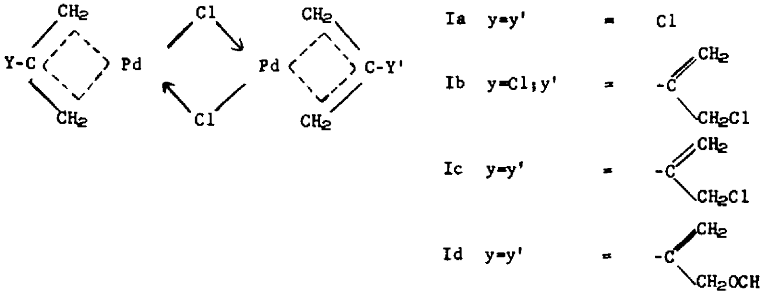
Abstract—A series of π-allylic palladium complexes has been prepared directly from allene. The polarity of the solvents used in the preparations has been found to have a significant effect upon the structure and composition of these complexes. NMR data in support of the proposed structure are tabulated.

THE preparation of π-allylic palladium complex compounds has been reported using allyl alcohols,[2a,b] allyl halides[2c,d,e] and conjugated dienes.[2f] Structural studies have led to the conclusion that these π-allylic complexes occupy two ligand positions of the palladium and that, in the solid state at least, the plane described by the three carbon allyl moiety is perpendicular to that of the palladium–chlorine system.[3a,b] NMR studies have confirmed the delocalized π-bonded structure in nonpolar solvents[4a,b,c] but in a polar solvent, dimethyl sulfoxide, transformation to a σ-bonded structure has been reported.[4d]

We now wish to report that novel π-allylic complexes may be prepared directly from allene. When allene is bubbled into a solution of dichloro bis-benzonitrile palladium (II),[5] a rapid reaction occurs and Ia, di-μ-chloro-di-π-(β-chloro-allyl) dipalladium (II)[4c] is isolated. When an inverse method of addition is used (i.e. dichloro bis-benzonitrile palladium (II) introduced as a solid to allene in benzene), the major product is Ib, di-μ-chloro-π-(β-chloroallyl)-π′-(β-(3-chloro-1-propen-2-yl)-allyl)-dipalladium (II). When allene is bubbled into a benzonitrile solution of dichloro bis-benzonitrile palladium (II) the product is Ic, di-μ-chloro-di-π-(β-(3-chloro-1-propen-2-yl)-allyl)-dipalladium (II).



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[1] Part of the material reported herein was the subject of a preliminary communication. *Tetrahedron Letters* 301 (1964).

[2a] J. Smidt and W. Hafner, *Angew. Chem.* **71**, 284 (1959); [b] I. I. Moiseev, E. A. Fedorovskaya and Ya K. Syrkin, *Russ. J. Inorg. Chem.* **4**, 1218 (1959); [c] R. Hüttel and J. Kratzer. *Angew. Chem.* **71**, 456 (1959); [d] E. O. Fischer and G. Burger, *Z. Naturforschung* **16b**, 702 (1961); [e] R. Hüttel, J. Kratzer and M. Bechter, *Chem. Ber.* **94**, 766 (1961); [f] B. L. Shaw, *Chem. Ind.* 1190 (1962).

[3a] J. M. Rowe, *Proceeding Chem. Soc.* **1962,** 66; [b] V. F. Levdik and M. A. Porai-Koshits, *Zh. Strukturnoi Khim* **3**, 472 (1962).

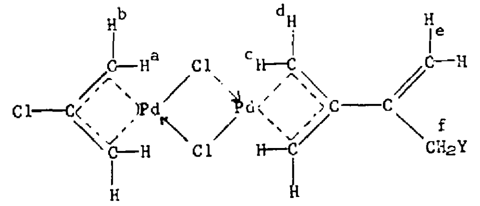
[4a] H. C. Dehm and J. C. W. Chien, *J. Amer. Chem. Soc.* **82**, 4429 (1960); [b] B. L. Shaw and N. Sheppard, *Chem. & Ind.* 517 (1961); [c] S. D. Robinson and B. L. Shaw, *J. Chem. Soc.* **4806** (1963); [d] J. C. W. Chien and H. C. Dehm, *Chem. & Ind.* **745** (1961).

[5] M. S. Kharasch, R. C. Seyler and F. R. Mayo, *J. Amer. Chem. Soc.* **60**, 882 (1938).

When allene is bubbled into a solution of dichloro bis-benzonitrile palladium (II) in methanol, two products are isolated, Ic and Id, di-μ-chloro-di-π-(β-(3-methoxy-1-propen-2-yl)-allyl) dipalladium (II) in approximately equal amounts. This is in contrast to the recently reported work of Lupin and Shaw[6] in which the chloro compound (Ic) was the only product isolated from the reaction of allene with sodium chloropalladite in methanol.

NMR spectral data which supports the structural assignments are given in Table 1 below. Because of the low solubility of these complexes, in some cases it was necessary to use hexadeuterodimethyl sulfoxide as a solvent. This solvent causes a change in bonding ($\pi \rightarrow \sigma$)[4c] but the structural integrity of the carbon skeleton is maintained. Data on the unsubstituted di-μ-chloro-di-π-allyl dipalladium (II) is included for comparison. Lupin and Shaw[6] have recently reported NMR data on iodobridged- and acetylacetonate-complexes containing the Ic carbon skeleton and their assigments agree with our previously postulated structure.[1]

TABLE 1. Proton NMR Data



Y : Cl,OCH$_3$

Compound	Solvent	H_a	H_b	H_c	H_d	H_e	H_f	
Ia	Dimethyl sulfoxide-d_6	−4·13		—	—	—	—	
	Benzonitrile	−3·27(1)	−4·22(1)	—	—	—	—	
Ib	Dimethyl sulfoxide-d_6	−4·13(4)		−3·54 (4) (z)	−4·11	−5·59(2) −5·76	−4·43(2)	
	Benzonitrile	−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)	
	Benzene	−2·30(2)	−3·79(v)	−2·41 −2·46(2)	−3·79(v)	−4·87 −5·04(2)	−3·79(v)	
Ic	Dimethyl sulfoxide-d_6	—	—	−3·42 (4) (z)	−4·29	−5·58(2) −5·77	−4·42(2)	
Id	$CDCl_3$	—	—	−2·83(2)	−4·10 or −4·15(w)	−5·35 −5·55(2)	−4·10 or −4·15(w)	CH_3O −3·41 (3)
$(C_3H_5PdCl)_2$	Dimethyl sulfoxide-d_6	−3·86(4)		—	—	—	—	β-hydrogen −5·88(1) pentet
	Benzonitrile	−2·96(2) (x)	−4·01(2) (y)	—	—	—	—	−5·37(1) heptet
	Benzene	−2·41(2) (x)	−3·57(2) (y)	—	—	—	—	−4·62(1) heptet
	$CDCl_3$	−2·88(2) (x)	−3·88(2) (y)	—	—	—	—	−5·18(1) heptet

NMR data is presented as ppm relative to a tetramethyl silane standard.
Relative peak intensities in parentheses.
v — peaks incompletely resolved; total relative intensity, 6.
w — peaks incompletely resolved; total relative intensity, 4.
x — Doublet, J = 12 c/s.
y — Doublet, J = 7 c/s.
z — Broad, saddle shaped peaks.

The reaction of dichloro-bis-benzonitrile palladium (II) with tetramethyl allene in benzene solution afforded II, di-μ-chloro-di-π-(β-chloro-α,α,α′,α′-tetramethyl allyl)-dipalladium (II) in good yield. Apparently steric factors have little importance in this reaction.

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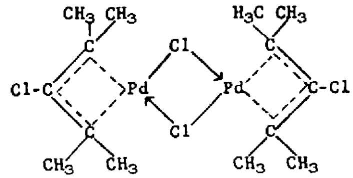
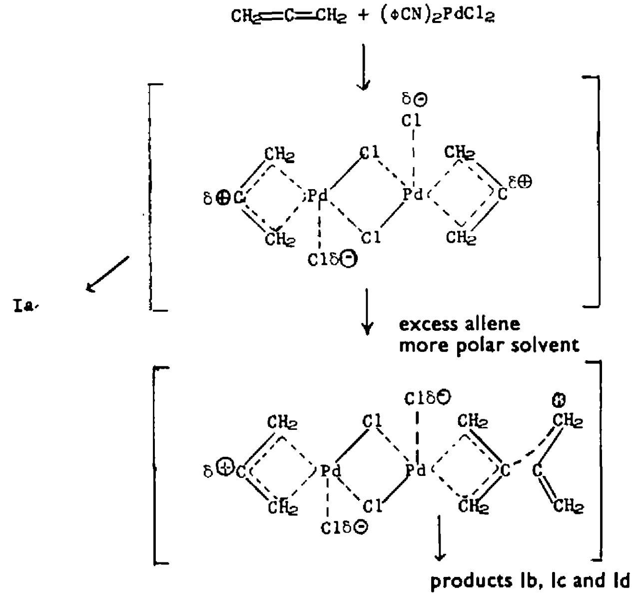
[6] M. S. Lupin and B. L. Shaw, *Tetrahedron Letters* 883 (1964).



It is possible that the reaction proceeds by one of the routes discussed below with the polarity of the solvent and the relative amounts of allene and dichloro bis-benzonitrile palladium (II) acting as determining factors in the product formation.



The allene insertion mechanism recently postulated by Heck[7] for this reaction also offers satisfactory explanation for the product (Ia) obtained in benzene, but is less satisfactory in its unmodified form in explaining the formation of Id which is obtained along with Ic in methanol solution, since solvolysis of the chloro compound, Ic, in methanol at 25° for 20 hr afford only 20% Id with 66% Ic recovered unchanged, while in the reaction of dichloro bis-benzonitrile palladium (II) with allene in methanol at 25°, 42% Ic and 46% Id are isolated after only 5 min reaction time. However, an insertion reaction mechanism for this reaction is possible if, prior to insertion, a methoxy palladium chloride or a methanol solvated palladium chloride is formed. The Heck mechanism could then be written as below with insertion across the Pd—O rather than the Pd—Cl bond.

Apparently the insertion reaction does not occur on the central carbon atom in the methoxy system, since no 2-methoxy-π-allyl palladium derivatives are observed. Since the chloro compound Ic is also observed, the chloride insertion mechanism of Heck is also occurring.

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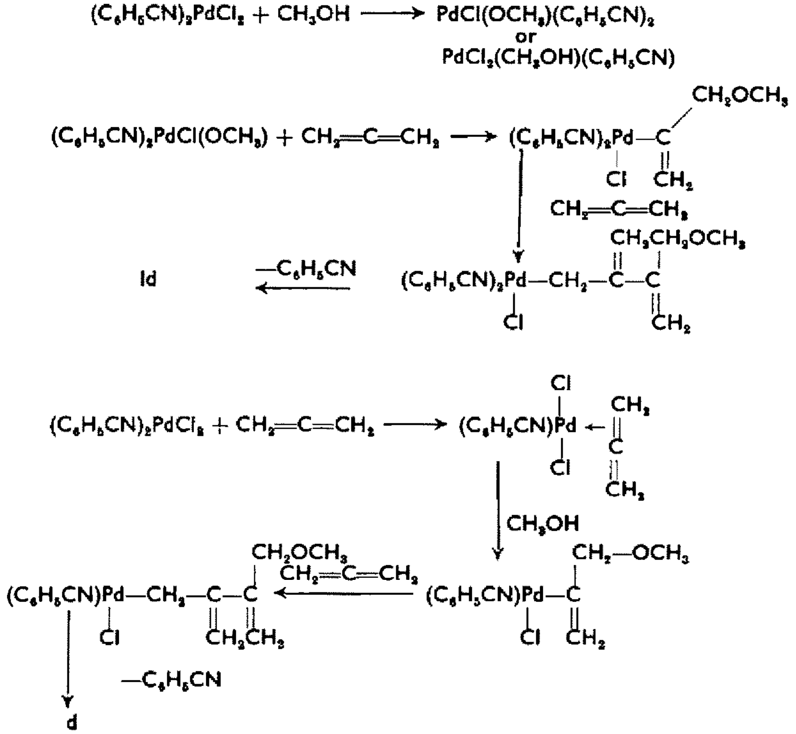
[7] R. F. Heck, *Summer Symposium on the Mechanism of Inorganic Reactions.* American Chemical Society, Division of Inorganic Chemistry, Preprint 180 (1964).

Another mechanistic possibility is an external attack of methanol preferentially on the α-carbon of the allene π-complex with dichloro bis-benzonitrile palladium (II) followed by an insertion-type reaction.



Since Lupin and Shaw[6] report an "excellent yield" of the chloro complex Ic and find no methoxy complex Id when sodium chloropalladite is reacted with allene in methanol, it is probable that the benzonitrile in the complex plays some part in promoting methanol incorporation into the allene system.

EXPERIMENTAL

Allene was obtained from the Matheson Company and used without further purification. Tetramethyl allene was obtained from Columbia Organic Chemicals Company and $PdCl_2$ from Matheson, Coleman and Bell. Dichloro bisbenzonitrile palladium(II) was prepared by the method of Kharasch, Seyler and Mayo.[5]

All mps are uncorrected. Microanalyses were by J. C. Edwards and associates. NMR spectra were taken on a Varian Associates Model A-60 instrument and data are reported in ppm (δ) relative to an internal tetramethyl silane standard.

Di-μ-chloro-di-π-(β-chloroallyl)-dipalladium(II), Ia. Allene was bubbled into a solution of 1·00 g (2·61 mmole) dichloro bisbenzonitrile palladium(II) in 100 ml benzene for 5 min at 25°. During this time the solution changed in color from deep red-brown to pale yellow. The benzene solution was then evaporated under vacuum to small volume and 100 ml low boiling pet ether added. The resulting solid was filtered, washed with pet ether and air-dried yielding 419 mg (81·4%) of Ia dec. pt. 180–185°. Recrystallization from benzene–heptane afforded pure Ia dec. pt. 182–185°. [Found: C, 16·4; H, 2·1; Cl, 32·2; Residue 56·7. $C_6H_8Cl_4Pd_2$ requires: C, 16·6; H, 1·9; Cl, 32·6%; Residue (as PdO) 56·3.] NMR spectral data are reported in Table 1.

Di-μ-chloro-π-(β-chloroallyl)-π′-(β-(3-chloro-1-propen-2-yl)-allyl) dipalladium (II), Ib. Dichloro bis-benzonitrile palladium(II) (3·246 g, 8·47 mmole) was added in portions as a solid to 125 ml benzene through which allene was bubbling at 25°. The Pd salt dissolved rapidly to give a yellow solution. This solution was evaporated to small volume and 100 ml low boiling pet ether added. The resulting precipitate was filtered, washed with pet ether and air-dried yielding 1·893 g (94·7%) of Ib m.p. 150–152°. Recrystallization from benzene afforded pure Ib, m.p. 153–155°. (Found: C, 23·3; H, 3·1; Cl, 29·6; Residue 52·2. $C_9H_{12}Cl_4Pd_2$ requires: C, 22·8; H, 2·6; Cl, 29·9%; Residue as PdO, 51·6). NMR spectral data are reported in Table 1.

Di-μ-chloro-di-π-(β-(3-chloro-1-propen-2-yl)-allyl)-dipalladium(II), Ic. Allene was bubbled into a solution of 541 mg (2·54 mmoles) $PdCl_2$ in 25 ml benzonitrile at 25°. During the course of the reaction, the solution changed in colour from dark red-brown to yellow brown. Upon addition of 150 ml pet ether a solid formed which was filtered, washed with pet ether and air-dried yielding 640 mg (97·9%) of Ic, dec. pt. 165–170°. Recrystallization from benzene-heptane afforded pure Ic, dec. pt. 179–181° in 78·5% yield. (Found: C, 28·1; H, 3·2; Cl, 27·1; Residue 47·7. $C_{12}H_{16}Cl_4Pd_2$ requires: C, 28·0; H, 3·1; Cl, 27·5%; Residue as PdO, 47·5). NMR spectral data are reported in Table 1.

Reaction of dichloro bis-benzonitrile palladium (II) *with allene in methanol.* Allene was bubbled into a solution of 1·00 g (2·6 mmoles) dichloro bis-benzonitrile palladium(II) in 125 ml methanol at 25°. During the course of the reaction the solution changed in colour from brownish black to pale yellow and a preciptate formed. The total reaction mixture was evaporated to dryness and the residue (1·10 g) was taken up in 8 ml benzonitrile. The insoluble residue was filtered, washed with a small amount of benzonitrile and air-dried yielding 199 mg (29·7%) of Ic, dec. pt. 180–185°. (Upon admixture with an authentic sample of Ic the dec. pt. was undepressed.) The filtrate was then evaporated to smaller volume and chromatographed on "Florisil" (Floridin Co., Magnesium Silicate). The fraction eluted with 4:1 benzene:heptane (81·5 mg, 12·1%) appeared from its NMR spectrum to be more Ic. Further elution with 5:1 benzene:chloroform afforded 72·4 mg of intermediate fractions containing Ic and Id followed by 305·6 mg (46·3%) of pure Id, m.p. 123·5–125°. Recrystallization from benzene-heptane afforded pure Id, m.p. 123·5–124·5°. (Found: C, 33·5; H, 4·8; Cl, 14·4. $C_{14}H_{22}Cl_2O_2Pd_2$ requires: C, 33·2; H, 4·4; Cl, 14·0%.) NMR spectral data are reported in Table 1.

Di-μ-chloro-di-π-(β-chloro-α,α,α′,α′-tetramethyl allyl)-dipalladium(II); II. To a solution of 769 mg (2·01 mmoles) dichloro bis-benzonitrile palladium(II) in 110 ml benzene at 25° was added 7·21 g tetramethylallene. Over a period of 5 min the solution changed in colour from red-brown to pale yellow. The solution was evaporated to small volume and heptane added. The resulting solid was filtered, washed with heptane and air-dried yielding 423 mg (77·2%) of II, dec. pt. 137–140°. Recrystallization from chloroform-heptane afforded pure II, dec. pt. 140–141°. (Found: C, 30·8; H, 4·9; Cl, 26·4. $C_{14}H_{24}Cl_4Pd_2$ requires: C, 30·7; H, 4·4; Cl, 25·9%). The NMR spectrum (in $CDCl_3$) shows two methyl peaks of equal intensity at 1·62 and 1·64 c/s relative to a tetramethyl silane internal standard.