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Preliminary communication

REACTION OF ACETYLENES WITH TRANSITION METALS

VIII*. π-ALLYLPALLADIUM COMPLEXES FROM ACETYLENES AND ALKENES

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Summary

Coupling of diarylacetylenes with alkenes in the presence of dichlorobis-(benzonitrile)palladium gives chloro(*syn*-1-chloro-*anti*-1-aryl-*syn*-3-alkyl)-π-allylpalladium complexes.

Many routes to π-allylpalladium complexes have been explored with success [2—5], but little is known of their preparation by coupling of acetylenes with alkenes*** [7]. We now describe an easy general method for the synthesis of a wide variety of π-allylpalladium complexes, from acetylenes, alkenes, and dichlorobis(benzonitrile)palladium (BNP).

A solution of BNP (1.0 mmol) in benzene or chloroform (15 ml) was treated with alkene (1—10 mmol) at room temperature, and acetylene (1.0 mmol) dissolved in the same solvent (2—3 ml), was then added. The mixture was kept for 1—24 h at room temperature and then worked up. Some of the complexes obtained from diarylacetylenes****, namely diphenyl- (I), phenyl-mesityl- (III) and phenylxylylacetylene (II) with ethylene, isobutene and t-butylethylene are listed in Table 1.

The structures of the new complexes IV—X thus obtained were assigned on the basis of spectral data (Table 2) coupled with elemental analyses and

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*For Part VII, see Ref. 1.

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***Hosokawa et al. [6] reported shortly on the preparation of the *anti*-1-chloro-*syn*-1-t-butyl-2-phenyl-*syn*-3-methyl-π-allylpalladium complex from $(C_2H_4PdCl_2)_2$ and t-butylphenylacetylene.

****We found that monoaryl- and monoalkyl-acetylenes undergo the same reaction, yielding π-allyl-palladium complexes by coupling at the less substituted end of the unsaturated bonds.

TABLE 2

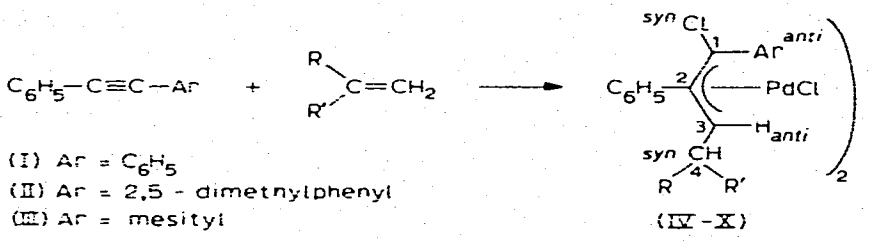
NMR SPECTRAL DATA FOR NEW π-ALLYLPALLADIUM COMPLEXES

Compound	Solvent	NMR (δ (ppm)) [a]							
		H(3)	3- or 4-CH_3	t-Bu	CH_3	CH	CH_3 (aryl)	aromatic	$J_{3,4}$ (Hz)
IV	CCl_4	4.38 q	1.18 d					7.20–7.85 m	6.0
V	$CDCl_3$	4.36 tr		0.80 s	1.63 d			7.15–7.80 m	7.0
VI	CCl_4	4.00 d	0.83d 1.16d			2.00 broad		7.15–7.80 m	6.0
VII	CCl_4	3.93 q	1.11 d				2.33 s	6.83–8.08 m	6.0
VIII	CCl_4	4.00 q		0.78 s	1.45–1.72d		2.46 s	6.85–8.00 m	7.0
IX	$CDCl_3$	3.65 q	1.10 d				2.24s 2.35s 3.10–3.24	6.73s, 6.80s(Ms); 7.30–8.20 m(Ph)	6.0
X	$CDCl_3$	3.58 tr		0.80 s	1.46 d		2.28s 2.50s 3.25s	6.76s, 6.91s(Ms); 7.51s, 8.11s(Ph)	6.0

[a] s, singlet; d, doublet; tr, triplet; q, quartet; m, multiplet; Ms, mesityl.

TABLE 1

FORMULAE AND M.P.'s FOR NEW π-ALLYLPALLADIUM COMPLEXES



(I) Ar = C_6H_5
(II) Ar = 2,5 - dimetnylphenyl
(III) Ar = mesityl

(IV-X)

Compound	Ar	R	R'	m.p. (°C)	Yield (%)
IV [a]	phenyl	H	H	140	26
V	phenyl	t-Bu	H	190	57
VI	phenyl	CH_3	CH_3	178	81
VII	2,5-dimethylphenyl	H	H	155	48
VIII [b]	2,5-dimethylphenyl	t-Bu	H	200	28
IX	mesityl	H	H	165	51
X	mesityl	t-Bu	H	175	38

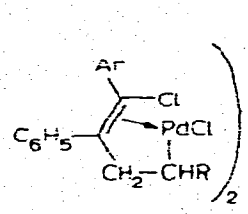
[a] The same results were obtained by using $(C_2H_4 \cdot PdCl_2)_2$ and diphenylacetylene. [b] Together with VIII an isomeric complex with interchanged phenyl and 2,5-dimethylphenyl groups was obtained in 14% yield.

chemical behaviour*. All the data are inconsistent with the isomeric σ-Pd structure XI but in accord with the π-allylpalladium formulas IV—X.

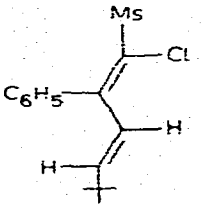
For assignment of the configuration at C(1) and C(3) we considered the chemical shift values in comparison with those of other π-allylpalladium complexes [3,6,8] **. A *syn*-configuration for the 3-alkyl groups was assigned on the basis of the normal chemical shift (δ 1.10—1.18 ppm) [3]. The chemical shift of the *anti*-H(3) allylic protons (δ 3.55—4.38 ppm) in the 1-aryl derivatives IV—X, more shielded than those of the *anti*-1-chloro-π-allylpalladium complexes [6,8] *, led us to assign a *syn* orientation to the chlorine in the 1-aryl complexes IV—X and consequently an *anti* orientation for the aryls at C(1). This is supported also by the unshielded values (δ 7.15—8.11 ppm) of the aromatic ring protons [9]. The variation of the δ values of H(3) in the range of 0.80 ppm offers additional support for the above-proposed configurations. Thus in the complexes IX and X the very bulky mesityl group which, molecular models show can only lie perpendicular to the π-allylic plane, exhibit on H(3) the shielding effect of the aromatic

* Reduction with $NaBH_4$ of the complexes IV, V, IX and X gave the expected mixtures of alkenes and alkanes, as well as the chloroalkenes, as shown by NMR spectra and elemental analyses.
Treatment of IV with thallium(I) acetylacetonate (Tlacac) using the procedure of Robinson and Shaw [11] yields the acetylacetonato derivative $C_{16}H_{14}Cl(acac)Pd^{II}$. NMR ($CDCl_3$, δ, ppm): 1.11 (d, 3H, allylic CH_3, J 6.0 Hz), 1.98 (s, 6H, 2 CH_3 from acetylacetonato group), 4.10 (quartet, 1 allylic H, H(3)), 5.28 (s, 1 allylic H from acetylacetonato group), 6.90—7.65 (m, 10 aromatic H).

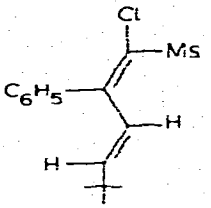
** *anti*-1-Chloro-*syn*-1-t-butyl-π-allyl complexes obtained from t-butylacetylene and alkenes show H(3) signals at δ 4.80—5.10 ppm.
syn-1-Chloro-*anti*-1-aryl-π-allyl complexes obtained from phenylacetylene and alkenes show H(3) signals at δ 3.90—4.45 ppm.



(XI)



(XII)



(XIII)

Ms = mesityl

ring (δ 3.55—3.58 ppm). On the other hand, the free rotation of the less bulky phenyl group is responsible for the downfield shifted H(3) signal (δ 4.00—4.38 ppm) in the 1,2-diphenyl complexes IV—VI. The intermediate δ values (3.93—4.00 ppm) in the C(1)-xylyl derivatives VII and VIII reflect a limited oscillation of this group.

From the reaction of phenylmesitylacetylene (III) with t-butylethylene, in addition to complex X a diene with m.p. 140°C was isolated, for which NMR and UV spectra* indicated structure XII. This is configurationally different at C(1) from the isomeric diene XIII (m.p. 99°C) ** obtained by decomposition of complex X on heating with basic methanol [10]. The fact that the two dienes are not interconvertible in acidic media or in the presence of electrophilic catalysts shows that XII does not result from XIII, which is the normal decomposition product of complex X.

The occurrence of the *cis*-1,2-diaryl-substituted diene XII can be explained by HPdCl elimination from the σ-Pd complex XI (resulted by *cis*-chloropalladation), earlier suggested in general terms as an intermediate in the coupling of acetylenes with alkenes [7]. The isolation of XII seems to be the first proof for this kind of a σ-Pd intermediate.

The transformation of the σ-Pd intermediate of the 1-aryl-substituted complexes into the π-allylic complexes, with inversion of configuration at C(1), will be the subject of further investigations.

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*Compound XII. NMR (CCl_4, δ, ppm): 1.06 (s, 9H, t-butyl), 2.11 (s, 3H, *p*-CH_3), 2.20 (s, 6H, *o,o*-CH_3). 5.38 and 6.68 (2 olefinic H, H(3) and H(4), AB system with J_{AB} 16.0 Hz), 6.58 (s, 2 aromatic H from mesityl), 6.90—7.20 (m, 5 aromatic H). UV (EtOH): λ_{max} 237.9 nm (log ε 4.377), 248.1 (4.355).

**Compound XIII. NMR (CCl_4, δ, ppm): 0.83 (s, 9H, t-butyl), 2.31 (s, 9H, CH_3 groups from mesityl), 5.16 and 5.76 (d, 2 olefinic H, H(3) and H(4), AB system with J_{AB} 16.5 Hz), 6.85 (s, 2 aromatic H from mesityl), 7.10—7.50 (m, 5 aromatic H). UV (EtOH): λ_{max} 239.4 nm (log ε 4.365), 250—260 (sh).