

π -ALLYLIC COMPLEXES FROM ALLENES

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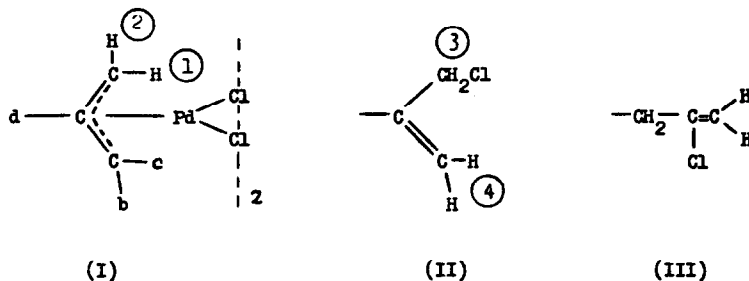
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The recent note (1) on the reaction of allene with dichlorobisbenzotriolepalladium(II) to give π -allylicpalladium complexes prompts us to report on a similar, more extensive investigation. Following our work on the preparation of π -allylicpalladium complexes from 1,3-dienes (2,3) we are investigating similar reactions with allenes and report on results for allene, methylallene and 1,1-dimethylallene.

Treatment of benzene solutions of dichlorobisbenzotriolepalladium(II) with allene, methylallene and 1,1-dimethylallene gives chloro-bridged complexes of the type $[\text{Pd}_2\text{Cl}_2(\text{all})_2]$ (I) $b=\text{C}=\text{H}$; $b=\text{H}$, $\text{C}=\text{CH}_3$; $b=\text{C}=\text{CH}_3$



respectively; $d=\text{Cl}$ in each case. Treatment of sodium chloropalladite in methanol with allene gives an excellent yield of a π -allylic complex $[\text{Pd}_2\text{Cl}_2(\text{C}_6\text{H}_8\text{Cl})_2]$ identical with a sample prepared by dichlorobisbenzotriolepalladium(II) with allene in benzotriole

solution (1). Allene and potassium bromopalladite in methanol gives the corresponding bromo complex $[\text{Pd}_2\text{Br}_2(\text{C}_6\text{H}_8\text{Br})_2]$.

n.m.r. results (see below) suggest that the chloro complex has the structure (I) with $b=c=H$ and substituent d has structure (II) rather than (III), an X-ray determination of the structure of this complex is being carried out by Dr. G. E. Pringle and Mr. T. L. Broadbent of this department. These bridged complexes undergo typical reactions e.g. metathesis of bridging chlorine by bromine, iodine or thiocyanate, bridge splitting reactions with pyridine or ammonia and the formation of mononuclear complexes with acetylacetonate (see Robinson and Shaw (3)).

Because of poor solubility the only n.m.r. data given by Schultz (1) for the compound $[\text{Pd}_2\text{Cl}_2(\text{C}_6\text{H}_8\text{Cl})_2]$ were determined in dimethyl sulphide, a solvent which converts π -allylic into σ -allylic structures. We also find this complex is insoluble in common organic solvents but the corresponding iodo-bridged $[\text{Pd}_2\text{I}_2(\text{C}_6\text{H}_8\text{Cl})_2]$ and acetylacetonate complexes $[\text{Pd}(\text{acac})(\text{C}_6\text{H}_8\text{Cl})]$ are soluble in deuteriochloroform and carbon tetrachloride, respectively. The n.m.r. data for these complexes are given below with the protons numbered as in (I) and (II) and the relative intensities given in parentheses. All the peaks in these two n.m.r. spectra were singlets but for the complex $[\text{Pd}_2\text{Cl}_2(\text{C}_5\text{H}_4\text{Cl})_2]$ (I, $d=\text{Cl}$, $b=c=H$) in deuteriochloroform we find protons of types (1) and (2) couple, with $J_{12}=2\text{c/sec.}$, the first time this type of coupling has been reported in π -allylic-palladium complexes. The n.m.r. data on our other complexes are not reported here but agree with the assigned structures.

Compound	τ_1	τ_2	τ_3	τ_4	
$[\text{Pd}_2\text{I}_2(\text{C}_6\text{H}_8\text{Cl})_2]$ in CHCl_3	7.10(2)	5.82(1)	5.59(2)	4.57(1)	4.38(1)
					τ_{H} τ_{CH_3}
$[\text{Pd}(\text{acac})(\text{C}_6\text{H}_8\text{Cl})]$ in CCl_4	7.34(2)	6.19(2)	5.75(2)	4.54(1)	4.36(1)
					4.82(1) 8.12(6)

REFERENCES

1. R. G. Schults, Tetrahedron Letters, 301 (1964).
2. B. L. Shaw, Chem. and Ind., (London) 1190 (1962).
3. S. D. Robinson and B. L. Shaw, J. Chem. Soc., 4806 (1963).