

THE FORMATION OF ALLENES VIA Pd^{II} AND Pt^{II} COMPLEXES

J. LUKAS, J. P. VISSER and A. P. KOUWENHOVEN

Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research N.V.) (The Netherlands)

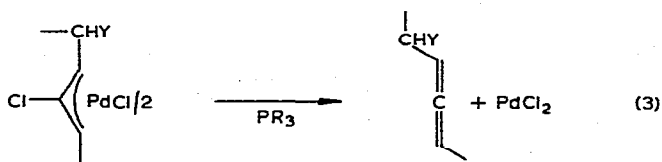
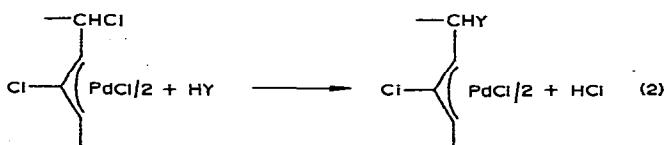
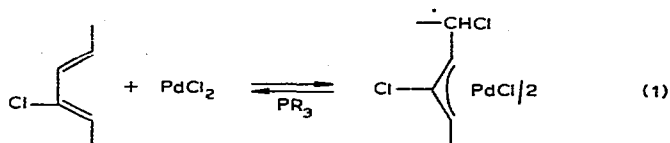
(Received July 18th, 1972)

SUMMARY

4-Methoxy-1,2-butadiene has been prepared from chloroprene via a 2-chloro- π -allylpalladium complex. Attempts to synthesize a similar platinum complex from 2-chloroallyl chloride led to insertion of the metal into the vinylic carbon-chlorine bond.

RESULTS AND DISCUSSION

A method for the conversion of conjugated into cumulated dienes (allenes) would be of interest in view of the scarcity of useful routes leading to the latter class of compounds. A combination of the reactions outlined in the scheme below should provide such a route:



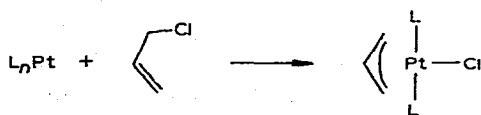
A 2-chloro-1,3-diene reacts with palladium chloride to give a 1-chloroalkyl-2-chloroallyl complex (eqn. 1), an addition reaction which is well known for conjugated dienes¹. The 1-chloroalkyl group is very reactive. Upon treatment with coordinating

compounds the chloro substituent returns to the metal, generating the starting diene and PdCl_2L_2 (1)². With nucleophiles, solvolysis occurs readily (2)³. Once the chlorine at the 1-alkyl group has been replaced, the reaction with coordinating compounds gives rise to elimination of the chlorine on the *meso*-carbon atom, a known reaction which leads to allenes⁴.

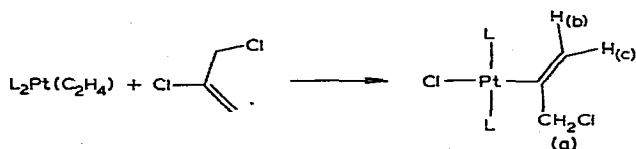
When bis(triphenylphosphine)palladium chloride (2.5 g) was dissolved in chloroprene (30 ml) and stirred for 30 min a light yellow complex, 1-chloromethyl-2-chloroallylpalladium chloride, was formed (1.07 g, 61% yield). This complex solvolyzed quantitatively in methanol within 15 min. to give 1-methoxymethyl-2-chloro- π -allylpalladium chloride. The latter compound was also prepared directly from chloroprene (8 ml), bis(triphenylphosphine)palladium chloride (16 g), and methanol (100 ml), in 30% yield (70% conversion). The 1-methoxymethyl complex reacted with an excess of tri-*n*-butylphosphine to give 4-methoxy-1,2-butadiene (67% yield).

It proved impossible to carry out other solvolytic reactions with the diene adduct. Usually, a retroreaction took place and chloroprene was formed. Attempts to replace the chlorine ligand by acetate and cyanide were equally unsuccessful.

For platinum complexes the sequence of reactions (1)–(3) is unknown. In order to ascertain whether step(3) is feasible for platinum compounds it was necessary to devise a synthesis for a 2-chloro- π -allylplatinum complex. A route analogous to that reported for 2-alkyl- π -allylplatinum complexes seemed the most appropriate⁵.



Thus 2,3-dichloropropene was added at 10° to bis(triphenylphosphine)(ethene)platinum in benzene; a white solid crystallized (75% yield), and was shown by analysis to have the formula $(\text{PPh}_3)_2(\text{C}_3\text{H}_4\text{Cl})\text{PtCl}$. The NMR spectrum revealed to our surprise, that the platinum had not inserted into the allylic but into the vinylic carbon-chlorine bond, to yield [1-(chloromethyl)viny]bis(triphenylphosphine)platinum chloride.



($\delta(\text{H}_a)$ 3.13 ppm, $J(\text{Pt}-\text{H}_a)$ 16 Hz; $\delta(\text{H}_b)$ 4.78 ppm, $J(\text{Pt}-\text{H}_b)$ 71 Hz; $\delta(\text{H}_c)$ 5.53 ppm, $J(\text{Pt}-\text{H}_c)$ 120 Hz; 220 MHz, solvent CDCl_3 , -10°). Upon being heated to 40° in chloroform or to 150° in the crystalline state the complex was converted quantitatively into allene and bis(triphenylphosphine)platinum dichloride.

REFERENCES

- 1 B. L. Shaw, *Chem. Ind. (London)*, (1962) 1190; S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, (1963) 4806; *ibid.*, (1964) 5002.

- 2 J. Lukas, P. W. N. M. Van Leeuwen, H. C. Volger and A. P. Kouwenhoven, *Chem. Commun.*, (1970) 799 and paper in preparation.
- 3 J. Lukas and P. A. Kramer, *J. Organometal. Chem.*, 31 (1971) 111.
- 4 R. G. Schultz, *Tetrahedron*, 20 (1964) 2809; M. S. Lupin and B. L. Shaw, *Tetrahedron Lett.*, (1964) 883.
- 5 M. C. Baird and G. Wilkinson, *J. Chem. Soc. A*, (1967) 865.