Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

THE REACTION OF CYCLOPROPANE WITH ZEISE'S SALT

DAVID BASSET BROWN*
Bell Telephone Laboratories, Murray Hill, New Jersey 07974 (U.S.A.) and The University of Vermont, Burlington, Vermont 05401 (U.S.A.)

(Received March 13th, 1970)

SUMMARY

The addition of cyclopropane to H_2PtCl_6 yields the Pt–cyclopropane complex $PtCl_2(C_3H_6)$, whereas addition of cyclopropane to Zeise's acid $HPtCl_3(C_2H_4)$ in EtOH or to Zeise's dimer $[PtCl_2(C_2H_4)]_2$ in CH_2Cl_2, $CHCl_3$, or EtOH gives the isomeric olefin dimer $[PtCl_2(CH_3CH{=}CH_2)]_2$. The two isomeric complexes can be readily interconverted by bubbling either cyclopropane or propylene through solutions of either the olefin dimer or the cyclopropane complex, respectively. It is concluded that in the reaction of cyclopropane with Zeise's complex, the cyclopropane simultaneously opens to propylene and displaces ethylene from the complex.

INTRODUCTION

The unusual phenomenon of complexes containing a cyclopropane ring bonded to platinum has been the subject of a number of publications in the last decade. The first complex reported, and the parent compound in the series, was prepared by Tipper[1] in 1959 by bubbling cyclopropane through a solution of chloroplatinic acid in acetic anhydride, and has the composition $PtCl_2(C_3H_6)$, containing a recoverable cyclopropane ring. Irwin and McQuillin[2] have since prepared a number of similar complexes with penyl- and hexyl-substituted cyclopropanes by the reaction of the appropriate cyclopropane with Zeise's dimer, $[PtCl_2(CH_2{=}CH_2)]_2$, in dichloromethane. On the basis of its solubility, IR and NMR spectra, and reactions, Chatt and co-workers[3,4] suggested that $[PtCl_2(C_3H_6)]_n$ was a polymeric complex of Pt^{4+} in which platinum had inserted into the cylcopropane ring, and this formulation was substantiated by a structure determination[5] of the pyridine adduct which demonstrated that the adduct is 6-coordinate and that platinum has inserted into the ring. More recent evidence[6] indicates that the parent compound is in fact a chloride-bridged tetramer with a structure analogous to that of the platinum(IV) alkyls.

We report in this paper the unusual reaction of cyclopropane with Zeise's salt.

EXPERIMENTAL

Cyclopropane (Matheson) was used as received or purified of olefinic conta-

---

[*] Address correspondence to the author at the University of Vermont.

minants by bubbling through bromine water, bromine in carbon tetrachloride, or basic aqueous permanganate, and propylene (Matheson) and methyl-substituted cyclopropanes (Chemical Samples Co.) were used as received. Zeise's salt (Alfa Inorganics) was converted to the dimer by dissolution in ethanolic hydrochloric acid, filtration, and removal of solvent. IR spectra were obtained on Perkin–Elmer Model 457 and Model 21 spectrometers, and NMR spectra were obtained on a Varian A-60 spectrometer. Microanalyses were by Galbraith Laboratories.

Cyclopropane was bubbled for one hour through a solution of Zeise's acid [$HPtCl_3(C_2H_4)$ formed *in situ* from Zeise's salt, $KPtCl_3(C_2H_4)$] in ethanol. The resulting solution was maintained at 4° for three weeks, and, since no solid product had formed, was evaporated to dryness under vacuum at room temperature. The resulting orange product was shown by IR and NMR spectroscopy to be the propylene analog of Zeise's dimer. (Found: C, 11.66; H, 1.92; Cl, 23.14; Pt, 63.48. $C_3H_6Cl_2Pt$ calcd.: C, 11.70; H, 1.96; Cl, 23.01; Pt, 63.33%.)

The other reactions reported in this paper were performed in a similar fashion with only slight differences. Precipitates formed were filtered prior to solvent removal, which was done shortly after the reactions were completed.

RESULTS AND DISCUSSION

We have been investigating the unique products formed in the reaction of various methyl-substituted cyclopropanes with chloroplatinic acid in acetic anhydride. In an effort to find an alternate route to these materials, we attempted the reaction of 1,1-dimethylcyclopropane, *cis*-1,2-dimethylcyclopropane, and spiropentane with Zeise's acid in ethanol. Since there has been no report of the parent cyclopropane complex formed in this way, cyclopropane was bubbled through an identical solution. After standing for three weeks, there was no evidence for the formation of any cyclopropane complexes, which were expected to be insoluble. The solutions were all evaporated to dryness, and IR spectra indicated that in each of the first three cases the residue was Zeise's dimer[7]. The IR spectrum of the material derived from cyclopropane, however, was different, and was not that which has been reported[4] for the platinum–cyclopropane complex. Further investigation confirmed that the material is in fact the propylene analog of Zeise's dimer, $[PtCl_2(CH_3CH{=}CH_2)]_2$. Its IR and NMR spectra are in complete accord with those which have been reported[7,8] for the known propylene complex. Further, the material decomposes in dimethylsulfoxide to give free propylene (demonstrated by NMR), whereas under similar conditions the cyclopropane complex gives only free cyclopropane. Apparently, under the conditions used cyclopropane isomerizes and subsequently, or concurrently, displaces ethylene from Zeise's salt.

Further investigation indicates that this unusual reaction is not simply a result of the specific conditions used, *e.g.*, the presence of acid and the ethanol solvent. Bubbling cyclopropane through a dichloromethane solution of Zeise's dimer rapidly produces a bright yellow precipitate which can be shown to be the cyclopropane complex*. However, evaporation of the remaining solution yields the propylene

---

* The cyclopropane complex prepared in acetic anhydride varies in color from brown to yellow. When prepared in the fashion discussed here, it is always bright yellow, and gives rise to much sharper IR absorptions.

complex. In ethanol and chloroform, the reaction of $[PtCl_2(CH_2{=}CH_2)]_2$ and cyclopropane does not give a precipitate, and upon evaporation of the solution the product is primarily the propylene complex, along with some of the cyclopropane complex. There apparently is a fairly facile equilibrium established between the cyclopropane and propylene complexes in solution. Thus, if cyclopropane is bubbled through a carbon tetrachloride solution of the propylene complex, most of the material eventually precipitates as the cyclopropane complex. Similarly, bubbling propylene through a suspension of the cyclopropane complex in ethanol (in which it is slightly soluble) produces a solution containing the propylene complex.

It would be possible to explain all of the observed products on the basis of propylene contamination of the cyclopropane used, but this can be ruled out on several grounds. First, the gas (Matheson) is claimed to contain a minimum of 99% cyclopropane, and passes the USP test (less than 0.25 mole %) for unsaturated hydrocarbons. In agreement with the stated purity, no propylene is observed in the IR spectrum of the cyclopropane used, under conditions where it is estimated that as little as 0.3% propylene would be detectable. More direct evidence that $[PtCl_2(CH_3\text{-}CH{=}CH_2)]_2$ does not result from propylene in the starting materials is obtained by carrying out the reaction under conditions where propylene should be eliminated. Thus, the propylene complex is still formed using cyclopropane which has first been passed through bromine water, bromine in carbon tetrachloride, or basic aqueous permanganate, all reagents which should selectively react with propylene. The reaction of Br_2/CCl_4 with pure propylene under similar flow conditions is quantitative, so that in this instance at least propylene in the product must originate from cyclopropane.

The isomerization of cyclopropane itself has been observed only under rather severe conditions, such as high temperatures[9], reactions with recoil tritium atoms[10], and catalytically on acidic surfaces[11]. There is, however, precedent for substituted cyclopropanes isomerizing to various olefinic products. For example, the reaction of methylenecyclopropane with diiron enneacarbonyl gives about 2% of butadieneiron tricarbonyl[12], and *exo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene rearranges quantitatively in the presence of catalytic amounts of $IrCl(CO)(PPh_3)_2$ to give 5-methylenebicyclo[2.2.1.]hept-2-ene[13]. The much more common ring-opening reaction gives rise to π-allyl complexes, and such reactions have been observed for several different types of substituted cyclopropanes[2,14,15]. The formation of the propylene complex observed in this work substantiates claims for similar complexes as intermediates in ring-opening reactions. The aqueous reaction of palladium(II) chloride and phenylcyclopropane gives 35% of phenylacetone. It is postulated that this product arises from *trans*-propenylbenzene as an intermediate, and in fact *trans*-propenylbenzene is found in the reaction mixture[16]. Similarly, the reaction of bromocyclopropane and di-μ-chlorobis(ethylene)dipalladium dichloride in refluxing benzene gave π-allylpalladium chloride, and allyl bromide was considered a likely intermediate[17].

The actual sequence of events in the reaction of Zeise's complex and cyclopropane to form the propylene analog of Zeise's complex is not clear. It is likely that the reaction does not proceed through the cyclopropane complex as an intermediate, since this material is practically insoluble in many of the solvents used, and since there has been no evidence for the formation of either propylene or the propylene complex in the reactions of the cyclopropane complex. The most likely mechanism is a concerted reaction in which cyclopropane is converted into propylene at the same time as it displaces ethylene from Zeise's salt, and this would be consistent with the reported failure to observe allyl bromide in solution in the isomerization of cyclopropyl bromide[17].

ACKNOWLEDGEMENT

I am grateful to M. B. Robin for penetrating discussions. Portions of this work performed at the University of Vermont were supported by the National Science Foundation.

REFERENCES

1 C. F. H. Tipper, *J. Chem. Soc.*, (1955) 2045.
2 W. J. Irwin and F. J. McQuillin, *Tetrahedron Lett.*, 16 (1968) 1937.
3 D. M. Adams, J. Chatt and R. G. Guy, *Proc. Chem. Soc.*, (1960) 179.
4 D. M. Adams, J. Chatt, R. G. Guy and N. Sheppard, *J. Chem. Soc.*, (1961) 738.
5 N. A. Bailey, R. D. Gillard, M. Keeton, R. Mason and D. R. Russell, *Chem. Commun.*, (1966) 396.
6 S. E. Binns, R. H. Cragg, R. D. Gillard, B. T. Heaton and M. F. Pilbrow, *J. Chem. Soc. A*, (1969) 1227.
7 J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, (1953) 2939.
8 H. P. Fritz, K. E. Schwarzhans and D. Sellmann, *J. Organometal. Chem.*, 6 (1966) 551.
9 H. M. Frey, *Advan. Phys. Org. Chem.*, 4 (1966) 147.
10 E. K. C. Lee and F. S. Rowland, *J. Phys. Chem.*, 66 (1962) 2622.
11 R. M. Roberts, *J. Phys. Chem.*, 63 (1959) 1400.
12 R. Noyori, T. Nishimura and H. Takaya, *J. Chem. Soc. D*, (1969) 89.
13 H. C. Volger, H. Hogeveen and M. M. P. Gaasbeek, *J. Amer. Chem. Soc.*, 91 (1969) 2137.
14 R. Noyori and H. Takaya, *J. Chem. Soc. D*, (1969) 525.
15 T. Shono, T. Yoshimura, Y. Matsumura and R. Oda, *J. Org. Chem.*, 33 (1968) 876.
16 R. J. Ouellette and C. Levin, *J. Amer. Chem. Soc.*, 90 (1968) 6889.
17 A. D. Ketley, J. A. Braatz, J. Craig and R. Cole, *Preprints, Div. of Petrol. Chem., 157th Meeting Amer. Chem. Soc.*, Minneapolis, 1969, B142.