Platinum(0) Complexes of Short-lived Cyclic Allenes

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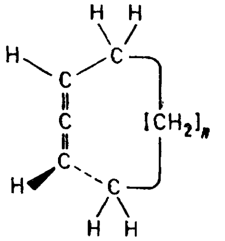
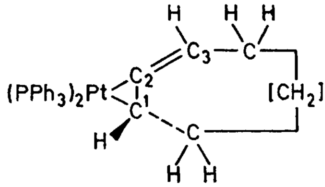
Summary Platinum(0) complexes of cyclonona-1,2-diene, cyclo-octa-1,2-diene, and cyclohepta-1,2-diene have been prepared; the co-ordinating ability of these allenes increases with decreasing ring size.

RECENT work has shown that co-ordination to Pt greatly enhances the stability of strained ring systems such as cyclopropenes.[1] We have now succeeded in trapping thermally unstable cyclic allenes by means of a Pt complex.

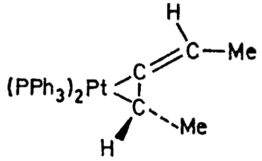
The linearity of the three carbon atoms of the C=C=C group imposes a lower limit on the ring size of cyclic allenes. The smallest cyclic allene isolated is cyclonona-1,2-diene (I).[2] Evidence for the formation of smaller cyclic allenes as intermediates was obtained from i.r. data and from the structures of the reaction products formed on dimerization. Thus, in the reaction of 8,8-dibromobicyclo[5,1,0]octane with methyl-lithium[3] and in the dehydrobromination of 1-bromocyclo-octene[4] the occurrence of cyclo-octa-1,2-diene (II) was established. Evidence for the formation of the even more strained cyclohepta-1,2-diene (III) was reported in the dehydrohalogenations of 1-chloro- and 1-bromo-cycloheptene.[5,6]



(I) $n = 4$
(II) $n = 3$
(III) $n = 2$



(IV) $n = 4$
(V) $n = 3$
(VI) $n = 2$

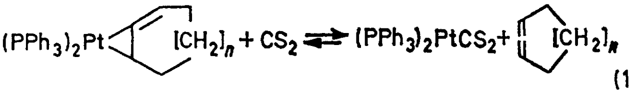


(VII)

Generation of (II)[3] in the presence of bis(triphenylphosphine)(ethylene)platinum gave bis(triphenylphosphine)-(cyclo-octa-1,2-diene)platinum (V), which was isolated as an off-white, air-stable, crystalline compound (m.p. 151—153° decomp.). The cyclohepta-1,2-diene complex (VI, m.p. 156—159° decomp.) was obtained by a similar ligand exchange (cyclohepta-1,2-diene was generated *via* dehydrobromination of either 1-bromocycloheptene or 1,2-dibromocycloheptane).

Comparison of the n.m.r. spectra† of (V) and (VI) with those of complexes of stable allenes (IV) and (VII) shows unambiguously that allenes (II) and (III) are indeed co-ordinated. The protons at C^1 and C^3 were clearly identified; the ^{195}Pt–H and P–H spin–spin couplings and the chemical shifts of these protons are characteristic of the proposed structure.

The allenes can be displaced by a stronger binding ligand, such as CS_2 (equation 1). In this way cyclo-octa-1,2-diene was liberated from its complex at −60 °C. The structure of (II) was demonstrated by the characteristic pattern of the olefinic protons in the n.m.r. spectrum, which was very similar to that of cyclonona-1,2-diene. At higher temperatures (II) started to dimerize (k_2 at 3 °C = $2{\cdot}3 \times 10^{-3}$ l mol^{-1} s^{-1}; $CDCl_3$–CS_2 5:1). More severe conditions were required to remove cyclohepta-1,2-diene from its complex. At 35 °C the decomposition of (VI) with CS_2 in $CDCl_3$ took several hours and resulted in the formation of dimer(s) of (III). Apparently, at lower temperatures the concentration of the free allene in the equilibrium (equation 1) was so small that hardly any dimerization occurred. Addition of tetraphenylcyclopentadienone, capable of undergoing a rapid cycloaddition with (III), caused a rapid conversion of the allene complex in the presence of CS_2 into $L_2Pt(CS_2)$. With 3-methylthiiren 1,1-dioxide, which is known to be a stronger co-ordinating ligand than CS_2,[7] cyclohepta-1,2-diene was removed from its complex at −25 °C. However, dimer(s) rather than the free allene were again obtained.



(1)

These experiments show that cyclohepta-1,2-diene gives a much stronger co-ordination with Pt^0 than CS_2. In addition, it may be concluded that the co-ordinating ability of the cyclic allene increases with decreasing ring size owing to the release of strain upon co-ordination, which will be greater for smaller rings.

Since the efficiency of the trapping of generated allene by Pt^0 complexes is determined by the rate of dimerization of the allene and the rate of complex formation, the efficiency drops with decreasing ring size of the allene. Indeed, whereas the trapping of cyclo-octa-1,2-diene, was quantitative, in the trapping of cyclohepta-1,2-diene, as well as the complex, a considerable amount of dimer(s) was formed. It was, therefore, not surprising that with cyclohexa-1,2-diene,[8] dimerization rather than complex formation occurred.

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† The chemical shifts in $CDCl_3$ of the C^1–H of compounds (IV)—(VII) (δ in p.p.m.), with, in parentheses $J(^{195}\text{Pt–C}^1\text{H})$ in Hz, are, respectively, 2·43(65), 2·55(65), 2·52(62), and 2·33(71). Similarly, the chemical shifts of the C^3–H of compounds (IV)—(VII), with, in parentheses firstly $J(^{195}\text{Pt–C}^3\text{H})$ and secondly $J(\text{P–C}^3\text{H})$ both in Hz, are, respectively, 4·93(73, 11), 4·96(74, 12), 5·33(65, 8·5), and 4·78(68, 11).

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