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HYDRIDO COMPLEXES OF ZIRCONIUM
III. REACTIONS WITH ACETYLENES TO GIVE ALKENYLZIRCONIUM DERIVATIVES

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SUMMARY

The zirconium hydride $(C_5H_5)_2Zr(H)Cl$ reacts with both mono and disubstituted acetylenes by addition of Zr–H across the triple bond. Generally *trans*-alkenyl derivatives result although in some cases mixtures of isomers are formed. With monosubstituted acetylenes $(C_5H_5)_2ZrH_2$ behaves similarly giving di(*trans*-alkenyl)-zirconium compounds, but with diarylacetylenes hydrogen is evolved and tetraarylbutadiene complexes result.

INTRODUCTION

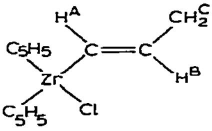
In Parts I[1] and II[2] the preparations of several derivatives of zirconium with bridging hydrido ligands were reported, as well as their reactions with carboxylic acids and ketones. These hydrides react also with acetylenes and olefins giving highly coloured alkenyl- and alkylzirconium derivatives which are extremely sensitive to oxygen and to water. In this paper the reactions of $(C_5H_5)_2ZrH_2$ and $(C_5H_5)_2Zr(H)Cl$ with mono- and disubstituted acetylenes are described.

RESULTS AND DISCUSSION

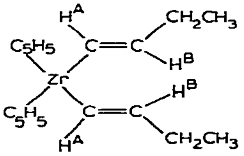
Despite the insolubility of $(C_5H_5)_2ZrH_2$ and $(C_5H_5)_2Zr(H)Cl$, both hydrides dissolved readily when boiled in benzene in the presence of acetylenes, the colour darkening to reddish-brown or black. In most cases the reaction was complete in several minutes. Dry acetylene reacted rapidly giving black solid products, but the composition of these was somewhat variable. Better results were obtained with substituted acetylenes.

From $(C_5H_5)_2Zr(H)Cl$ and 1-butyne a pale brown oily product was obtained, the infrared spectrum of which showed a C=C stretching band at 1560 cm^{-1} and no triple bond absorption. The PMR spectrum confirmed structure (I), the H^A proton being evident as one half of an AB quartet at δ 6.74 (J_{AB} 18 Hz) in which each signal was further split into a triplet ($J \sim 2$ Hz) by long range allylic coupling to the CH_2 of the ethyl group. The large AB coupling (J 18 Hz) indicated that the double bond was *trans*. The broadened quintet and triplet due to H^C and H^D were centred at δ 1.93

(J 7.2 Hz) and 0.90 (J 7.6 Hz) respectively. H^B was obscured by several small sharp peaks around the major cyclopentadienyl resonance at δ 5.92. These were probably due to small amounts of other isomeric forms.



(I)



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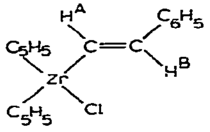


(III)

When $(C_5H_5)_2Zr(D)Cl$ was used instead of the hydride, the infrared spectrum of the product (I, $H^B = D$) showed the C=C stretch at 1525 cm^{-1}. The ethyl resonances in the PMR spectrum occurred now as a broadened quartet centred at δ 1.96 (J 8 Hz) and a triplet at δ 0.92 (J 8 Hz), but H^A showed as a broad band at δ 6.72 split into a multiplet by weak coupling with deuterium and with the allylic protons. Irradiation of this band and consequent sharpening of the CH_2 quartet at δ 1.96 demonstrated the weak coupling of H^A with the CH_2 protons.

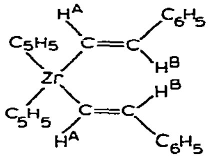
From the dihydride $(C_5H_5)_2ZrH_2$ and 1-butyne an oil was obtained, showing a broad absorption in the C=C stretch region of the infrared (1580 cm^{-1}) and broad multiplets in the PMR spectrum due to C_2H_5 at δ 1.00 and 2.25 and due to C_5H_5 at δ 5.90. The resonances due to H^A and H^B were split and distributed under the C_5H_5 band. It would appear from analysis that the product has structure (II) but the complicated PMR spectrum indicates the presence of isomers and extensive interference between the cyclopentadienyl and the 1-butenyl ligands.

Phenylacetylene behaved similarly with both hydrides, although in all cases the double bond stretching frequency around 1580 cm^{-1} in the infrared spectrum was masked by the aromatic absorption in this area. The product from $(C_5H_5)_2Zr(H)Cl$ and $C_6H_5C{\equiv}CH$ was a viscous oil, the PMR spectrum of which showed extensive splitting of all of the proton resonances. The C_5H_5 occurred as a multiplet centred at δ 5.76 and the C_6H_5 as a multiplet at δ 7.21. Protons H^A and H^B [structure (III)] could not be detected, but in the spectrum of the corresponding compound (III), $H^B = D$) from $(C_5H_5)_2Zr(D)Cl$, H^A showed as a peak at δ 7.62, split into a triplet by small coupling with deuterium (J 3 Hz).

From $(C_5H_5)_2ZrH_2$ and $C_6H_5C{\equiv}CH$ in the molar ratio 1/2, a black solid corresponding to structure (IV) was obtained. This was monomeric in boiling benzene; protons H^A and H^B could not be detected in the PMR spectrum since they were masked by multiplets at δ 5.78 (C_5H_5) and 6.98 (C_6H_5). A similar black product (IV, $H^B = D$) was obtained from $(C_5H_5)_2ZrD_2$, showing a substantially unchanged PMR spectrum. The C_5H_5 peak was a strong sharp singlet at δ 5.78 accompanied by several very small sharp bands at δ 6.07, 5.96, 5.71, 5.63, 5.48, 5.26 and 5.12. It seems likely that the compound is 90% of one isomer, the rest being a mixture of the other possible isomers.

A by-product from this reaction was a green solid, insoluble in benzene, tetrahydrofuran, dimethyl sulphoxide and other solvents, and showing a strong sharp band in the infrared spectrum at 1825 cm^{-1} indicative of a co-ordinated triple bond. Analysis indicated the loss of a cyclopentadienyl ligand giving a polymeric product of the type $(C_5H_5ZrC{\equiv}CC_6H_5)_n$. Loss of a cyclopentadiene in this way occurs readily and was observed often in reactions with disubstituted acetylenes.

With disubstituted acetylenes the two hydrides reacted in different ways; the hydridochloride added across the multiple bond and the dihydride eliminated hydrogen forming olefin complexes. Thus from $(C_5H_5)_2Zr(H)Cl$ and diphenylacetylene (tolan) in equimolar quantities an orange solid (V) was obtained, which was monomeric in boiling benzene.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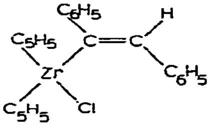
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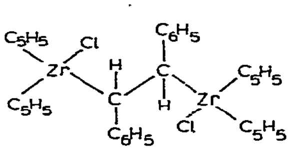
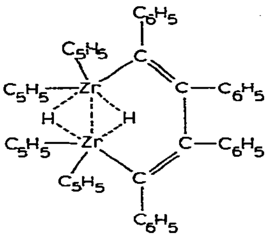

(VI)

Integrated intensities of the PMR peaks of (V) indicated that the proton on the double-bonded carbon was hidden under the multiplet due to C_6H_5 at δ 6.76. The similarity of this multiplet to that of *trans*-stilbene indicated that the major part of the product was the *trans*-adduct. Two sharp bands due to the cyclopentadienyl ligands were present at δ 5.90 and 5.77 in the intensity ratio 3/1, so that 25% *cis*-isomer could be present.

From $(C_5H_5)_2Zr(H)Cl$ and tolan in the molar ratio 2/1, a crimson-coloured solid was obtained containing no double bond. Addition of the second mole of hydride had apparently occurred giving the saturated compound (VI), which was extremely soluble in organic solvents.

The phenyl peak of (VI) in the PMR spectrum was again split into a multiplet centred at δ 6.76 and in the cyclopentadienyl region were two strong sharp bands (δ 5.90 and 5.78) together with two weaker sharp bands (δ 5.85 and 5.60). Since structure (VI) has two asymmetric centres the possibility of *threo* and *erythro* forms arises and the resonance bands between δ 5.60 and 5.90 may be connected with these, but no definite assignments have been made.

Reactions of the dihydride $(C_5H_5)_2ZrH_2$ with diphenyl- and di-*p*-tolylacetylene were characterized by the evolution of hydrogen and the loss of one cyclopentadienyl ligand from each zirconium atom on prolonged heating at 80°. When the mixture was boiled in benzene until the hydride had just dissolved, the product isolated at this stage corresponded to $[(C_5H_5)_2ZrH_n \cdot C_6H_5C{\equiv}CC_6H_5]_2$ in analysis and molecular weight. After heating the solution for a longer period the products isolated contained less carbon, and after one hour or more at 80° the product corresponded to $(C_5H_5Zr \cdot C_6H_5C{\equiv}CC_6H_5)_2$. Treatment of the monocyclopentadienyl product with acetone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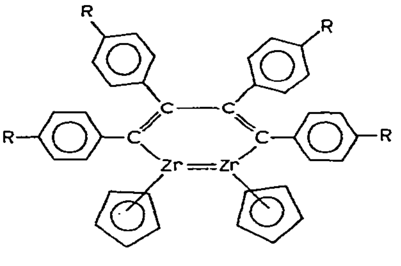
(VIII A) R = H
(VIII B) R = CH_3

gave large colourless crystals of *cis, cis*-1,2,3,4-tetraphenylbutadiene.

These results indicate the formation of an initial complex, for which structure (VII) is a reasonable possibility, since not all of the hydrogen has been lost at this stage.

Both cyclopentadienyl groups were still present on each zirconium and showed a single resonance line in the PMR spectrum. Complete hydrogen evolution was a slow process which probably paralleled the loss of one cyclopentadienyl ligand from each zirconium atom to give what is believed to be the dizirconabenzene complex (VIII).

The product (VIIIA) from diphenylacetylene and the dihydride or dideuteride showed a singlet cyclopentadienyl resonance at δ 6.00 and a multiplet due to the phenyl groups with at least eight bands between δ 6.64 and 7.10. The PMR spectrum of the di-*p*-tolylacetylene compound (VIIIB) showed two methyl peaks of equal intensity at δ 1.75 and 1.96, a sharp singlet at δ 5.94 due to the cyclopentadienyl protons and two multiplets due to the two AA'BB' systems of the phenyl rings (Fig. 1). To satisfy the coordination requirements of the zirconium it is probable that a double bond exists between the metal atoms.

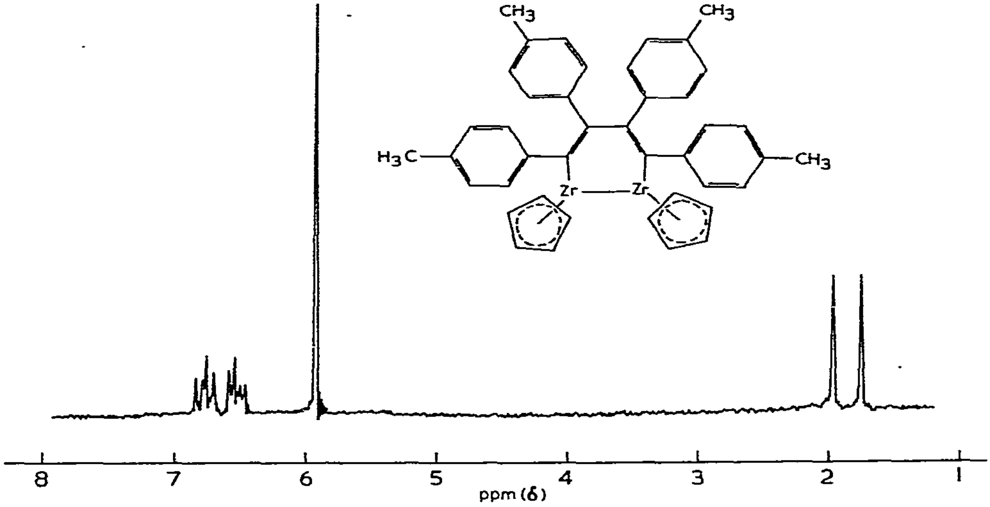

Fig. 1. PMR spectrum of compound (VIIIB) in deuterobenzene.

PMR spectra

The PMR spectra of many of the compounds just described were characterized by a multiplicity of resonance bands in both the cyclopentadienyl and the phenyl regions. Since most of the alkenes were *trans*-isomers, multiplets of the type shown by *trans*-stilbene would be expected. Multiplets in the cyclopentadienyl region are probably due to the formation of isomeric forms of the alkenes attached to zirconium, although the possibility of steric interference between the substituent on the alkene and the cyclopentadienyl ligands should not be overlooked[3,4]. Consideration of the possible molecular conformations of most of the products shows that such interference is possible. Only in one class of complex, namely the tetraarylbutadiene compounds, is interference not possible and in these cases single PMR resonance bands were observed for the cyclopentadienyl protons.

EXPERIMENTAL

General

All solid compounds were handled in a nitrogen-filled glovebox and all reactions were carried out under purified argon in a Schlenk tube system. Molecular weights were determined ebulliometrically in a Gallenkamp ebulliometer modified to take a 3-ml cell with N_2 inlet. PMR spectra were measured on a Varian HA 100 instrument in C_6D_6. Infrared spectra were run on a Perkin–Elmer 137 spectrophotometer calibrated with polystyrene.

Materials

Zirconium hydrides were prepared as described in Part I of this series[1]. 1-Butyne, phenylacetylene and diphenylacetylene were commercial products; phenylacetylene was distilled before use, the others were used without further treatment. Di-*p*-tolylacetylene was prepared from 4,4'-dimethylbenzil[5].

Analyses

Zirconium was determined by ignition to the oxide. Carbon and hydrogen were determined by the Australian Microanalytical Service, on pelleted samples sealed in aluminium capsules. In those cases in which the products were oils, encapsulation was not possible and analyses for carbon and hydrogen could not be determined.

Reaction of acetylenes with zirconium hydrides

General reaction. The hydride (5 mmole) and the acetylene (5 or 10 mmoles as required) were refluxed in benzene (50 ml) until the hydride dissolved. In the case of 1-butyne the gas was bubbled through the refluxing benzene. The solution, usually red-brown or black, was then filtered, solvent was removed under reduced pressure and the product was washed with petrol several times. Those products which were oils or low-melting solids could generally not be purified beyond this stage owing to their extreme sensitivity to heat, oxygen and moisture.

$(C_5H_5)_2Zr(Cl)CH{=}CHC_2H_5$. From $(C_5H_5)_2Zr(H)Cl$ and $C_2H_5C{\equiv}CH$, a yellow-brown oil. (Found: Zr, 29.5. $C_{14}H_{17}ClZr$ calcd.: Zr, 29.23%.)

$(C_5H_5)_2Zr(Cl)CH{=}CHC_6H_5$. From $(C_5H_5)_2Zr(H)Cl$ and $C_6H_5C{\equiv}CH$, a brown-black low-melting solid which could not be purified further. (Found: C, 62.5; H, 5.4; Zr, 24.9. $C_{18}H_{17}ClZr$ calcd.: C, 60.06; H, 4.76; Zr, 25.3%.)

$(C_5H_5)_2Zr(CH{=}CHC_2H_5)_2$. From $(C_5H_5)_2ZrH_2$ and $C_2H_5C{\equiv}CH$, brown-black oil. (Found: Zr, 28.3. $C_{18}H_{24}Zr$ calcd.: Zr, 27.50%.)

$(C_5H_5)_2Zr(CH{=}CHC_6H_5)_2$. From $(C_5H_5)_2ZrH_2$ and $C_6H_5C{\equiv}CH$, black solid. (Found: C, 72.3; H, 5.3; Zr, 21.3; mol.wt., 436. $C_{26}H_{24}Zr$ calcd.: C, 73.03; H, 5.66; Zr, 21.33%; mol.wt., 428.)

Compound (V). From $(C_5H_5)_2Zr(H)Cl$ and $C_6H_5C{\equiv}CC_6H_5$, an orange solid. (Found: C, 66.3; H, 4.5; Zr, 21.1; mol.wt., 465. $C_{24}H_{21}ClZr$ calcd.: C, 66.12; H, 4.85; Zr, 20.91%; mol.wt., 436.)

Compound (VI). From $(C_5H_5)_2Zr(H)Cl$ (2 moles) and $C_6H_5C{\equiv}CC_6H_5$, a crimson solid which was never obtained completely pure. [Found: C, 60.7; H, 4.6; Zr, 24.8. $C_{34}H_{32}Cl_2Zr_2$ calcd.: C, 58.84; H, 4.65; Zr, 26.28%.)

Compound (VII). From $(C_5H_5)_2ZrH_2$ and $C_6H_5C{\equiv}CC_6H_5$, a brown-black solid. (Found: C, 71.3; H, 5.5; Zr, 21.8; mol.wt., 825. $[C_{24}H_{21}Zr]_2$ calcd.: C, 71.96; H, 5.28; Zr, 22.77%; mol.wt., 801.)

Compound (*VIIIA*). From $(C_5H_5)_2ZrH_2$ and $C_6H_5C{\equiv}CC_6H_5$, red-brown solid. (Found: C, 67.8; H, 5.4; Zr, 24.9; mol.wt., 668. $[C_{19}H_{15}Zr]_2$ calcd.: C, 68.21; H, 4.52; Zr, 27.27%; mol.wt., 669.)

When the product was dissolved in air-free acetone and set aside for two days, long colourless needles of *cis,cis*-1,2,3,4-tetraphenylbutadiene, m.p. 185°, were deposited. (Found: C, 93.9; H, 6.3. $C_{28}H_{22}$ calcd.: C, 93.82; H, 6.18%.)

Compound (*VIIIB*). From $(C_5H_5)_2ZrH_2$ and $CH_3C_6H_4C{\equiv}CC_6H_4CH_3$, red-brown solid. (Found: C, 68.9; H, 5.3; Zr, 25.5; mol.wt., 650. $[C_{21}H_{19}Zr]_2$ calcd.: C, 69.55; H, 5.27; Zr, 25.16%; mol.wt., 725.)

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