Reactions of Titana- and Zircona-cyclopentadienes with Alkynes

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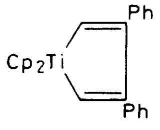
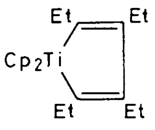
Expanded metallacycles of up to 17 members have been obtained from insertion reactions of acetylenic molecules into the M–C bonds of various substituted dicyclopentadienyl-titana- and -zircona-cyclopentadienes; in one case, a zirconacyclononatetraene with mixed phenyl and methyl substituents was isolated.

Earlier we reported that the apparent mechanism of polymerisation of acetylenes by Cp_2MCl_2–$EtAlCl_2$ (Cp = η^5-cyclopentadienyl, M = Ti, Zr) involved the formation of a metallacyclopentadiene species, followed by successive insertions of alkynes into the metal–carbon bonds, producing expanded metallacycles.[1] In the course of the reaction of but-2-yne catalysed by Cp_2ZrCl_2–$EtAlCl_2$, the presence of dicyclopentadienyl-2,3,4,5-tetramethylzirconacyclopentadiene, a known compound,[2] was detected by ^{1}H n.m.r. spectroscopy. We have now isolated and characterized some of these expanded metallacycles of titanium and zirconium.

Various metallacyclopentadienes (**1**)—(**5**) were prepared by reported methods,[2,3] and allowed to react with alkynes in 2—8 relative molar amounts.



(**1**)



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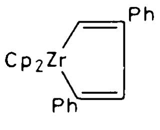

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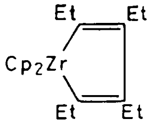
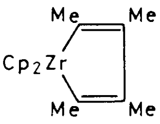
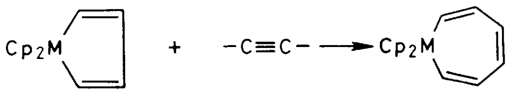


(**4**)



(**5**)



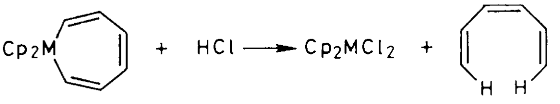
(1)

Substituents are Ph and Et

When small amounts of alkynes were used (2—4 molar excess), metallacycloheptatrienes were obtained. The compounds were isolated in 10—50% yields, based on the starting metallacycle, by repeated chromatography on Florisil or alumina columns, using CCl_4 and non-polar hydrocarbons as the eluants, and their solution n.m.r. and mass spectra recorded. Representative examples are shown in Table 1. The general reaction to produce the metallacycloheptatrienes is as in equation (1).

In order to determine whether the products were metallacycles rather than separately co-ordinated alkynes or smaller units of polyene attached to the metal, they were treated with HCl–$CHCl_3$, leading to the quantitative reaction (2). The hexatrienes thus obtained were examined by n.m.r. and mass spectrometry. The triphenylhexatriene had m.p. 133—134 °C (lit.[4] for 1,3,6-triphenylhexatriene 134 °C), *m/z* 308 (M^+), and a ^{1}H n.m.r. signal at δ 7.1 (m, aromatic and olefinic H). The hexaethylhexatriene was isolated as a colourless liquid, *m/z* 248 (M^+), ^{1}H n.m.r. δ 2.1 and 0.9 (both, 6 × Et, 30H), and 5.3 (t, vinylic H, 2H). The vinylic signal was not observed in the spectrum of the hexaethyl-titana- or -zircona-cycloheptatriene complexes, showing that both ends of the organic ligand are attached to the metal.

Larger metallacycles were also prepared by the same methods, using a greater excess of alkyne (Scheme 1). Spectral properties of the expanded metallacycles and the polyenes recovered after reaction with HCl–$CHCl_3$ are given in Table 2. The mass spectrum of compound (E) also showed fragmentation peaks at *m/z* 312 and 221, corresponding to $C_8H_2(CH_3)_4$-$(C_6H_5)_2^+$ and Cp_2Zr^+, respectively.



(2)

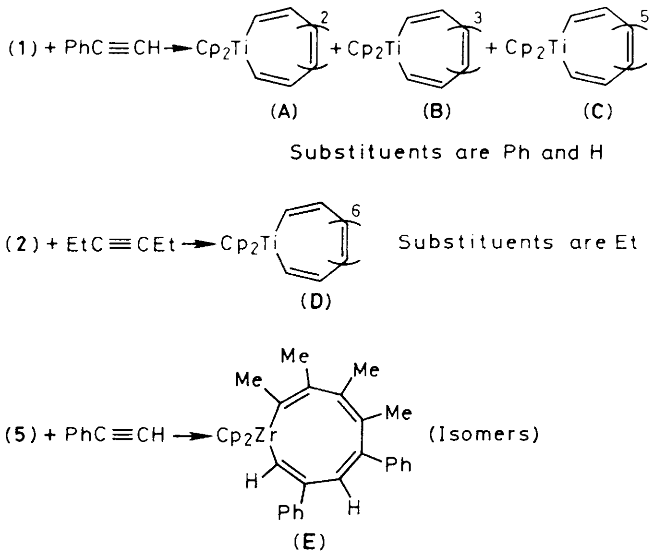
Substituents are Ph and Et

Table 1. ^{1}H N.m.r. and mass spectrometry of the metallacycloheptatrienes.

Starting metallacycle	Alkyne	Metallacycloheptatriene substituents	*m/z*	^{1}H N.m.r. (δ)
(**2**)	EtC≡CEt	Et_6	424 (M^+)	6.5 (s, Cp, 10H), 2.1 (m, CH_2, 12H), 0.8 (m, CH_3, 18H)
(**3**)	PhC≡CH	Ph_3	306 ($C_6H_3Ph_3^+$), 221 (Cp_2Zr^+)	7.0 (m, aromatic and olefinic, 18H), 6.1 (s, Cp, 10H)
(**4**)	EtC≡CEt	Et_6	467 (M^+)	6.1 (s, Cp, 10H), 2.1 (overlapping q, CH_2, 12H), 0.9 (overlapping t, CH_3, 18H)

Table 2

	Metallacycle		Polyene from metallacycle	
Compound	*m/z* (M^+)	^{1}H N.m.r. (δ)	*m/z* (M^+)	^{1}H N.m.r. (δ)
(A)	586	7.2 (m, aromatic and olefinic, 24H), 6.2 (s, Cp, 10H)	410	7.2 (m, aromatic and olefinic)
(B)	688	7.2 (m, aromatic and olefinic, 30H), 6.2 (s, Cp, 10H)	512	7.2 (m, aromatic and olefinic)
(C)	892	7.2 (m, aromatic and olefinic, 42H), 6.2 (s, Cp, 10H)	716	7.2 (m, aromatic and olefinic)
(D)	834	6.6 (s, Cp, 10H), 2.2 (m, CH_2, 32H), 1.2 (m, CH_3, 48H)	658	5.3 (t, vinylic, 2H), 2.1 (m, CH_2, 32H), 0.9 (m, CH_3, 48H)
(E)	533	7.2 (m, aromatic, 10H), 6.05 (Cp, 10H), 5.6, 5.7 (s, vinylic, 2H), 1.4 (m, CH_3, 12H)	314	7.2 (m, aromatic, 10H), 6.3 (m, olefinic, 4H), 1.1—1.6 (m, CH_3, 12H)



Scheme 1

Lei and Teuben[5] have shown that acetylenic molecules can insert into Ti–vinyl bonds to produce conjugated dienes. The fact that metallacycles of up to 17 members can be produced from smaller ones indicates that a similar insertion mechanism occurs in these reactions. Under investigation is the possibility that an analogous mechanism may occur in Ziegler–Natta polymerisation of olefins by certain catalysts.

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