

## ALKYLZIRCONIUM-(III) AND -(IV) COMPLEXES

T. CUENCA and P. ROYO

*Departamento de Química Inorgánica, Universidad de Alcalá de Henares (Spain)*

(Received April 22nd, 1985)

### Summary

The complex  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}]_2$  is oxidized by acetylenes  $\text{PhC}\equiv\text{CR}$  ( $\text{R} = \text{H}, \text{Ph}$ ) to give dimeric alkenediylzirconium(IV) derivatives and can be methylated with  $\text{LiMe}$  and  $\text{AlMe}_3$ . The methyl complex obtained in the reaction with  $\text{LiMe}$  is a diamagnetic solid characterized as  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrMe}]_2$  by  $^1\text{H}$  NMR spectroscopy. This compound is reversibly acylated by  $\text{CO}$ , and the equilibrium can be displaced by simultaneous oxidation to give the  $\eta^2$ -acetylzirconium(IV) complex  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\eta^5\text{-COMe})_2(\mu\text{-O})]$ . The analogous insertion of  $\text{CyNC}$  ( $\text{Cy} = \text{cyclohexyl}$ ) goes to completion, and the resulting diamagnetic dimer  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\eta^2\text{-CMe=NCy})_2]$  has been characterized by IR and NMR spectroscopy. The methylzirconium(III) complex is a strong reducing agent, being oxidized by  $\text{AgClO}_4$  with deposition of metallic silver and by  $\text{I}_2$  to give  $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrI}_2$  and  $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrIME}$ .

### Introduction

The formation of various paramagnetic alkylzirconium(III) complexes has been demonstrated by ESR studies on chemical, photochemical or electrochemical reductions of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrR}_2$  and  $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrClR}$  [1,2,3] but only one type of organozirconium(III) dinitrogen complex has been isolated [4].

An earlier paper described the isolation and reactivity of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}]_2$  [5]. We report here the oxidation of this complex with alkynes and the NMR characterization of a diamagnetic methylzirconium(III) complex and its behaviour in oxidation and insertion reactions with  $\text{CO}$  and  $\text{CyNC}$  ( $\text{Cy} = \text{cyclohexyl}$ ).

### Results and discussion

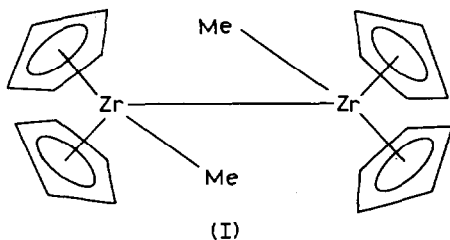
#### *Methylzirconium(III)*

We examined two methods of obtaining methylzirconium(III), namely the reduction of chloromethylzirconium(IV) and the methylation of the chlorozirconium(III) complexes.

$(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrClMe}$  was made as previously described [6]. We also tried to make it by reaction of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$  with  $\text{LiMe}$  and  $\text{AlMe}_3$ . The reaction with 1 mol of  $\text{LiMe}$  gives the expected complex along with a smaller amount of the dimethyl derivative, the starting dichloride, and the  $\mu$ -oxo complex produced by hydrolysis. The subsequent separation lowers the yield, so that the method is not satisfactory. The reaction with  $\text{AlMe}_3$  does not give the expected methyl complex, but only the dimethyl derivative along with unreacted starting dichloride.

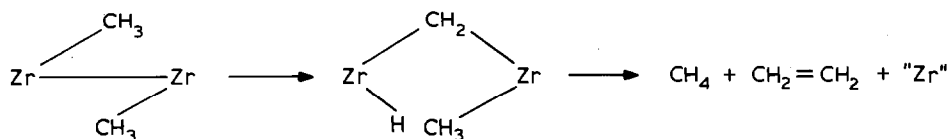
Reduction of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrClMe}$  with  $\text{Na/Hg}$  in THF takes place without change of colour and gives unidentified diamagnetic zirconium(IV) derivatives, as reported for other alkyl zirconium(III) complexes characterized by ESR at low temperatures in electrochemical reductions [2]. Different behaviour is observed for the methylation of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}]_2$  [5].

The reaction of a toluene red solution of the halozirconium(III) complex with one equivalent of  $\text{LiMe}$ , followed by filtration and evaporation of the solvent, gives a red oil which cannot be crystallized, but after several days under vacuum gives a deep red diamagnetic solid. The  $^1\text{H}$  NMR spectrum of the solution obtained when this oil is extracted with benzene- $d_6$  is clean and shows only two singlets with an intensity ratio 10/3 at  $\delta$  5.80 and 0.37 ppm which must be assigned respectively to the  $(\eta^5\text{-C}_5\text{H}_5)$  and Me protons of a methylzirconium(III) complex. No toluene signals are observed in this spectrum. When the same reaction is carried out in THF, a similar red oil is obtained, which shows exactly the same spectrum except that THF signals are always present, as two multiplets at  $\delta$  3.76 and 1.56 ppm. The chemical shift observed for the Me protons suggests the presence of a terminal methyl group [7], corresponding with a structure which must contain a zirconium-zirconium bond.



The reaction of a pentane suspension of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}]_2$  with one mol of  $\text{AlMe}_3$  (toluene 10%) gives a red solution, which after filtration and evaporation of the solvent yields a red oil. The  $^1\text{H}$  NMR spectrum of the solution obtained by extraction of this oil with benzene- $d_6$  shows two singlets, with an intensity ratio 10/3 at  $\delta$  5.80 ppm due to the  $(\eta^5\text{-C}_5\text{H}_5)$  ring and at  $\delta$  0.42 ppm, along with a singlet at  $\delta$  3.00 ppm due to  $\text{CH}_3\text{O-Al}$  produced by traces of oxygen and a multiplet at  $\delta$  -0.34 ppm due to  $\text{Me-Al}$ . The position of the methyl-zirconium singlet at  $\delta$  0.42 ppm suggests the presence of  $\text{Zr-Me-Al}$  species [8]. It appears that the reactions with  $\text{LiMe}$  and  $\text{AlMe}_3$  both give the same methylzirconium(III) complex, but the product from the  $\text{AlMe}_3$  reaction cannot be freed from aluminum-containing products. Benzene solutions of the complex prepared from  $\text{AlMe}_3$  remain unchanged at least for 3 days under argon. The red solid obtained from  $\text{LiMe}$  is fairly stable under argon, but its high sensitivity to air prevented analysis. Its red benzene solution decomposes under argon, the colour going through black to yellow in 10-12 h; important changes are observed in the  $^1\text{H}$  NMR spectrum, which shows

complex multiplets in the region of the Me and ( $\eta^5\text{-C}_5\text{H}_5$ ) protons. The  $^{13}\text{C}$  NMR spectrum recorded after this 12 h period shows a multiplet between  $\delta$  110.54 and 112.71 and a singlet at 179.9 ppm. The presence of this low field resonance suggests that decomposition takes place through an intermediate species containing a methylene bridge [9].



The gas evolved during decomposition was studied by gas chromatography and identified as a mixture of methane with a smaller amount of ethylene.

### Acetylene complexes

Addition of alkynes  $\text{PhC}\equiv\text{CR}$  ( $\text{R} = \text{H}, \text{Ph}$ ) to toluene solutions of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}]_2$  gives pale yellow orange solutions which after evaporation of the solvent give crystalline  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}]_2(\mu\text{-PhC}=\text{CR})$  (II:  $\text{R} = \text{H}$ ; III:  $\text{R} = \text{Ph}$ ); the analytical data are shown in Table 1.

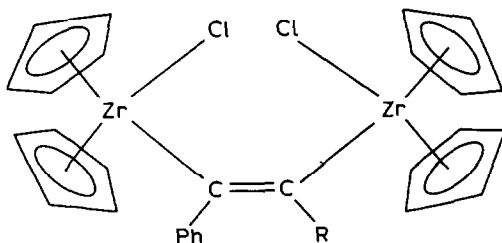
The  $^1\text{H}$  NMR spectrum of complex III shows a low field singlet at  $\delta$  6.00 ppm, corresponding to a zirconium(IV) derivative with all the ( $\eta^5\text{-C}_5\text{H}_5$ ) rings equivalent, and two multiplets at  $\delta$  6.94 and 7.41 ppm due to phenyl protons of the acetylene. The  $^{13}\text{C}$  NMR spectrum of III shows a singlet at  $\delta$  113.68 ppm for ( $\eta^5\text{-C}_5\text{H}_5$ ) a singlet at  $\delta$  113.02 ppm for two equivalent acetylenic carbon atoms, and signals at  $\delta$  128–130 ppm coincident with those from the solvent (toluene).

The  $^1\text{H}$  NMR spectrum of complex II exhibits two low field singlets of the same intensity at  $\delta$  6.00 and 6.07 ppm showing that the zirconium(IV) compound contains inequivalent  $\eta^5\text{-C}_5\text{H}_5$  rings, and two multiplets at  $\delta$  7.34 and 7.41 ppm due to phenyl protons of the acetylene. No signal is observed for the acetylenic proton.

TABLE 1  
ANALYTICAL DATA FOR ZIRCONIUM COMPLEXES

Complex	Colour	Analyses (Found (Calcd.) (%))	
		C	H
$(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}(\overline{\text{PhC}=\text{CH}})\overline{\text{ClZr}}(\eta^5\text{-C}_5\text{H}_5)$ (II)	orange-red	53.45 (53.71)	4.62 (4.34)
$(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}(\overline{\text{PhC}=\text{CPh}})\overline{\text{ClZr}}(\eta^5\text{-C}_5\text{H}_5)_2$ (III)	orange-red	58.84 (59.02)	4.53 (4.37)
$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\eta^2\text{-COMe})]_2(\mu\text{-O})$ (VI)	Yellow	52.22 (52.48)	4.59 (4.80)
$(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrI}_2$ (VII)	Yellow-orange	25.73 (25.26)	2.44 (2.12)
$(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrIme}$ (VIII)	Yellow	35.39 (36.35)	3.00 (3.60)

These data are consistent with a dimeric structure with both zirconium atoms bonded to an alkenediyl group.

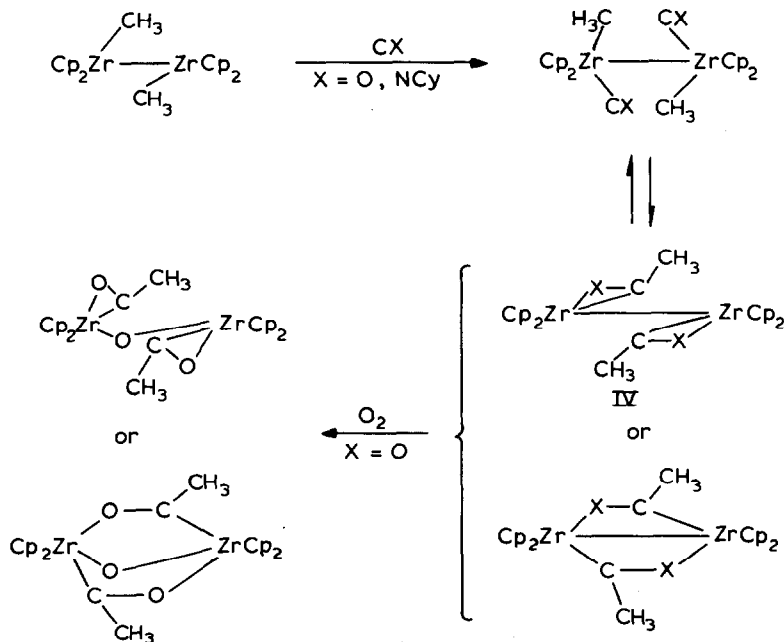


When  $R = \text{Ph}$  all the ( $\eta^5\text{-C}_5\text{H}_5$ ) rings are equivalent, whereas when  $R = \text{H}$  the rings bonded to a different metal atom are inequivalent.

In keeping with this proposed structure, complex III reacts with  $\text{HCl}$  to give  $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$  and a solution which contains *cis*-stilbene (as shown by GLC). It must thus be concluded that the chlorozirconium(III) complex reduces acetylenes to give the corresponding alkenediyl derivatives.

### Reactions of the methylzirconium(III) complex with CO and CyNC

When CO is bubbled at room pressure through a benzene solution of I, the  $^1\text{H}$  NMR spectrum shows two new singlets at  $\delta$  5.50 and 2.37 ppm in an intensity ratio of 10/3, along with the two more intense singlets due to the starting compound at  $\delta$  5.80 and 0.37 ppm, also in an intensity ratio of 10/3. Using available data [10] we can assign these two singlets to an  $\eta^2$ -acyl derivative (IV) formed reversibly in the second step of the reaction sequence shown in Scheme 1.



SCHEME 1

The equilibrium for this reversible reaction is shifted towards the acyl derivative when dry oxygen is bubbled through the red solution, and the colour changes immediately to yellow. After filtration, concentration and cooling at  $-40^{\circ}\text{C}$  a crystalline yellow solid is obtained and this has been identified as  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{COCH}_3)_2](\mu\text{-O})$  (VI), as indicated by the analytical data shown in Table 1, and the spectroscopic features discussed below.

The IR spectrum of II shows an absorption at  $1500\text{ cm}^{-1}$  which must be assigned to the  $\nu(\text{CO})$  stretching vibration of a  $\eta^2\text{-COCH}_3$  group [10] and a broad band at  $700\text{--}800\text{ cm}^{-1}$  due to the  $\nu(\text{ZrO})$  bond. The  $^1\text{H}$  NMR spectrum in benzene- $d_6$  shows two singlets at  $\delta$  6.17 and 2.09 ppm, respectively, assigned to the  $(\eta^5\text{-C}_5\text{H}_5)$  and Me protons of the oxidized  $\mu$ -oxozirconium complex (VI). We cannot distinguish between chelate or bridge  $\eta^2\text{-COCH}_3$  groups on the available data.

In a similar reaction the addition of cyclohexyl isocyanide to a toluene solution of I gives a red solution, which after filtration and evaporation under vacuum for 1 week yields a red solid. This solid is highly sensitive to air, and so analytical data could not be obtained but it is stable under argon as a solid and in solution.

The IR spectrum shows an absorption band at  $1628\text{ cm}^{-1}$  assignable to the  $\nu(\text{CN})$  stretching vibration displaced to lower frequencies  $250\text{--}300\text{ cm}^{-1}$  with respect to other  $\text{MRC}=\text{NR}$  systems [11]. This displacement suggests the presence of a dihapto  $\eta^2\text{-CR}(\text{NR})$  group. The  $^1\text{H}$  NMR spectrum shows a complex multiplet due to the cyclohexyl protons and two singlets at  $\delta$  5.42 and 2.04 ppm in an intensity ratio of 10/3 which must be assigned to the  $(\eta^5\text{-C}_5\text{H}_5)$  and Me groups of a zirconium(III) complex. In contrast to the acylation, this insertion reaction goes to completion and no signal of the starting complex is observed.

The complex immediately turns yellow in air but a  $\mu$ -oxozirconium(IV) complex could not be isolated because simultaneous cleavage of the Zr-C bond occurs.

### Reactions with oxidants

Complex I reacts with  $\text{AgClO}_4$  with deposition of metallic silver, the colour of the solution changing from red to yellow, this solution was not further investigated as simultaneous cleavage of the Zr-Me bond takes place.

Complex I is also readily oxidized by iodine to give solutions from which a mixture of two iodo compounds was isolated. These were separated by extraction with pentane. The insoluble residue was recrystallized and identified as  $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrI}_2$  (VII) [7] (see analytical data in Table 1); its  $^1\text{H}$  NMR spectrum shows a singlet at  $\delta$  6.03 ppm. Evaporation of pentane from the soluble fraction gives yellow crystalline  $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrI}(\text{CH}_3)$  (VIII) (see analytical data in Table 1); its  $^1\text{H}$  NMR spectrum shows two singlets (intensity 10/3) at  $\delta$  6.09 and 0.34 ppm. Complex V is formed even when a deficiency of  $\text{I}_2$  is used, revealing the ease of cleavage of the Zr-Me bond.

### Experimental

All experiments were performed under argon or vacuum using Schlenk type glassware, with solvents previously distilled, were degassed and dried immediately.  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}]_2$  was prepared as previously reported [5]. Commercial LiMe (Alfa),  $\text{AlMe}_3$  (Ethyl Co.),  $\text{PhC}\equiv\text{CR}$  (Alfa) were used without further purification.

TABLE 2  
 IR AND NMR DATA FOR ZIRCONIUM COMPLEXES

Complex	$\nu(\text{C}=\text{X})$ ( $\text{cm}^{-1}$ ) (X = O, NCy)	NMR <sup>a</sup>	
		<sup>1</sup> H	<sup>13</sup> C
$[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrMe}]_2$ (I)		5.80(10), s, Cp 0.37(3), s, Me	
$(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}(\overline{\text{PhC}=\text{CH}})\text{ClZr}(\eta^5\text{-C}_5\text{H}_5)_2$ (II)		6.00(10), s, Cp 6.07(10), s, Cp 7.11–7.34(6), m, Ph	
$(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}(\overline{\text{PhC}=\text{CPh}})\text{ClZr}(\eta^5\text{-C}_5\text{H}_5)_2$ (III)		6.00(10), s, Cp 7.01–7.49(12), s, Ph	113.02, s, C=C 113.68, s, Cp 128–130, m, Ph
$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\eta^2\text{-COMe})]_2$ (IV)		5.50(10), s, Cp 2.37(3), s, COMe	
$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\eta^2\text{-MeCNCy})]_2$ (V)	1628	5.42(10), s, Cp 2.04(3), s, MeCN- 1.10–1.50, m, Cy	
$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{COMe})]_2(\mu\text{-O})$ (VI)	1500	6.17(10), s, Cp 2.09(3), s, COMe	
$(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrI}_2$ (VII)		6.03, s, Cp	
$(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrIme}$ (VIII)		6.09(10), s, Cp 0.34(3), s, Me	

<sup>a</sup> Data presented as chemical shift ( $\delta$ ), (relative intensity), multiplicity, assignment. Recorded in benzene-*d*<sub>6</sub>.

CyNC was prepared as described elsewhere [12]. IR spectra were recorded on a Perkin–Elmer 599 spectrophotometer (in the range 4000–200  $\text{cm}^{-1}$ ) using Nujol mulls or KBr pellets. NMR spectra were recorded on a Varian FT80A spectrometer. Gas-chromatography was carried out in a Perkin–Elmer Sigma 3B apparatus. C, H analyses were carried out with a Perkin–Elmer 240B microanalyzer.

Infrared and NMR spectral data for compounds I–VIII are given in Table 2.

#### Methylation of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}]_2$

(a) A solution of 0.513 g (1.00 mmol) of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}]_2$  in 50 ml of toluene was treated with 1.25 ml of a 1.6 M solution of LiMe in ether (2.00 mmol). The mixture was stirred for 5 h at room temperature. LiCl was filtered off and the solution evaporated to dryness. The residue was kept under vacuum for 4 days, then characterized by <sup>1</sup>H NMR spectroscopy.

The same reaction occurs in THF in a shorter time.

(b) A toluene (50 ml) solution of 0.513 g (1.00 mmol) of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}]_2$  was treated with 2.00 mmol of AlMe<sub>3</sub> (10% toluene solutions). After stirring for 5 h the solution was filtered and evaporated under vacuum to give a red oil, which was characterized by <sup>1</sup>H NMR spectroscopy.

The reaction was better carried out using a suspension of the zirconium complex in pentane. After filtration the solution was handled similarly.

*Reaction of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}]_2$  with  $\text{PhC}\equiv\text{CR}$  ( $R = \text{H}, \text{Ph}$ )*

An excess of the acetylene (0.75 mmol) was added to a toluene (50 ml) solution of 0.513 g (1.00 mmol) of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}]_2$ . The colour slowly changed from red into orange overnight. The solution was filtered and evaporated to dryness. The residue was repeatedly washed with diethyl ether then recrystallized from toluene, to give complex II or III. Yields: 50–60%.

*Reaction of complex I with CO*

When CO gas was bubbled for 0.5 h through a benzene- $d_6$  (50 ml) solution of I, prepared as above, no change in colour was observed. This solution was studied by  $^1\text{H}$  NMR spectroscopy. When oxygen was then slowly bubbled through the colour changed from red to yellow.

After filtration the solution was evaporated to 10 ml, and cooling at  $-40^\circ\text{C}$  gave a crystalline solid which was identified as VI. Yield. 70%.

*Reaction of complex I with CyNC*

0.22 g (2.00 mmol) of CyNC were added to a toluene (50 ml) solution of I (1.00 mmol) and the mixture was stirred for 4 h without apparent change in colour. After evaporation a red oil was obtained, and this gave a red solid when kept under vacuum. The solid was characterized by IR and  $^1\text{H}$  NMR spectroscopy as complex V.

*Reaction of complex I with  $\text{I}_2$*

A toluene (10 ml) solution of 0.63 g (1.00 mmol) of  $\text{I}_2$  was added to a toluene solution of I, prepared as above, containing 1 mmol of I. The colour changed immediately from red to yellow-orange, and stirring was continued for 2 h. The solution was evaporated to dryness and the solid residue was extracted with pentane. The insoluble residue gave VII after recrystallization from toluene. The pentane solution gave yellow crystals of VIII on evaporation.

### Acknowledgements

The authors greatly appreciate financial support from Comisión Asesora de Investigación Científica y Técnica (Spain) R. 2001/83.

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