

## PREPARATION AND CHEMICAL BEHAVIOUR OF HALODICYCLOPENTADIENYL-ZIRCONIUM(III) AND -HAFNIUM(III)

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### Summary

Reduction of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{MCl}_2$  (M = Zr, Hf) with one equivalent of Na/Hg gives  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{M}(\mu\text{-Cl})_2]$ . The zirconium(III) complex is also obtained from reactions between LiCp and  $[\text{ZrCl}_3\text{L}_2]_2$  ( $\text{L}_2 = 2\text{P-n-Bu}_3$ , dppe) or solutions of  $\text{ZrCl}_4$  previously reduced with Na/Hg. These zirconium(III) and hafnium(III) complexes are oxidized by  $\text{AgBF}_4$  or  $\text{TlBF}_4$  to the cationic  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{M}(\mu\text{-Cl})_2]^{2+}$  complexes, which react with monodentate ligands to give  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{MCIL}]^+$  (L =  $\text{OPPh}_3$ ,  $\text{NHPH}_2$ ) and with bidentate ligands to give dinuclear cationic derivatives  $\{[(\eta^5\text{-C}_5\text{H}_5)_2\text{MCl}]_2(\mu\text{-L-L})\}^{2+}$  (L-L-dppe, 2,2'-bipyridine). Similar complexes can also be obtained from  $(\eta^5\text{-C}_5\text{H}_5)_2\text{MCl}_2$  by halide abstraction with a silver salt. Oxidation of zirconium(III) and hafnium(III) derivatives with halogens gives  $(\eta^5\text{-C}_5\text{H}_5)_2\text{MCIX}$  (X = Cl, Br) and  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}(\text{OPPh}_3)]\text{I}_3$ . Conductivity, magnetic susceptibility and IR and NMR data are discussed.

### Introduction

The reduction of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$  by  $\text{LiPR}_2$  [1], Na-Hg, or  $\text{NaC}_{10}\text{H}_8$ , 1,1'-bipyridine sodium [2] or electrochemically [3] has been reported previously. Photolysis of zirconozene(IV) alkyls, chlorides and hydrides gave various zirconium(III) species, which were characterized by ESR spectroscopy [4], and thermal decomposition of zirconozene(II) derivatives gave several dimeric zirconium(III) complexes [5]. The complex  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}]_2$  has been recently prepared [6] by comproportionation between the corresponding zirconium(IV) dihalide and zirconium(II) dicarbonyl and some other zirconozene(III) alkyls have been described [7,8]. However, only a very few zirconium(III) compounds are known and they are mostly rather ill-characterized. The hafnium(III) analogues are even more rare [9].

TABLE 1  
ANALYTICAL DATA AND CONDUCTIVITY MEASUREMENTS

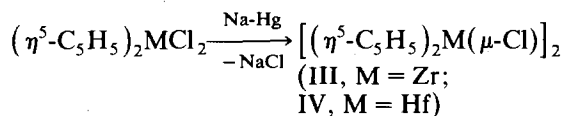
Complex	Analyses (Found(calcd)(%)			$\Lambda_{\max}^a$ ( $\text{ohm}^{-1} \text{mol}^{-1} \text{cm}^2$ )
	C	H	N	
III $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\mu\text{-Cl})]_2$	46.73 (46.76)	4.38 (3.92)		
IV $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Hf}(\mu\text{-Cl})]_2$	34.23 (34.90)	3.47 (2.93)		
V $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\mu\text{-Cl})]\text{BF}_4$	32.64 (33.21)	3.53 (3.34)		168
VI $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Hf}(\mu\text{-Cl})]\text{ClO}_4$	26.72 (27.06)	3.14 (3.98)		177
VII $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}(\text{OPPh}_3)]\text{ClO}_4$	52.48 (52.98)	4.16 (3.98)		104
VIII $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}(\text{NHPh}_2)]\text{ClO}_4$	50.01 (50.26)	4.56 (3.99)	3.23 (2.66)	97
IX $\{[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}]_2(\mu\text{-dppe})\}(\text{ClO}_4)_2$	49.71 (50.60)	3.97 (4.30)		178
X $\{[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}]_2(\mu\text{-bipy})\}(\text{ClO}_4)_2$	43.70 (43.90)	3.95 (4.09)	1.91 (2.85)	163
XI $[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfCl}(\text{OPPh}_3)]\text{ClO}_4$	47.32 (45.56)	4.10 (3.47)		103
XII $\{[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfCl}]_2(\mu\text{-bipy})\}(\text{ClO}_4)_2$	34.05 (34.50)	3.19 (2.68)	3.24 (2.68)	169
XIII $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$	41.07 (41.15)	3.42 (3.85)		
XIV $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrClBr}$	35.74 (35.64)	3.25 (2.97)		
XV $(\eta^5\text{-C}_5\text{H}_5)_2\text{HfCl}_2$	31.49 (31.58)	2.79 (2.62)		
XVI $(\eta^5\text{-C}_5\text{H}_5)_2\text{HfClBr}$	29.37 (28.30)	2.62 (2.36)		
XVII $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}(\text{OPPh}_3)]\text{I}_3$	36.44 (36.72)	2.92 (2.75)		100

<sup>a</sup> Ca.  $5 \times 10^{-4} M$  in acetone.

## Results and discussion

### Syntheses of metal(III) complexes

When a yellow solution of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{MCl}_2$  (I, M = Zr; II, M = Hf) was added to one equivalent of 10% sodium amalgam, the solution became deep-red and reaction is complete in 1 h in THF or 5–6 h in toluene. After filtration the solution was evaporated to give an oil, which was kept for 24 h under reduced pressure to yield deep red solids, which were shown to be complexes III and IV on the basis of structural studies and their analytical compositions, shown in Table 1.

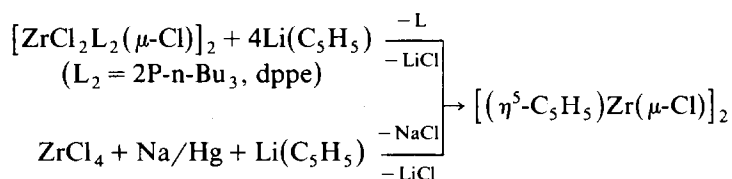


The same products are obtained if  $\text{PMe}_2\text{Ph}$  or dppe is previously added to the

reacting solutions, and the unchanged free ligand can be readily eliminated by washing with diethyl ether and hexane.

Complex III has been unambiguously isolated and characterized by Floriani [6] from the reaction between  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{CO})_2$  and  $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$ . Many other attempts to make III by a similar reduction have been reported to give impure solids with a variable analytical composition, and an olive-green adduct  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}]_2 \cdot \text{C}_6\text{H}_6$  which was obtained by extraction with benzene [2]. We never observed the formation of this green solid; and extraction with benzene of our oily residues gives red solutions, which upon evaporation also leave oils which after being kept under reduced pressure for several days give red solids, with analytical compositions accurately correct for samples from several runs of III and IV. Our complex III is red, not green as described by Floriani [6], but similar colour variations have been observed for other zirconium derivatives [10].

In order to confirm the nature of our complexes we tried to obtain them by a different method. It has been reported [11] that  $\text{TlCp}$  is reduced to thallium metal by  $[\text{ZrCl}_3\text{L}_2]_2$ ; we have carried out a similar reaction using  $\text{LiCp}$  and found that substitution and ligand elimination take place to give the same red complex III.



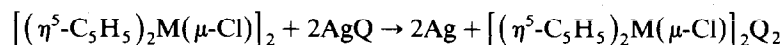
This method is not satisfactory because the need to remove  $\text{LiCl}$  and the free phosphine results in lower yields. A better method involves addition of  $\text{Li}(\text{C}_5\text{H}_5)$  to toluene solutions of  $\text{ZrCl}_4$  previously reduced with one equivalent of  $\text{Na/Hg}$ . The resulting red solutions after evaporation to dryness and extraction with toluene give the same red complex III.

Both zirconium(III) and hafnium(III) complexes are stable under argon but are oxidized by traces of oxygen quite readily as solids and, rapidly, in solution, to give the  $\mu$ -oxometal(IV) complexes, as indicated by a broad IR absorption around  $750 \text{ cm}^{-1}$ .

#### *Oxidation with silver(I) or thallium(I)*

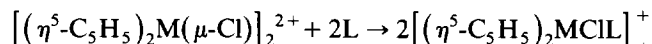
The reactions of III and IV with silver(I) and thallium(I) salts were examined.

Addition of one equivalent of  $\text{AgBF}_4$  or  $\text{AgClO}_4$  to toluene solutions of III and IV gave a brown black solid which after extraction with acetone gave metallic silver and yellow solutions. The latter on evaporation yielded green-yellow ( $\text{M} = \text{Zr}$ ) or pale yellow ( $\text{M} = \text{Hf}$ ) crystals of V and VI, as indicated by the analytical data in Table 1

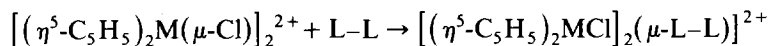


(V:  $\text{M} = \text{Zr}$ ,  $\text{Q} = \text{BF}_4$ ; VI:  $\text{M} = \text{Hf}$ ,  $\text{Q} = \text{ClO}_4$ )

The addition of various ligands to THF solutions of V and VI gave, after evaporation, the cationic complexes VII–XII, (see analytical data in Table 1):



(VII:  $\text{M} = \text{Zr}$ ,  $\text{L} = \text{OPPh}_3$ ; VIII:  $\text{M} = \text{Zr}$ ,  $\text{L} = \text{NHPPh}_2$ ; XI:  $\text{M} = \text{Hf}$ ,  $\text{L} = \text{OPPh}_3$ )

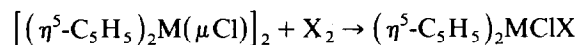


(IX: M = Zr; L-L = dppe; X: M = Zr; L-L = bipy; XII: M = Hf; L-L = bipy)

The same oxidation is brought about by TIBF<sub>4</sub>, and metallic thallium is deposited. Similar behaviour has been described [11] for other zirconium(III) compounds. When the oxidation is carried out with Tl(C<sub>5</sub>H<sub>5</sub>), metal is also formed but the expected  $\sigma\text{-C}_5\text{H}_5\text{Zr(IV)}$  complex cannot be isolated, and workup of the yellow solution always results in decomposition.

#### *Oxidation with halogens*

Addition of a solution of Cl<sub>2</sub> or Br<sub>2</sub> to THF solutions of III and IV in an M/X<sub>2</sub> molar ratio of 2/1 produced pale yellow solutions which on evaporation under reduced pressure gave crystals of halogeno complexes XIII–XVI, as indicated by the analytical data shown in Table 1 and according to the following equation:



(XIII: M = Zr, X = Cl; XIV: M = Zr, X = Br; XV: M = Hf, X = Cl;

XVI: M = Hf, X = Br)

The dichloro complexes XIII and XV were characterized by comparison with authentic samples obtained as described previously [12]. Complexes XIV and XVI have been reported as products of redistribution reactions [ref. 12].

Analogous reactions take place with I<sub>2</sub>, but the resulting iodo complexes are highly reactive so readily hydrolysed, and cannot be obtained as pure compounds. However, when III is oxidized with an additional mole of I<sub>2</sub> in the presence of OPPh<sub>3</sub>, a blue precipitate was formed, and after being dried under vacuo this was characterized as  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl(OPPh}_3)]^+ \text{I}_3^-$  (XVII).

### **Structural studies**

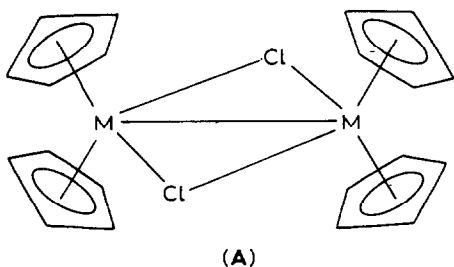
#### *Complexes III–IV*

These complexes were found to be diamagnetic in the solid state at room temperature under dry N<sub>2</sub>. This behaviour confirms the presence of a metal–metal bond.

The IR absorptions at 3050–3010, 1018–1022, 1010–1015 and 810–850 cm<sup>-1</sup> characteristic of ( $\eta^5\text{-C}_5\text{H}_5$ ) ligands reveal the presence of such ligands. There are no absorptions in the region between 400–250 cm<sup>-1</sup>, suggesting that both chlorine atoms are engaged in bridging.

The low thermal stability of the complexes and their high reactivity towards traces of oxygen make it difficult to study the <sup>1</sup>H and <sup>13</sup>C NMR spectra. Complex III gives a <sup>1</sup>H spectrum with a singlet at  $\delta$  5.13 ppm and a <sup>13</sup>C spectrum showing a singlet at  $\delta$  113.75 ppm in benzene-*d*<sub>6</sub>, due to the ( $\eta^5\text{-C}_5\text{H}_5$ ) rings. In our experiments, the singlets of  $\delta$  5.85 and 114.8 ppm due to some  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}]_2(\mu\text{-O})$  were always present.

These data enable us to formulate III and IV as dimers, with a metal–metal bond and two chlorine bridges in the same plane and four equivalent ( $\eta^5\text{-C}_5\text{H}_5$ ) rings occupying pseudotetrahedral positions (structure A).



This formulation agrees with previous proposals [3,6] and fits in with Lahuer-Hoffman's predictions [13] for this type of complexes.

#### Cationic metal(IV) complexes

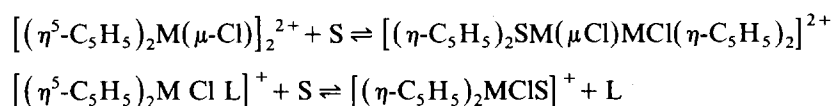
All these complexes are diamagnetic at room temperature, as expected for metal(IV) derivatives.

IR characteristic absorptions for the various ligands are observed. It is noteworthy that there are: (a) absorption bands between  $350\text{--}410\text{ cm}^{-1}$  for complexes containing N-M bonds; (b) a strong broad absorption for complexes containing free  $\text{ClO}_4^-$  between  $1050\text{--}1100\text{ cm}^{-1}$ ; and (c) the strong  $\nu(\text{P}=\text{O})$  absorption noted for free  $\text{OPPh}_3$  at  $1200\text{ cm}^{-1}$  is absent for complexes VII and VI, indicating that a shift to lower frequency brings this band under the stronger  $\text{ClO}_4^-$  band.

$^1\text{H}$  NMR were recorded, in acetone- $d_6$ , for zirconium complexes only. The single ( $\eta^5\text{-C}_5\text{H}_5$ ) resonance expected for all the cationic derivatives is observed at  $\delta 6.40$  and  $6.44$  ppm for VIII and X, respectively whereas the remaining compounds except IX show two singlets. This second resonance observed at  $\delta 6.47$  (V),  $6.43$  (VII) probably arises from the presence in solution of solvated species.

Complex IX shows a doublet due to the splitting produced by the phosphorous ligand,  $J(\text{P-H})$  2.4 Hz.

The solvation equilibria do not significantly change the total number of ions in solution as shown by conductivity measurements. The conductivities shown in Table 1 for complexes VII, VIII and XI are in the region expected for 1/1 electrolytes [14], whereas those for IX, X, XII are close to the values characteristic of 2/1 electrolytes. Thus, the solvation equilibria must be of the type represented in the following equations:



The complexes with bidentate ligands remain unchanged, and only one singlet  $^1\text{H}$  NMR is observed.

The results enable us to formulate V and VI as dimer dications containing two chlorine bridges.

Thus the oxidation of metal(III) dimers involves only the cleavage of the metal-metal bond. The chlorine bridges are readily cleaved by O, N or P donors, to give mononuclear cationic species with monodentate ligands  $[(\eta\text{-C}_5\text{H}_5)_2\text{MCIL}]^+$  (VII, VIII, XI). The corresponding reaction with bidentate ligands gives dinuclear

cations (IX, X, XII) with the ligand bridging between the two metal atoms.

The properties of complex XVII, obtained by oxidation with  $I_2$ , are similar to those described for VIII.

#### *Neutral metal(IV) complexes*

Complexes XIII–XVI are diamagnetic at room temperature and non conducting in acetone, as expected.

IR and NMR data for XIII and XV agree with those described elsewhere [12, 15]. The  $^1H$  ( $\eta^5-C_5H_5$ ) resonance for XIV appears as a singlet at  $\delta 5.85$  ppm.

#### **Experimental**

All experiments were performed under argon using Schlenk-type glassware. Solvents were distilled under  $N_2$ , dried by standard methods, and degassed before use. The starting complexes  $(\eta^5-C_5H_5)_2MCl_2$  ( $M = Zr, Hf$ ) and  $[ZrCl_3L_2]_2$  ( $L = 2P-n-Bu_3, dppe$ ) were synthesized as described elsewhere [11,12]. The C, H, and N analysis were carried out on a Perkin–Elmer 240B microanalyzer. Conductivity measurements were carried out in a LF-42 conductimeter.

Infrared spectra between 4000 and 200  $cm^{-1}$  were recorded as Nujol mulls on a 505 Perkin–Elmer spectrophotometer. The  $^1H$  and  $^{13}C$  NMR spectra were recorded on a Varian FT-80A instrument in benzene- $d_6$ , acetone- $d_6$ , or chloroform- $d$ . Magnetic susceptibilities were measured by the Faraday method at room temperature with a Bruker magnet system.

#### $[(\eta^5-C_5H_5)_2M(\mu-Cl)]_2$ (III, IV)

(a) A mixture of 1 mmol of  $(\eta^5-C_5H_5)_2MCl_2$  and 1.05 mmol of 10% sodium amalgam in 60 ml of THF or toluene was stirred for 1 h (THF) or 6 h (toluene). The deep red solutions were filtered, and the solvent was evaporated off under reduced pressure to leave red oils. After 48 h under vacuum these gave red solids, which were identified as complexes III and IV. Yields were 60%.

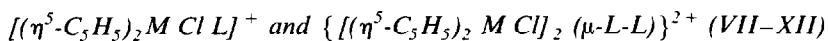
(b) A second method involved addition of a solution of 2 mmol of  $Li(C_5H_5)$  in 20 ml of THF to a suspension of 0.5 mmol of  $[ZrCl_3L_2]_2$  ( $L_2 = 2P-n-Bu_3, dppe$ ) in 100 ml of toluene. A red solution was formed during 0.5 h of stirring at room temperature, and this was filtered and evaporated. The residue was repeatedly washed with hexane and identified as complex III.

(c) A solution of 1 mmol  $ZrCl_4$  in 100 ml of toluene was added to one equivalent of Na-Hg (10%). After 48 h stirring the dark-brown suspension was treated with a solution of 2 mmol of  $Li(C_5H_5)$  in 20 ml of THF. The red solution obtained was filtered and worked up as above, to give complex III.

#### $[(\eta^5-C_5H_5)_2M(\mu-Cl)]_2^{2+}$ (V, VI)

To a solution of 1 mmol of III or IV in 50 ml of THF was added 1 mmol of  $AgBF_4$ ,  $AgClO_4$  or  $TiBF_4$ . The mixture was stirred at room temperature for 2 h then the black metallic residue was filtered off and the solvent evaporated to give a crystalline green-yellow (Zr) or yellow (Hf) solid, identified as IV and V.

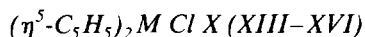
When the solvent was toluene, the solid filtered off contained IV and V, which were insoluble in this solvent. After extraction with acetone, V and VI were obtained on evaporation. Yields 70% ( $M = Zr$ ), 45% ( $M = Hf$ ).



The procedure was similar in all cases.

Method (a): THF solutions of V or VI, obtained as described above were treated with 1.1 mmol of a monodentate ligand, L (OPPh<sub>3</sub> or NHPPh<sub>2</sub>) or 0.55 mmol of a bidentate ligand L-L (dppe or 2,2'-bipyridine), and the mixture was stirred at room temperature for 2 h. After filtration the solvent was removed by evaporation under reduced pressure to give VII–XII as crystalline solids. Yields were 66–80%.

Method (b): A mixture of 0.292 g (1 mmol) of III, 0.31 g (1.1 mmol) of OPPh<sub>3</sub> and 0.207 g (1 mmol) of AgClO<sub>4</sub> in 50 ml of THF was stirred at room temperature for 2 h. The precipitate was filtered off and the solution evaporated to give crystals of VII, which were repeatedly washed with diethyl ether, pentane, and toluene, then dried under vacuum. Yield 70%.



The procedure was similar in all cases. The THF solutions of 0.6 mmol of III or IV obtained as described above were treated with a CCl<sub>4</sub> solution of Cl<sub>2</sub> or Br<sub>2</sub> containing 0.60 mmol of the halogen, and the mixture was stirred at room temperature for 0.5 h. The solvent was evaporated off under reduced pressure, and the solid left was recrystallized from toluene to give XIII–XVI. Yields 70–85%.

A similar reaction with I<sub>2</sub> always gave solids which could not be characterized as the pure iodo complex. When 2 mmol of OPPh<sub>3</sub> was added to 1 mmol of III before an excess (3 mmol) of I<sub>2</sub> was introduced, a blue precipitate was obtained, and this filtered off washed with toluene and pentane, and dried under reduced pressure. It was identified as XVII. Yield 55%.

### Acknowledgements

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