

## Synthetic, Chemical Spectroscopic (Infrared and Electronic) and Magnetic Studies on Dizirconium enneaisopropoxide Complexes of Iron(II)

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### Abstract

Bimetallic alkoxide derivatives of iron(II) with zirconium of the types  $[\text{Fe}\{\text{Zr}_2(\text{OPr}^i)_9\}_2]$ ,  $[\text{ClFe}\{\text{Zr}_2(\text{OPr}^i)_9\}]$ ,  $[(\text{RO})\text{Fe}\{\text{Zr}_2(\text{OPr}^i)_9\}]$ , and  $[(\text{acac})\text{Fe}\{\text{Zr}_2(\text{OPr}^i)_9\}]$  have been synthesized and characterized by elemental analyses, infrared and electronic spectral as well as magnetic susceptibility studies.

### Introduction

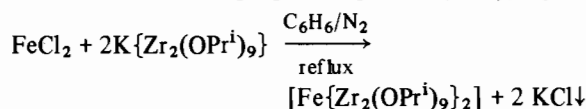
Simple alkoxides of iron(II) [1],  $\{\text{Fe}(\text{OR})_2\}_n$ , have been found to be insoluble, nonvolatile and polymeric. During the last few years, we have been interested in exploring the alkoxide chemistry of the later transition metals [2–8] with emphasis on the synthesis and physicochemical studies of some novel hydrocarbon soluble, volatile and monomeric bimetallic alkoxide derivatives of later 3d metals. In this paper we are reporting the synthesis of a number of new bimetallic alkoxides of iron(II) with zirconium and their characterization by infrared, electronic and magnetic studies.

It may be interesting to mention that the ligand,  $\{\text{Zr}_2(\text{OPr}^i)_9\}^-$  exhibited an ambidentate behaviour towards metal ions. For example, it behaves as a bidentate ligand in complexes of the types  $[\text{Fe}\{\text{Zr}_2(\text{OPr}^i)_9\}_3]$  [9],  $[\text{Ca}\{\text{Zr}_2(\text{OPr}^i)_9\}_2]$  and  $[\text{Ba}\{\text{Zr}_2(\text{OPr}^i)_9\}_2]$  [10], whereas tridentate ligation is shown in compounds such as  $[\text{Co}\{\text{Zr}_2(\text{OPr}^i)_9\}_2]$  [11],  $[\text{Ni}\{\text{Zr}_2(\text{OPr}^i)_9\}_2]$  [12] and  $[\text{Cu}\{\text{Zr}_2(\text{OPr}^i)_9\}_2]$  [13].

### Results and Discussion

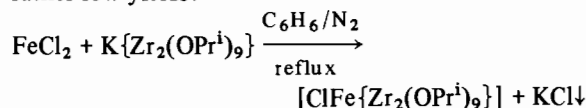
Bimetallic tetraisopropoxyaluminates of a number of metals including iron(II) have generally been prepared in benzene isopropanol mixture by the interaction of the relevant metal halides with potassium tetraisopropoxyaluminate. Attempts to synthesize iron(II) dizirconium enneaisopropoxide under similar

conditions led to a mixture of  $\text{Fe}(\text{OPr}^i)_2$  and  $\text{Zr}(\text{OPr}^i)_4 \cdot \text{Pr}^i\text{OH}$ . However, interaction of iron(II) chloride with potassium dizirconium enneaisopropoxide in 1:2 molar ratio in benzene (without isopropanol) yielded the hydrocarbon soluble and volatile bimetallic isopropoxide  $[\text{Fe}\{\text{Zr}_2(\text{OPr}^i)_9\}_2]$ :

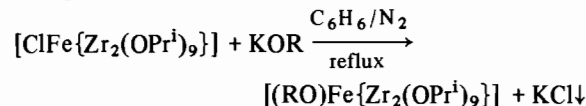


Inability to isolate the bimetallic derivative involving zirconium by the above reaction in the presence of isopropanol may be due to the crystallizing tendency of  $\text{Zr}(\text{OPr}^i)_4 \cdot \text{Pr}^i\text{OH}$  in isopropanol. In order to test this hypothesis, the volatilized bimetallic isopropoxide  $[\text{Fe}\{\text{Zr}_2(\text{OPr}^i)_9\}_2]$  was refluxed in a minimum amount of isopropanol and cooled to room temperature, when crystalline  $\text{Zr}(\text{OPr}^i)_4 \cdot \text{Pr}^i\text{OH}$  and insoluble brown–red solid  $\text{Fe}(\text{OPr}^i)_2$  separated out.  $\text{Zr}(\text{OPr}^i)_4 \cdot \text{Pr}^i\text{OH}$  could be separated from this insoluble mixture by dissolution in benzene.

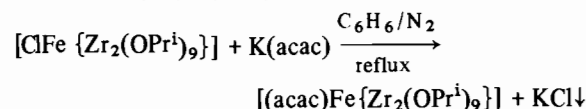
Interaction of iron(II) chloride with potassium dizirconium enneaisopropoxide in a 1:1 molar ratio resulted in chloride bimetallic iron(II) isopropoxide,  $[\text{ClFe}\{\text{Zr}_2(\text{OPr}^i)_9\}]$ , which can be volatilized in rather low yields:



The chloride in  $[\text{ClFe}\{\text{Zr}_2(\text{OPr}^i)_9\}]$  could easily be replaced by alkoxide and acetylacetonate groups:



where R = Me, Et,  $\text{Pr}^i$ ,  $\text{Bu}^n$ ,  $\text{Bu}^t$



All these bimetallic isopropoxide complexes (Table I) are volatile and soluble in common organic solvents.

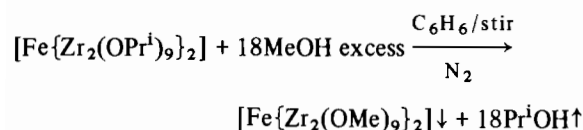
\*Author to whom correspondence should be addressed.

TABLE I. Analytical and Physical Data on Dizirconiumneaisopropoxide Derivatives of Iron(II)

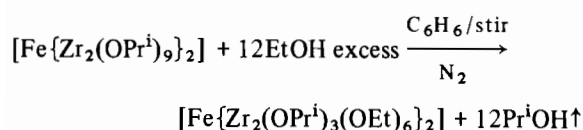
Reactants (g)	Products (g)	Colour and appearance	Found (calc.) (%)		Bath temperature (°C/mm)	$\mu_{\text{eff}}$ (BM)
			OR	Zr		
FeCl <sub>2</sub> (0.32 g, 2.53 mmol) + 2K[Zr <sub>2</sub> (OPr <sup>t</sup> ) <sub>9</sub> ] (3.80 g, 5.04 mmol)	[Fe-Zr <sub>2</sub> (OPr <sup>t</sup> ) <sub>9</sub> ] <sub>2</sub> 3.75 (4.21)	brown solid	71.32 (71.66)	24.86 (24.58)	200/0.2	5.15
[Fe-Zr <sub>2</sub> (OPr <sup>t</sup> ) <sub>9</sub> ] <sub>2</sub> (2.46 g) + MeOH excess	[Fe-Zr <sub>2</sub> (OMe) <sub>9</sub> ] <sub>2</sub> 1.62 (1.70)	yellowish powdery solid	57.10 (57.01)	37.40 (37.28)	*	5.18
[Fe-Zr <sub>2</sub> (OPr <sup>t</sup> ) <sub>9</sub> ] <sub>2</sub> (2.32 g) + EtOH excess	[Fe-Zr <sub>2</sub> (OEt) <sub>9</sub> ] <sub>2</sub> 1.93 (1.93)	red-brown solid	65.62 (65.81)	29.48 (29.65)	210/0.2	5.08
[Fe-Zr <sub>2</sub> (OPr <sup>t</sup> ) <sub>9</sub> ] <sub>2</sub> (2.78 g) + Pr <sup>n</sup> OH excess	[Fe-Zr <sub>2</sub> (OPr <sup>n</sup> ) <sub>9</sub> ] <sub>2</sub> 2.73 (2.75)	brown solid	24.96 (24.58)	3.71 (3.76)	220/0.2	5.02
[Fe-Zr <sub>2</sub> (OPr <sup>t</sup> ) <sub>9</sub> ] <sub>2</sub> (2.53 g) + Bu <sup>n</sup> OH excess	[Fe-Zr <sub>2</sub> (OBu <sup>n</sup> ) <sub>9</sub> ] <sub>2</sub> 2.96 (2.96)	yellowish brown solid	21.33 (21.03)	3.30 (3.22)	240/0.2	5.12
[Fe-Zr <sub>2</sub> (OPr <sup>t</sup> ) <sub>9</sub> ] <sub>2</sub> (3.42 g) + Bu <sup>t</sup> OH excess	[Fe-Zr <sub>2</sub> (OPr <sup>t</sup> )(OBu <sup>t</sup> ) <sub>6</sub> ] <sub>2</sub> 3.81 (3.83)	brown sticky solid	14.20 (14.08)	22.10 (21.73)		5.22
[Fe-Zr <sub>2</sub> (OPr <sup>t</sup> ) <sub>9</sub> ] <sub>2</sub> (3.16 g) + Am <sup>t</sup> OH excess	[Fe-Zr <sub>2</sub> (OPr <sup>t</sup> )(OAm <sup>t</sup> ) <sub>6</sub> ] <sub>2</sub> 3.87 (3.88)	brown sticky solid	12.51 (12.61)	19.75 (19.46)		5.19
FeCl <sub>2</sub> (0.28 g, 2.21 mmol) + K[Zr <sub>2</sub> (OPr <sup>t</sup> ) <sub>9</sub> ] (1.66 g, 2.20 mmol)	[ClFe-Zr <sub>2</sub> (OPr <sup>t</sup> ) <sub>9</sub> ] 1.77 (1.78)	brown solid	65.91 (66.02)	21.36 (21.18)	210/0.2	3.83
[ClFe-Zr <sub>2</sub> (OPr <sup>t</sup> ) <sub>9</sub> ] (2.55 g, 3.17 mmol) + KOMe (0.24 g, 3.14 mmol)	[(MeO)Fe-Zr <sub>2</sub> (OPr <sup>t</sup> ) <sub>9</sub> ] 2.53 (2.54)	yellowish brown solid	77.66 (77.77)	21.68 (21.29)	215/0.2	3.49
[ClFe-Zr <sub>2</sub> (OPr <sup>t</sup> ) <sub>9</sub> ] (2.46 g, 3.05 mmol) + KOBu <sup>n</sup> (0.34 g, 3.0 mmol)	[(Bu <sup>n</sup> O)Fe-Zr <sub>2</sub> (OPr <sup>t</sup> ) <sub>9</sub> ] 2.40 (2.57)	brown solid	62.90 (63.08)	21.88 (21.64)	195/0.2	3.52
[ClFe-Zr <sub>2</sub> (OPr <sup>t</sup> ) <sub>9</sub> ] (2.18 g, 2.71 mmol) + KOPr <sup>t</sup> (0.26 g, 2.64 mmol)	[(Pr <sup>t</sup> O)Fe-Zr <sub>2</sub> (OPr <sup>t</sup> ) <sub>9</sub> ] 2.24 (2.46)	brown solid	71.18 (71.26)	22.23 (21.99)	195/0.2	3.54
[ClFe-Zr <sub>2</sub> (OPr <sup>t</sup> ) <sub>9</sub> ] (2.52 g, 3.13 mmol) + KOBu <sup>t</sup> (0.35 g, 3.12 mmol)	[(Bu <sup>t</sup> O)Fe-Zr <sub>2</sub> (OPr <sup>t</sup> ) <sub>9</sub> ] 2.60 (2.64)	brown solid	63.00 (63.08)	21.92 (21.64)	200/0.2	3.58
[ClFe-Zr <sub>2</sub> (OPr <sup>t</sup> ) <sub>9</sub> ] (3.42 g) + Kacac (0.41 g)	[(acac)Fe-Zr <sub>2</sub> (OPr <sup>t</sup> ) <sub>9</sub> ] 3.62 (3.69)	reddish brown solid	61.15 (61.20)	21.23 (20.99)	210/0.2	5.16

**Alcoholysis Reactions**

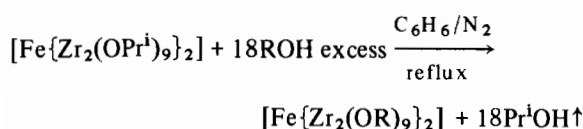
Complete replacement of the isopropoxy groups in  $[\text{Fe}\{\text{Zr}_2(\text{OPr}^i)_9\}_2]$  could be achieved with excess methanol even at ambient temperatures leading to the formation of the insoluble methoxy derivative:



However, stirring of the isopropoxy derivative with excess ethanol led to the formation of mixed ethoxy-isopropoxy derivative of the following type:

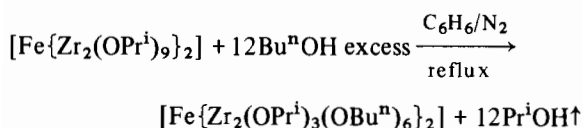


Under refluxing conditions, the formation of methoxy and ethoxy derivatives was much faster and a total replacement of the isopropoxy groups could be achieved in both cases:

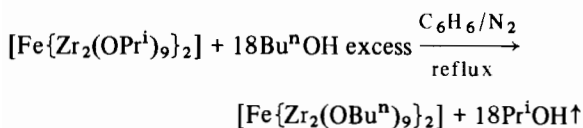


where R = Me, Et

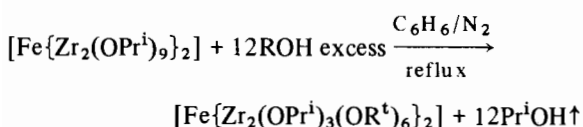
By comparison, the reaction with n-butanol resulted in a mixed alkoxy derivative of the composition  $[\text{Fe}\{\text{Zr}_2(\text{OPr}^i)_3(\text{OBu}^n)_6\}_2]$  even under refluxing conditions:



However, by carrying out the above reaction with n-butanol or n-propanol under refluxing conditions in benzene with continuous fractionation of liberated isopropanol azeotropically, all the isopropoxy groups could be replaced:



Interaction of  $[\text{Fe}\{\text{Zr}_2(\text{OPr}^i)_9\}_2]$  with excess of tert-butyl or tert-amyl alcohols with continuous azeotropic removal of the liberated isopropanol with benzene could lead finally to the formation of only mixed isopropoxy-tert-alkoxy derivatives:



where  $\text{R}^t = \text{Bu}^t, \text{Am}^t$

All the bimetallic alkoxy complexes are hydrocarbon soluble and volatile (under reduced pressure) except the methoxy derivative,  $[\text{Fe}\{\text{Zr}_2(\text{OMe})_9\}_2]$ ; all of these are air- and moisture-sensitive coloured solids (Table I).

The results of the alcoholysis experiments with the bimetallic isopropoxide tend to show that six of the nine isopropoxy groups in the  $\{\text{Zr}_2(\text{OPr}^i)_9\}$  unit are more easily replaceable and the facility of further replacement decreases with the increasing steric requirements of the substituent alkoxy group.

**Electronic Spectral Studies**

The absorptions observed in the reflectance spectra of the new bimetallic alkoxy derivatives,  $[\text{Fe}\{\text{Zr}_2(\text{OR})_9\}_2]$  and some allied compounds are recorded in Table II.

In spite of extensive work [14] on high spin iron(II) complexes, very little information is available on neutral  $\text{FeO}_n$  (where  $n = 6, 5,$  or  $4$ ) systems to which the above complexes obviously belong and therefore, the above preliminary data on the electronic spectra are being cited for record and qualitative correlation with the alcoholysis behaviour of the complexes.

Iron(II) complexes are known in a wide variety of stereochemistries and spin states out of which six, four, and five coordination states are more common in decreasing order of importance. For high spin six coordinate complexes, the octahedral ground state is  ${}^5\text{T}_{2g}$  and the only spin allowed excited state is  ${}^5\text{E}_g$ . The Jahn-Teller distortions in the excited states, however, result in splitting into  ${}^5\text{A}_1 + {}^5\text{B}_1$  states in  $D_{4h}$  symmetry.

The alcoholysis data tend to indicate that three out of nine OR groups in  $[\text{Fe}\{\text{Zr}_2(\text{OR})_9\}_2]$  complexes can be replaced with comparative facility and these may be considered to be constituting bridges between iron and zirconium atoms. Construction of a few simple models indicates clearly that out of these three bridging groups, one would be under severe strain and hence elongated; this

TABLE II. Reflectance Absorptions of some Bimetallic Alkoxy Derivatives of Iron(II)

Compound	$\nu_{\text{max}}$ ( $\text{cm}^{-1}$ )
I R = Me	12230, 8430
II R = Et	(10480) 8520, 7420, 5390
III R = Pr <sup>n</sup>	(9802), (7930), 6585, 5110
IV R = Bu <sup>n</sup>	(9715), (7895), 6470, 5085
V R = Pr <sup>i</sup>	(9480), (7960), 6510, 5150
VI [(Bu <sup>n</sup> O)Fe{Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> }]	10855, 6340, (5125), 4290
VII [(Bu <sup>t</sup> O)Fe{Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> }]	10555, (7860), 6590, 5100, (4290)
VIII [(acac)Fe{Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> }]	(9715), 7930, 6585, 5045

TABLE III. Significant Infrared<sup>a</sup> Frequencies (cm<sup>-1</sup>) and Magnetic Data of Dizirconiumneaisopropoxide Complexes of Fe(II)

Compounds	$\nu(\text{Fe}-\text{O})$	$\nu(\text{Zr}-\text{O})$	$\nu(\text{C}-\text{O})$	$\mu_{\text{eff}}$ (BM)
[Fe{Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> } <sub>2</sub> ]	405, 475	585	1015, 960	5.15
[Fe{Zr <sub>2</sub> (OMe) <sub>9</sub> } <sub>2</sub> ]	450, 470	570	1020, 950	5.18
[Fe{Zr <sub>2</sub> (OEt) <sub>9</sub> } <sub>2</sub> ]	425, 455	510, 555	1020, 965	5.08
[Fe{Zr <sub>2</sub> (OPr <sup>n</sup> ) <sub>9</sub> } <sub>2</sub> ]	415, 465	570	968, 1012	5.02
[Fe{Zr <sub>2</sub> (OBu <sup>n</sup> ) <sub>9</sub> } <sub>2</sub> ]	415, 450	580	960, 1010	5.12
[Fe{Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>3</sub> (OBu <sup>t</sup> ) <sub>6</sub> } <sub>2</sub> ]	420, 470	530, 570	960, 1020	5.22
[Fe{Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>3</sub> (OAm <sup>t</sup> ) <sub>6</sub> } <sub>2</sub> ]	430, 480	535, 575	960, 1020	5.19
[ClFe{Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> }]	410, 455	515, 565	950, 1000	3.83
[(MeO)Fe{Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> }]	455, 480	545	1030, 1085	3.49
[(Bu <sup>n</sup> O)Fe{Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> }]	455, 465	515, 565	910, 1015, 1040	3.52
[(Pr <sup>i</sup> O)Fe{Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> }]				
[(Bu <sup>t</sup> O)Fe{Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> }]	440, 470	580	950, 970, 1015	3.58
[(acac)Fe{Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> }]	430, 480	575	940, 960, 1025	5.16

<sup>a</sup>In Nujol mull.

strain tends to increase with the steric requirements of the alkoxy group.

On the basis of extensive studies of the electronic spectra [14] of iron(II) complexes, it has been shown that such distortions due to elongation along the *z* axis brings about splitting of <sup>5</sup>E<sub>g</sub> terms resulting in absorptions at lower wavenumbers. These lower range absorptions are also characteristic of four-coordination iron(II) complexes.

The spectroscopic data displayed in Table II, therefore, indicate [Fe{Zr<sub>2</sub>(OMe)<sub>9</sub>}<sub>2</sub>] to be in a six-coordination state and the higher homologues to be either highly distorted six-coordination tetragonal systems or four-coordination species. The latter alternative would render {Zr<sub>2</sub>(OPr<sup>i</sup>)<sub>9</sub>}<sup>-</sup> moieties effectively bidentate in nature. These conclusions are similar to those observed for the corresponding nickel(II) derivatives [12].

### Magnetic Studies

Iron(II) complexes can exist in a high spin state with four unpaired electrons or in a low spin state with all electrons paired. The room temperature magnetic moments of the complexes of the type [Fe{Zr<sub>2</sub>(OR)<sub>9</sub>}<sub>2</sub>] have been found to lie in the range 5.02–5.22 BM against the expected value of 4.89 BM for high spin iron(II) (Table III).

The observed magnetic moments for octahedral iron(II) complexes [15] are in the range 5.20–5.40 BM due to a larger orbital contribution in comparison to the tetrahedral complexes (4.90–5.40 BM); for example, octahedral Fe(acac)<sub>2</sub> [16] (where acac = acetylacetonate) exhibits a magnetic moment 5.40 BM, whereas tetrahedral Fe(dpm)<sub>2</sub> [16] (where dpm = dipivaloylmethyl) shows a magnetic moment, 5.0 BM. The variable temperature magnetic moments of [Fe{Zr<sub>2</sub>(OPr<sup>i</sup>)<sub>9</sub>}<sub>2</sub>] (Table IV) showed lowering of magnetic moment values with decrease in temperature and the observed  $\mu_{\text{eff}}$  is 3.80 BM at 77.5 K.

TABLE IV. Temperature Dependence of Magnetic Moment of [Fe{Zr<sub>2</sub>(OPr<sup>i</sup>)<sub>9</sub>}<sub>2</sub>]

Temperature (K)	$\mu_{\text{eff}}$ (BM)
77.4	3.80
86.6	3.86
109.0	4.07
131.0	4.24
175.0	4.52
196.0	4.67
220.0	4.89
295.0	5.15

For the [(acac)Fe{Zr<sub>2</sub>(OPr<sup>i</sup>)<sub>9</sub>}] derivative with a plausible five-coordinate geometry (assuming {Zr<sub>2</sub>(OPr<sup>i</sup>)<sub>9</sub>} moiety behaving as a tridentate ligand), the observed magnetic moment of 5.16 BM is similar to those observed for other five-coordinate iron(II) complexes.

For [XFe{Zr<sub>2</sub>(OPr<sup>i</sup>)<sub>9</sub>}] (X = Cl, OMe, OPr<sup>i</sup>, OBu<sup>n</sup>, OBu<sup>t</sup>), the observed magnetic moments are in a much lower range, *i.e.* 3.83 (X = Cl), 3.54 (X = OPr<sup>i</sup>), 3.52 (X = OBu<sup>n</sup>), and 3.58 (X = OBu<sup>t</sup>) BM; this could be explained on the basis of their Fe( $\mu$ -X)-Fe bridged configuration.

### Infrared Spectral Studies

The tentative IR assignments (Table III) have been made on the basis of published data about metal alkoxides [17a–e]. These bimetallic alkoxide derivatives exhibit structurally significant bands at 940–1060  $\nu(\text{C}-\text{O})$ M, 510–585  $\nu(\text{Zr}-\text{O})$ , and 415–480  $\nu(\text{Fe}-\text{O})$  cm<sup>-1</sup>. In addition to the absorptions found for isopropoxides at 1145  $\pm$  15 and 1165  $\pm$  5 cm<sup>-1</sup>, the spectra of these complexes contain a strong doublet at 1365 and 1370 cm<sup>-1</sup> characteristic of gem-dimethyl groups [17a]. In the acetylacetonate

derivative ( $[(\text{acac})\text{Fe}\{\text{Zr}_2(\text{OPr}^i)_9\}]$ ), the band due to  $\nu(\text{C}=\text{O})$  observed at  $1590\text{ cm}^{-1}$ , shows a lowering of about  $23\text{ cm}^{-1}$ , compared to the parent acetylacetone ( $\nu(\text{C}=\text{O})$ ,  $1613\text{ cm}^{-1}$ ) indicating the coordination of the carbonyl oxygen [18] to the Fe(II) centre. In the chloride bimetallic complex  $[\text{ClFe}\{\text{Zr}_2(\text{OPr}^i)_9\}]$  the band at  $310\text{ cm}^{-1}$  can be attributed to the bridging  $\nu(\text{Fe}-\text{Cl})$  [17a; 19a, b].

## Experimental

General procedures and instruments were as described in our earlier paper [9]. Iron(II) was estimated by the volumetric method [20]. Owing to the air-sensitivity of the derivatives all preparations and other operations were carried out under a dry and oxygen-free nitrogen atmosphere. For brevity, details of only typical reactions of each type have been given below:

### (a) Synthesis of Iron(II) Bis-(dizirconiumneaisopropoxide)

A suspension of ferrous chloride (0.32 g, 2.5 mmol) in isopropanol ( $\sim 30\text{ ml}$ ), potassium dizirconiumneaisopropoxide (prepared from potassium (0.20 g, 5.13 mmol) and zirconium isopropoxide isopropanolate (3.92 g, 10.11 mmol)) were mixed in a three necked flask under nitrogen atmosphere and refluxed for about 6 h; isopropanol was distilled out at a bath temperature of  $\sim 120^\circ\text{C}$ , followed by dropwise addition of benzene into the system. Traces of isopropanol in the system were removed azeotropically with benzene. After adding more benzene ( $\sim 50\text{ ml}$ ), the reaction mixture was allowed to reflux for  $\sim 8\text{ h}$ . The mixture was allowed to cool down to room temperature and precipitated KCl (0.37 g; 4.97 mmol) was filtered out. The volatiles were removed under reduced pressure and the crude solid product (4.12 g, 2.52 mmol) volatilized at a bath temperature of  $200^\circ\text{C}$  (pressure of 0.2 mm), affording a dark brown solid product  $[\text{Fe}\{\text{Zr}_2(\text{OPr}^i)_9\}_2]$  (1.80 g, 50%).

### (b) Synthesis of Chloride Iron(II) Dizirconiumneaisopropoxide, $[\text{ClFe}\{\text{Zr}_2(\text{OPr}^i)_9\}]$

The title compound was prepared by the equimolar interaction of anhydrous  $\text{FeCl}_2$  and  $\text{K}\{\text{Zr}_2(\text{OPr}^i)_9\}$ , adopting the experimental procedure as described above for the preparation of the bis-product.

### (c) Reaction of Potassium Methoxide with Chloride Iron(II) Dizirconiumneaisopropoxide

To a reaction mixture of  $[\text{ClFe}\{\text{Zr}_2(\text{OPr}^i)_9\}]$  and KCl prepared (following procedure (a)) from the interaction of anhydrous ferrous chloride (0.43 g, 3.29 mmol) in isopropanol and potassium dizirco-

niumenneaisopropoxide prepared from potassium (0.13 g, 3.33 mmol) and zirconium isopropoxide isopropanolate (2.63 g, 6.78 mmol) was added a suspension of potassium methoxide (0.23 g, 3.33 mmol) in benzene ( $\sim 30\text{ ml}$ ). The mixture was refluxed for a few hours. After removing the precipitated KCl (0.30 g, 4.02 mmol) by filtration, excess solvent was removed under reduced and the yellowish grown product  $[(\text{MeO})\text{Fe}\{\text{Zr}_2(\text{OPr}^i)_9\}]$  (2.62 g, 96%) was volatilized in 50% yield at a bath temperature of  $215^\circ\text{C}$  under reduced pressure (0.2 mm).

### (d) Reaction of Potassium Acetylacetonate with Chloride Iron(II) Dizirconiumneaisopropoxide

Interaction of  $[\text{ClFe}\{\text{Zr}_2(\text{OPr}^i)_9\}]$  (3.42 g, 4.25 mmol) with  $\text{K}(\text{acac})$  (0.57 g, 4.12 mmol) resulted in the benzene soluble mixed acetylacetonato-alkoxide derivative of iron(II),  $[(\text{acac})\text{Fe}\{\text{Zr}_2(\text{OPr}^i)_9\}]$ , and in soluble potassium chloride. After removing the precipitated KCl (0.30 g, 4.02 mmol) by filtration, the excess solvent was stripped off under reduced pressure and the reddish brown product  $[(\text{acac})\text{Fe}\{\text{Zr}_2(\text{OPr}^i)_9\}]$  (3.69 g, 87%) was volatilized at a bath temperature of  $210^\circ\text{C}$  under reduced pressure (0.2 mm).

### (e) Alcoholysis Reactions:

#### (i) Reaction of $[\text{Fe}\{\text{Zr}_2(\text{OPr}^i)_9\}_2]$ with excess methanol (or ethanol)

Stirring of a benzene solution of  $[\text{Fe}\{\text{Zr}_2(\text{OPr}^i)_9\}_2]$  (2.46 g) with excess methanol ( $\sim 40\text{ ml}$ ) at room temperature for  $\sim 6\text{ h}$  resulted in the insoluble methoxy derivative  $[\text{Fe}\{\text{Zr}_2(\text{OME})_9\}_2]$  (1.60 g; 99%).

#### (ii) Reaction of $[\text{Fe}\{\text{Zr}_2(\text{OPr}^i)_9\}_2]$ with an excess of n-propanol

The isopropoxide derivative  $[\text{Fe}\{\text{Zr}_2(\text{OPr}^i)_9\}_2]$  (2.78 g) and an excess of n-propanol ( $\sim 40\text{ ml}$ ) in benzene ( $\sim 30\text{ ml}$ ) were refluxed with continuous azeotropic removal of the liberated isopropanol. When the liberation of isopropanol ceased the volatiles were removed under reduced pressure to afford a brown coloured solid product  $[\text{Fe}\{\text{Zr}_2(\text{OPr}^n)_9\}_2]$  (2.75 g, 99%), which could be volatilized at a bath temperature of  $220^\circ\text{C}$  under reduced pressure (0.2 mm).

#### (iii) Reaction of $[\text{Fe}\{\text{Zr}_2(\text{OPr}^i)_9\}_2]$ with an excess of tert-butanol (or tert-amyl alcohol)

To a benzene ( $\sim 40\text{ ml}$ ) solution of  $[\text{Fe}\{\text{Zr}_2(\text{OPr}^i)_9\}_2]$  (3.42 g) was added an excess of tert-butanol ( $\sim 40\text{ ml}$ ) and the reaction mixture was refluxed for  $\sim 24\text{ h}$  with continuous azeotropic removal of the liberated isopropanol from the reaction mixture until no more isopropanol could be detected in the azeotrope. For ensuring the comple-

tion of the reaction the mixture was refluxed for another 4 h with continuous removal of the tert-butanol–benzene azeotrope. After removing the volatiles, a brown coloured sticky product (3.80 g, 99.7%) was obtained, analysis of which corresponded to the formula  $[\text{Fe}\{\text{Zr}_2(\text{OPr}^i)_3(\text{OBU}^t)_6\}_2]$ .

Following the same procedure, reaction with an excess of tert-amyl alcohol yielded a brown sticky solid of formula  $[\text{Fe}\{\text{Zr}_2(\text{OPr}^i)_3(\text{OAm}^t)_6\}_2]$  (Table I).

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