

Synthesis and spectroscopic characterization of a new type of heterotrimetallic alkoxides of some bivalent metals

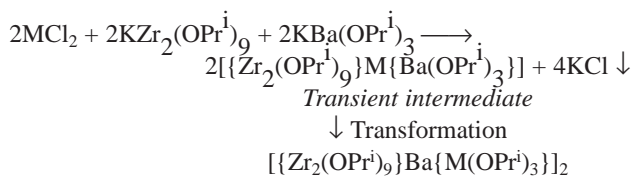
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Heterotrimetallic isopropoxides of the composition $\{Zr_2(OPr^i)_9\}Ba\{M(OPr^i)_3\}_2$ have been prepared by the *in situ* reactions of MCl_2 [M = Be, Mg, Zn, Sn(II), Co, Ni, Cu(II), $KZr_2(OPr^i)_9$ and $KBa(OPr^i)_3$ in equimolar amounts. Reaction of $\{Zr_2(OPr^i)_9\}Ba\{Zn(OPr^i)_3\}_2$ with *tertiary* butyl alcohol has been studied to gain an insight into its structure. All new derivatives have been characterised by elemental analyses, spectroscopic [IR, UV-VIS, and NMR (1H , ^{13}C , and ^{119}Sn)] studies and molecular weight measurements.

Keywords: heterotrimetallic isopropoxides, *t*-butoxo-isopropoxo derivatives.

In continuation of our earlier studies on heterometallic alkoxides of bivalent metals of main group¹⁻³ and later transition^{4,5} metals, we now report our studies on derivatives of the composition $\{Zr_2(OPr^i)_9\}Ba\{M(OPr^i)_3\}_2$ formed by the *in situ* interaction of MCl_2 [M = Be, Mg, Zn, Sn(II), Co, Ni, Cu(II)] with $KZr_2(OPr^i)_9$ and $KBa(OPr^i)_3$. A comparison of electronic spectral data for the precursor derivatives $\{Zr_2(OPr^i)_9\}MCl_2$ (M = Co, Ni) with those of the new heterotrimetallic isopropoxides of cobalt(II) and nickel(II) provide evidence for the shifting of the $Zr_2(OPr^i)_9$ group from a smaller atom to the atom of a larger size, such as barium (Scheme 1), due to its oxophilic nature and the tendency to attain a higher coordination number.

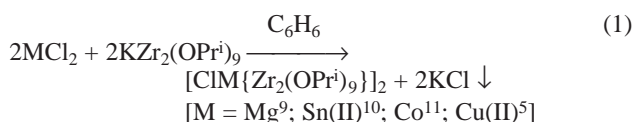


Scheme 1

Veith and co-workers^{6,7} first established this type of shifting of an alkoxometallate ligand from a smaller metal to barium, by single crystal X-ray analysis of the derivative $\{Zr_2(OPr^i)_9\}Ba\{Cd(OPr^i)_3\}_2$ isolated from the reaction mixture containing $\{Zr_2(OPr^i)_9\}CdI$ and $KBa(OPr^i)_3$. Heterometallic complexes with a similar molecular geometry have recently been shown to be attractive as precursors for the insertion of catalytic sites into inorganic matrices.⁸ These studies assume significant importance due to the recent quest for the production of mixed-metal oxide based electronic and ceramic materials by sol-gel/ MOCVD techniques.

Results and discussion

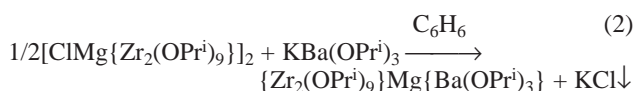
Reactions of metal chlorides with $KZr_2(OPr^i)_9$ in 1:1 molar ratio led to the formation of chloro-derivatives:



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[†] This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

The replacement of the chloride group in the Mg derivative (Eqn1) by $\{Ba(OPr^i)_3\}^-$ yields a derivative of composition $\{Zr_2(OPr^i)_9\}Mg\{Ba(OPr^i)_3\}$.



A more convenient route for the synthesis of heterotrimetallic isopropoxides is the *in situ* sequential interaction of MCl_2 with $KZr_2(OPr^i)_9$ and $KBa(OPr^i)_3$ as shown in Scheme 2.

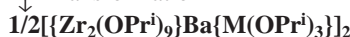
MCl_2 (in C_6H_6)

- (i) $KZr_2(OPr^i)_9$, stir for 6 h at room temperature
- (ii) $KBa(OPr^i)_3$, stir for 6 h at room temperature
- (iii) Filtration
- (iv) Removal of volatiles under reduced pressure
- (v) Recrystallisation from *n*-hexane and toluene at $-20^\circ C$



Transient intermediate

↓ Transformation



(1): M = Be; (2): Mg; (3): Zn;

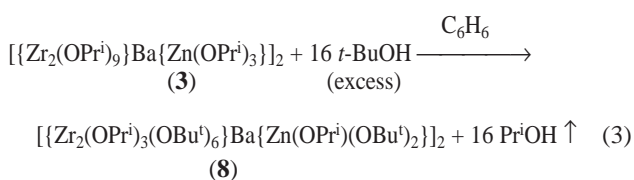
(4): Sn(II); (5): Co; (6): Ni; (7): Cu(II)

Scheme 2

The final outcome of the reactions illustrated by Scheme 2 is the shifting of the $Zr_2(OPr^i)_9$ unit from a smaller bivalent metal to the larger barium.

All these derivatives are highly moisture-sensitive, yellowish solids, soluble in common organic solvents and dimeric in nature.

Reaction of the derivative (3) with *tertiary* butyl alcohol lead to the formation of the *t*-butoxo-isopropoxo-derivative.



Interaction of coordinatively unsaturated four-coordinate derivatives (3), (5)–(7) with an excess of a donor solvent such as THF followed by stirring for ~2h yielded six-coordinate

Table 1 IR spectral (cm⁻¹) studies of heterotrimetallic alkoxides of some bivalent metals

Sample no.	Compound	$\nu(\text{OR})$	$\nu(\text{C-O})$	$\nu(\text{Ba-O})$	$\nu(\text{Zr-O})$	$\nu(\text{M-O})$ (Be, Mg, Zn, Sn, Co, Ni, Cu(II))
1	$\{[\text{Zr}_2(\text{OPr})_9]\text{Ba}\{\text{Be}(\text{OPr})_3\}_2$	1156s, 1110s	1015s, 998s	520 m	575m, 536m	830w, 806w
2	$\{[\text{Zr}_2(\text{OPr})_9]\text{Ba}\{\text{Mg}(\text{OPr})_3\}_2$	1164s, 1119s	992s, 963s	514 m	589m, 525m	477w, 462w
3	$\{[\text{Zr}_2(\text{OPr})_9]\text{Ba}\{\text{Zn}(\text{OPr})_3\}_2$	1162s, 1132s	1015s, 941s	500 m	58s, 544m	456s, 434m
4	$\{[\text{Zr}_2(\text{OPr})_9]\text{Ba}\{\text{Sn}(\text{OPr})_3\}_2$	1173s, 1143s	1032s, 986s	528 s	563m, 516m	417s, 410m
5	$\{[\text{Zr}_2(\text{OPr})_3(\text{OBU}^t)_6]\text{Ba}\{\text{Zn}(\text{OPr})_3(\text{OBU}^t)_2\}_2$	1203s, 1132s, 1115s	971s, 946s	518 s	591s, 563s	455m, 435s
6	$\{[\text{Zr}_2(\text{OPr})_9]\text{Ba}\{\text{Co}(\text{OPr})_3\}_2$	1143s, 1100s	1000s, 971s	529 m	557m, 547s	486m, 443m
7	$\{[\text{Zr}_2(\text{OPr})_9]\text{Ba}\{\text{Ni}(\text{OPr})_3\}_2$	1162s, 1132s	1029s, 971s	513 m	573m, 541m	471s, 426w
8	$\{[\text{Zr}_2(\text{OPr})_9]\text{Ba}\{\text{Cu}(\text{OPr})_3\}_2$	1140s, 1100s	1004s, 986s	528 s	586m, 531m	457m, 429m

Table 2 NMR (¹H and ¹³C) (δ, ppm) spectral studies of heterotrimetallic alkoxides of Be, Mg, Zn and Sn(II)

Sample no.	Compound	
1	$\{[\text{Zr}_2(\text{OPr})_9]\text{Ba}\{\text{Be}(\text{OPr})_3\}_2$	¹ H : 1.26 (d ($J = 6.15$ Hz), 24H, CHMe ₂ (t)); 1.46 (d ($J = 6.15$ Hz), 48H, CHMe ₂ (b)); 4.16 (br, 4H, CHMe ₂ (t)); 4.85 (br, 8H, CHMe ₂ (b))
2	$\{[\text{Zr}_2(\text{OPr})_9]\text{Ba}\{\text{Mg}(\text{OPr})_3\}_2$	¹ H : 1.21(d ($J = 6.1$ Hz), 24H, CHMe ₂ (t)); 1.41 (d ($J = 6.15$ Hz), 48H, CHMe ₂ (b)); 3.96 (br, 4H, CHMe ₂ (t)); 4.44 (br, 8H, CHMe ₂ (b))
3	$\{[\text{Zr}_2(\text{OPr})_9]\text{Ba}\{\text{Zn}(\text{OPr})_3\}_2$	¹ H : 1.27(d ($J = 6.15$ Hz) 24H, CHMe ₂ (t)); 1.39 (d ($J = 6.15$ Hz), 48H, CHMe ₂ (b)); 4.27 (sept ($J = 6.15$ Hz), 4H, CHMe ₂ (t)); 4.73 (sept ($J = 6.15$ Hz), 8H, CHMe ₂ (b)) ¹³ C : 25.89, 27.30 (CHMe ₂), 68.25, 71.07 (CHMe ₂)
4	$\{[\text{Zr}_2(\text{OPr})_9]\text{Ba}\{\text{Sn}(\text{OPr})_3\}_2$	¹ H : 1.31(d ($J = 6.10$ Hz), 48H, CHMe ₂ (t)); 1.49 (d ($J = 6.10$ Hz), 48H, CHMe ₂ (b)); 4.02 (br, 4H, CHMe ₂ (t)); 4.49 (br, 8H, CHMe ₂ (b)) ¹³ C : 27.14; 27.90 (CHMe ₂); 67.99, 71.02 (CHMe ₂)
5	$\{[\text{Zr}_2(\text{OPr})_3(\text{OBU}^t)_6]\text{Ba}\{\text{Zn}(\text{OPr})_3(\text{OBU}^t)_2\}_2$	¹ H : 1.32 (s, 72H, OCM ₃); 1.36 (d, 24H, CHMe ₂); 4.63 (sept, 4H, CHMe ₂)
6	$\{[\text{Zr}_2(\text{OPr})_9]\text{Ba}\{\text{Zn}(\text{OPr})_3(\text{THF})_2\}_2$	¹ H : 1.21 (d ($J = 6.15$ Hz), 24H, CHMe ₂ (t)); 1.36 (d ($J = 6.15$ Hz), 48H, CHMe ₂ (b)); 1.87 (br, 8H, β -H(THF)); 3.77(br, 8H, α -H(THF)); 4.05 (sept ($J = 6.15$ Hz), 4H, CHMe ₂ (t)); 4.48 (sept ($J = 6.15$ Hz), 8H, CHMe ₂ (b));

Table 3 Electronic spectra (cm⁻¹) of heterotrimetallic isopropoxides of Co, Ni and Cu(II)

Sample no.	Compound	In benzene	In tetrahydrofuran
1	$\{[\text{Zr}_2(\text{OPr})_9]\text{Ba}\{\text{Co}(\text{OPr})_3\}_2$	6516 (ν_2) ⁴ A ₂ → ⁴ T ₁ (F) 15277 (ν_3) ⁴ A ₂ → ⁴ T ₁ (P)	7375 (ν_1) ⁴ T ₁ g → ⁴ T ₂ g 15246 (ν_2) ⁴ T ₁ g → ⁴ A ₂ g 20044 (ν_3) ⁴ T ₁ g → ⁴ T ₁ g(P)
2	$\{[\text{Zr}_2(\text{OPr})_9]\text{Ba}\{\text{Ni}(\text{OPr})_3\}_2$	16994 and 18820 (ν_3) ³ T ₁ → ³ T ₁ (P) 16556 (ν_2) ³ A ₂ g → ³ T ₁ g(F)	9060 (ν_1) ³ A ₂ g → ³ T ₂ g(F) 23232 (ν_3) ³ A ₂ g → ³ T ₁ g (P)
3	$\{[\text{Zr}_2(\text{OPr})_9]\text{Ba}\{\text{Cu}(\text{OPr})_3\}_2$	15476 (ν_1) ² E → ² T ₂	20576 (ν_1) ² Eg → ² T ₂ g

derivatives of the composition $\{[\text{Zr}_2(\text{OPr})_9]\text{Ba}\{\text{M}(\text{OPr})_3(\text{THF})_2\}_2$ (M = Zn, Co, Ni, Cu(II)) which is confirmed by ¹H NMR spectra (Table 2) of the Zn derivative and electronic spectra (Table 3) of the Co, Ni, and Cu(II) derivatives.

IR spectral studies: Derivatives (1)–(7) show IR absorptions (cm⁻¹) (Table 1) in the regions: 1173–1100 $\nu(\text{OPr}^i)$ and 1032–963 $\nu(\text{C-O})$ (terminal and bridging). New absorption bands for metal-oxygen^{12,13} bonds appear in the regions 486–410 $\nu(\text{M-O})$ [M = Mg, Zn, Sn(II), Co, Ni, Cu(II)], 529–500 $\nu(\text{Ba-O})$, 591–516 $\nu(\text{Zr-O})$, and 830–806 $\nu(\text{Be-O})$. *Tertiary-butoxo-isopropoxo* derivative (8) exhibits absorptions (Table 1) characteristic of $\nu(\text{OBU}^t)$, $\nu(\text{OPr}^i)$, and $\nu(\text{M-O})$.

NMR spectral studies: ¹H NMR spectra (δ , ppm) (Table 2) of (1) – (4) exhibit two doublets in the regions: 1.21–1.31, 1.39–1.49 and two broad signals in the regions: 3.96–4.27, 4.44–4.85 due to terminal and bridging methyl and methine protons, respectively. The appearance of only two doublets

and two broad peaks instead of expected six is due to the fluxional behaviour of the molecules at ambient temperature. It is noteworthy that the nature of the spectra recorded at –80°C showed no change.

Derivative (8) shows ¹H NMR signals (Table 2) characteristic of the groups present therein.

¹³C NMR spectral studies of (3) and (4) show signals in the regions: 25.89–27.14 and 27.30–27.90 for terminal and bridging methyl carbons and signals at 67.99–68.25 and 71.02–71.07 ppm due to terminal and bridging methine carbon atoms (Table 2).

Appearance of a sharp ¹¹⁹Sn NMR signal at δ –260.75 ppm for the derivative (4) is indicative of five-coordinate tin(II) centre^{2,14} with a lone pair occupying one of the coordination positions.

Electronic spectra: The electronic spectrum (Table 3) of (5) in benzene solution shows bands in the visible region

Table 4 Preparative and analytical details of heterotrimetallic alkoxides of some bivalent metals

Sample no.	Reactant (g/mmoles)					Wt of KCl found (Calc.)	Product nature yield (g, %) ^a	Analysis : Found (Calc.)			
	MCl ₂	K	Zr(OPr ⁱ) ₄ .Pr ⁱ OH	K	Ba(OPr ⁱ) ₂			M=a bivalent metal	Ba	Zr	OPr ⁱ
1	(M = Be) (0.18, 2.27)	(0.098, 2.41)	(1.75, 5.50)	(0.096, 2.32)	(0.58, 2.27)	0.32 (0.33)	[{Zr ₂ (OPr ⁱ) ₉ }Ba{Be(OPr ⁱ) ₃ }] ₂ Yellow solid (2.30, 76%)	0.86 (0.87)	13.40 (13.23)	17.54 (17.58)	68.38 (68.34)
2	(M = Mg) (0.26, 2.76)	(0.11, 2.81)	(2.14, 5.52)	(0.11, 2.81)	(0.71, 2.78)	0.41 (0.41)	[{Zr ₂ (OPr ⁱ) ₉ }Ba{Mg(OPr ⁱ) ₃ }] ₂ Yellow solid (2.87, 73%)	2.26 (2.31)	12.84 (13.04)	17.07 (17.32)	67.09 (67.33)
3	(M = Zn) (0.38, 2.79)	(0.11, 2.81)	(2.16, 5.57)	(0.11, 2.81)	(0.71, 2.78)	0.19 (0.20)	[{Zr ₂ (OPr ⁱ) ₉ }Ba{Zn(OPr ⁱ) ₃ }] ₂ Yellow solid (2.90, 76%)	5.61 (5.97)	12.29 (12.55)	16.36 (16.67)	64.53 (64.79)
4	(M = Sn) (0.54, 2.85)	(0.12, 3.07)	(2.20, 5.67)	(0.12, 3.07)	(0.72, 2.81)	0.41 (0.42)	[{Zr ₂ (OPr ⁱ) ₉ }Ba{Sn(OPr ⁱ) ₃ }] ₂ Yellow solid (3.17, 81%)	10.19 (10.34)	11.79 (11.97)	15.56 (15.90)	-
5	(M = Co) (0.48, 3.70)	(0.15, 3.84)	(2.90, 7.48)	(0.15, 3.84)	(0.96, 3.75)	0.54 (0.56)	[{Zr ₂ (OPr ⁱ) ₉ }Ba{Co(OPr ⁱ) ₃ }] ₂ Purple solid (3.96, 76%)	5.19 (5.42)	12.41 (12.63)	16.63 (16.77)	65.09 (65.18)
6	(M = Ni) (0.36, 2.77)	(0.11, 2.81)	(2.18, 5.62)	(0.11, 2.81)	(0.72, 2.82)	0.40 (0.41)	[{Zr ₂ (OPr ⁱ) ₉ }Ba{(Ni(OPr ⁱ) ₃ }] ₂ Purple solid (3.00, 71%)	5.36 (5.40)	12.31 (12.63)	16.56 (16.77)	65.12 (65.20)
7	(M = Cu) (0.51, 3.79)	(0.15, 3.84)	(2.97, 7.66)	(0.15, 3.84)	(0.98, 3.83)	0.55 (0.56)	[{Zr ₂ (OPr ⁱ) ₉ }Ba{Cu(OPr ⁱ) ₃ }] ₂ Green solid (4.01, 79%)	5.67 (5.82)	12.43 (12.57)	16.51 (16.70)	-

^aRecrystallised from n-hexane and toluene mixture.

15277 cm^{-1} : $\nu_3[{}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{P})]$ and in near-infrared region 6516 : $\nu_2[{}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{F})]$. These transitions are characteristic for Co^{2+} in tetrahedral¹⁵ geometry. The spectrum of (5) in THF solution exhibits well defined bands at 7375 cm^{-1} : ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}(\nu_1)$; 15246 cm^{-1} : ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}(\nu_2)$; and 20044 cm^{-1} : ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$ (ν_3), consistent with Co^{2+} in an octahedral¹⁵ geometry with in $[\{\text{Zr}_2(\text{OPr}^i)_9\}\text{Ba}\{\text{Co}(\text{OPr}^i)_3(\text{THF})_2\}]_2$.

The derivative (6) exhibits well defined bands at 16994 cm^{-1} and 18820 cm^{-1} which can be assigned to the transition $\nu_3[{}^3\text{T}_1 \rightarrow {}^3\text{T}_1(\text{P})]$ of tetrahedral¹⁶ nickel(II). Interestingly, the electronic spectrum of (6) in THF solution exhibits bands at 9060: $\nu_1[{}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{F})]$; 16556: $\nu_2[{}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})]$ and 23232: $\nu_3[{}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})]$ consistent with an octahedral geometry around the nickel(II) atom arising from coordination of two THF molecules to the nickel centre, in $[\{\text{Zr}_2(\text{OPr}^i)_9\}\text{Ba}\{\text{Ni}(\text{OPr}^i)_3(\text{THF})_2\}]_2$.

The spectrum of (7) in benzene solution shows a broad band at 15476 cm^{-1} : $\nu_1({}^2\text{E} \rightarrow {}^2\text{T}_2)$, but in THF solution this band shifted to a higher side (20576 cm^{-1}) $\nu_1[{}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}]$. This can be explained by a change of geometry from tetrahedral^{17,18}, to distorted^{17,18} octahedral around the copper(II) atom, in $[\{\text{Zr}_2(\text{OPr}^i)_9\}\text{Ba}\{\text{Cu}(\text{OPr}^i)_3(\text{THF})_2\}]_2$.

Structural elucidation by X-ray crystallographic analysis has not been successful because of our failure to obtain crystallographically suitable crystals. However, on the basis of elemental analyses, spectroscopic measurements as well as X-ray crystallographic authentication of the analogue $[\{\text{Zr}_2(\text{OPr}^i)_9\}\text{Ba}(\mu\text{-OPr}^i)_2\text{Cd}(\mu\text{-OPr}^i)]_2$, the structure shown in (Fig. 1) for the derivatives (1)–(7) is plausible:

Experimental

All the experiments and manipulations were carried out under strictly anhydrous conditions. BDH grade benzene, isopropyl alcohol, *n*-hexane, tetrahydrofuran and toluene were dried and purified by the methods described in our earlier publication.¹⁹ Freshly cut and cleaned Ba metal (Aldrich) was used. $\text{ZnCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were made anhydrous by the thionyl chloride method.²⁰ $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ were dried by heating at 100°C under reduced pressure. Anhydrous SnCl_2 was obtained by treating $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ with acetic anhydride. BeCl_2 was sublimed prior to use. $\text{Zr}(\text{OPr}^i)_4 \cdot \text{Pr}^i\text{OH}$ was prepared by the literature method.²¹ Tertiary butyl alcohol was dried and purified by refluxing over sodium followed by distillation.

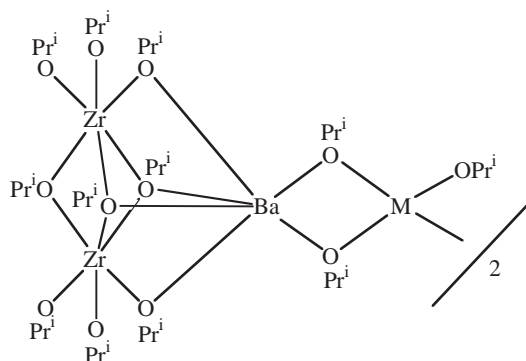


Fig. 1 Proposed structure for the derivatives (1)–(7)

Beryllium, barium, nickel, tin, zinc and zirconium in the derivatives (1)–(7) were determined²² gravimetrically as BeO , BaSO_4 , $\text{Ni}(\text{DMGH})_2$ (where $\text{DMGH}_2 = \text{dimethylglyoxime}$), SnO_2 , $\text{Zn}(\text{NH}_4)\text{PO}_4$ and $\text{Zr}(\text{C}_8\text{H}_7\text{O}_3)_4$, respectively. Cobalt, copper(II) and magnesium were determined²² volumetrically. Isopropoxy groups in the compounds were determined by the oxidimetric method.²³

${}^1\text{H}$ NMR (89.55 MHz), ${}^{13}\text{C}$ NMR (22.49 MHz) and ${}^{119}\text{Sn}$ NMR (33.35 MHz) spectra were recorded on a JEOL FX 90Q spectrometer. ${}^1\text{H}$ NMR in CDCl_3 were referenced with internal TMS ($\delta = 0$). ${}^{13}\text{C}$ NMR spectra were recorded in CCl_4 ($\delta = 96.10$) or C_6H_6 ($\delta = 128.16$) and solvents were referenced internally with solvent peaks given in parentheses. ${}^{119}\text{Sn}$ NMR spectra were recorded in

C_6H_6 and referenced externally with SnMe_4 ($\delta = 0$). IR spectra (4000–200 cm^{-1}) were recorded on a Nicolet Magna 550 spectrophotometer. The electronic spectra were recorded in C_6H_6 and THF solutions on a CARY-50 Bio-spectrophotometer.

Synthesis of $[\{\text{Zr}_2(\text{OPr}^i)_9\}\text{Ba}\{\text{Zn}(\text{OPr}^i)_3\}]_2$: To a benzene (20 ml) solution of $\text{KZr}_2(\text{OPr}^i)_9$ [which was freshly prepared from K (0.11g), Pr^iOH (10ml) and $\text{Zr}(\text{OPr}^i)_4$, Pr^iOH (2.16 g)] was added to a prestirred suspension of ZnCl_2 (0.38 g) in C_6H_6 (10 ml). After stirring the resulting reaction mixture for ~ 6 h at room temperature, freshly isolated $\text{KBa}(\text{OPr}^i)_3$ [prepared from K (0.11g), Pr^iOH (20 ml) and $\text{Ba}(\text{OPr}^i)_2$ (0.71g)] was added and the reaction mixture was again stirred at room temperature for ~6 h. After removal of the precipitated KCl (0.19g) by filtration, the volatile components from the filtrate were removed under reduced pressure to give a yellow solid (2.90 g), which was recrystallised from *n*-hexane and toluene at -20°C in 76% yield.

Analytical details and some physical properties are listed in Table 4.

Derivatives (1), (2), and (4)–(7) have also been prepared by the same method and further details are listed in Table 4.

Reaction of $[\{\text{Zr}_2(\text{OPr}^i)_9\}\text{Ba}\{\text{Zn}(\text{OPr}^i)_3\}]_2$ with an excess of *t*-BuOH: A benzene (60 ml) solution containing the derivative (3) (1.013 g) and anhydrous *t*-BuOH (3g) was refluxed under a fractionating column with the continuous removal of the liberated Pr^iOH (0.43 g) azeotropically, which was collected and determined periodically until the azeotrope showed negligible presence of an oxidisable material. From the yellowish solution, volatiles were removed under reduced pressure to obtain the product of composition $[\{\text{Zr}_2(\text{OPr}^i)_3(\text{OBu}^t)_6\}\text{Ba}\{\text{Zn}(\text{OPr}^i)(\text{OBu}^t)_2\}]_2$ (1.12 g). After recrystallisation from *n*-hexane and toluene at -20°C , the analytically pure product was obtained in 79% yield. Analysis (%): Found, Ba, 11.30; Zr, 15.05; Zn, 5.26. Calculated, Ba, 11.38; Zr, 15.12; Zn, 5.67.

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