

Pentadienyl chemistry of the heavy alkaline-earth metals revisited†

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Open-metallocenes of the heavy alkaline-earth metals $[(\eta^5\text{-Pdl}')_2\text{-M}(\text{thf})_n]$ ($\text{M} = \text{Ca}$ (**1**), Sr (**2**), $n = 1$; $\text{M} = \text{Ba}$ (**3**), $n = 2$; $\text{Pdl}' = 2,4\text{-tBu}_2\text{C}_5\text{H}_5$) are readily prepared by salt-metathesis between Ml_2 and KPdl' and characterized by NMR spectroscopy and X-ray diffraction studies.

Over the last decade organometallic calcium, strontium and barium complexes have attracted some interest,^{1–3} e.g. as precursors for metalorganic vapour deposition (MOCVD)^{4,5} or as catalyst systems in polymerisation and hydrofunctionalization reactions.^{6–9} Nevertheless, the isolation and characterization of these highly reactive compounds required the development of suitable ligands and synthetic techniques. In this context, the η^5 -coordinate cyclopentadienyl ligand has played a prominent role in stabilizing half-sandwich and metallocene complexes.^{10–16} More recently, these investigations have been extended to allyl systems, which can adopt both $\pi(\eta^3)$ and $\sigma(\kappa\text{C})$ bonding modes.^{17–25} Pentadienyls, with their ability to adopt κC -, η^3 - and η^5 -coordination modes, occupy an intermediate position between the cyclopentadienyl and allyl systems, and their coordination chemistry with transition metals has been well established.^{26–31} Surprisingly, reports on group 2 complexes (Be ,³² Mg ,³³ and Ca ³⁴) show only two of them are structurally characterized, $[(\kappa\text{C-}2,4\text{-Me}_2\text{C}_5\text{H}_5)_2\text{Mg}(\text{tmeda})]^{33}$ and $[(\eta^5\text{-Pdl}')_2\text{Ca}(\text{thf})]$ ($\text{Pdl}' = 2,4\text{-tBu}_2\text{C}_5\text{H}_5$; **1**).³⁴ Overby and Hanusa report that the Pdl' ligand provides only limited solubility, thus precluding the synthesis of the open metallocenes of the heavier homologues, Sr and Ba ,³⁴ but this is in contrast to the general observation that sterically demanding substituents such as $t\text{Bu}$ and SiMe_3 enhance solubility and stabilize the corresponding metal complexes. For instance, several heavy alkaline-earth metal complexes have

been successfully prepared with $t\text{Bu}$ -substituted cyclopentadienyl,^{5,35,36} pyrrolyl³⁷ and P-heterocyclic^{38,39} ligands, and all exhibit good solubility in aliphatic and aromatic hydrocarbon solvents. Within our research program on pentadienyl ligands,⁴⁰ we therefore decided to revisit the heavy alkaline-earth metals.

The potassium salt KPdl' ⁴¹ was prepared according to a modified literature procedure† and can be crystallized as its thf-adduct from saturated THF solutions at -30°C .† A snapshot of the molecular structure of $[(\text{thf})\text{K}(\mu\text{-}\eta^5\text{-}\eta^5\text{-Pdl}')_\infty]$ is shown in Fig. 1 and reveals that the U-shaped $\eta^5\text{-Pdl}'$ anion is coordinated in the solid state by two potassium cations to form a zigzag polymeric chain *via* a 2_1 screw axis. Selected bond distances and angles are listed in Table 1. The C–C bond distances within the pentadienyl moiety (C1–C5) follow the typical short–long–long–short pattern. The conformation angle χ is defined as the angle between the two planes, [centroid(C1–C5)–C3–M] and [centroid(C1'–C5')–C3'–M], and allows the mutual orientation of the two pentadienyl moieties to be quantified. In $[(\text{thf})\text{K}(\mu\text{-Pdl}')_\infty]$ the pentadienyl ligands adopt a nearly anti-ecliptic conformation with $\chi = 178.5^\circ$, thereby minimizing repulsive interactions between the sterically demanding $t\text{Bu}$ -groups.

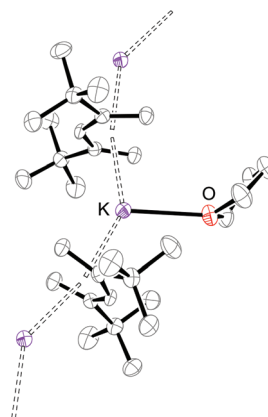







Fig. 1 ORTEP diagram of $[(\text{thf})\text{K}(\mu\text{-Pdl}')_x]$ (50% probability ellipsoids).

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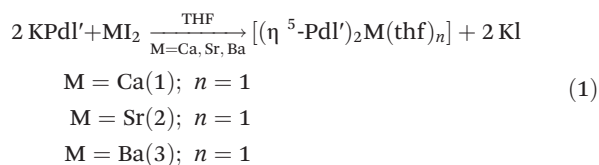
†Electronic supplementary information (ESI) available: Experimental, NMR, crystallographic and computational data. CCDC 982693–982696. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt00545g

Table 1 Selected bond distances and angles

							
	Idealized χ :	syn-eclipsed	gauche	staggered	gauche	anti-eclipsed	
		0°	60°	90°	120°	180°	
<hr/>							
	$[(\text{thf})\text{K}(\mu\text{-PdI}')]\text{x}$	1	2^a			3	
<hr/>							
M–C (pdl) (Å, range)	3.0166(19)–3.235(3)	2.7908(10)–2.6681(10)			2.786(3)–2.978(3)/2.800(3)–3.010(3)		2.9627(14)–3.1937(17)
M–C1/5 (pdl) (Å, average)	3.159(65)	2.722(54)			2.902(59)/2.907(78)		3.147(33)
M–C2/4 (pdl) (Å, average)	3.056(16)	2.768(31)			2.888(20)/2.896(27)		3.113(10)
M–C3 (pdl) (Å, average)	2.982(50)	2.728(28)			2.805(27)/2.817(23)		2.981(26)
M–C (pdl) (Å, average)	3.082 ± 0.083	2.738 ± 0.040			2.887 ± 0.053/2.884 ± 0.060		3.100 ± 0.068
M–PdI _{centroid} ^b (Å, average)	2.70	2.28			2.45/2.46		2.70
C1–C5 (Å, mean)	3.20	3.18			3.19/3.18		3.21
M–O (Å)	2.7577(18)	2.4074(7)			2.5383(17)/2.5224(17)		2.7488(11)/2.7943(12)
PdI _{centroid} –M–PdI _{centroid} ^b (°)	165.5	145.6			143.5/143.6		130.9
α^c	29.9	28.8			30.3/33.4		53.1
χ	178.5	175.0			176.1/176.0		124.8

^a Two independent molecules in the asymmetric unit. ^b PdI_{centroid} is the centroid of the pentadienyl ligand. ^c α is defined as the angle formed by the two dienyl planes.

In contrast to the previous report,³⁴ the salt metatheses of two equivalents of KPdl' with MI₂ (M = Ca, Sr, Ba) proceed smoothly at ambient temperature and yield the corresponding open-metallocenes $[(\eta^5\text{-PdI}')_2\text{M}(\text{thf})_n]$ (M = Ca (**1**), Sr (**2**), $n = 1$; M = Ba (**3**), $n = 2$) in crystalline form and moderate yields (eqn (1)).†



Nevertheless, we also found that the anionic PdI' ligand behaves as a strong base and readily undergoes radical coupling to 2,4,7,9-tetra-*tert*-butyl-1,3,7,9-decatetraene.^{41,42} Therefore, it is imperative for the synthesis of these complexes to use metal iodides MI₂ of high purity. Trace amounts of NH₃ or I₂ as a result of the MI₂ preparation must be removed, otherwise the yield of the salt metathesis reaction is dramatically reduced and insoluble material is obtained. However, pure open-metallocenes **1–3** are readily soluble in aliphatic hydrocarbons (pentane, hexane), aromatic solvents (benzene, toluene) and ethers (tetrahydrofuran, diethyl ether), and can readily be crystallized as their thf adducts from concentrated pentane solutions at –30 °C.‡ Since our synthetic protocol yields very soluble products, we also recorded ¹H and ¹³C{¹H} NMR spectra in C₆D₆ of these complexes and as expected, the NMR spectra of these complexes are very similar. In addition, no dynamic behaviour of the PdI' ligands is observed at ambient temperature in solution.†

The molecular structures of **2** and **3** are shown in Fig. 2, and relevant bond distances and angles are listed in Table 1. In addition significantly improved X-ray diffraction data for the open-calocene **1** were obtained, so we decided, for a

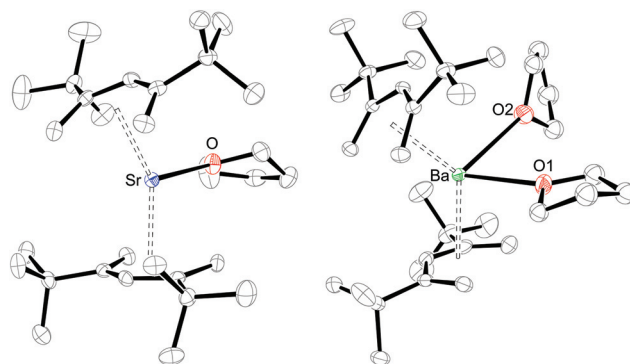


Fig. 2 ORTEP diagrams of **2** and **3** (50% probability ellipsoids). For **2** only one of the two independent molecules in the asymmetric unit is shown. For **3** the two thf molecules are disordered over two positions, but only one conformation is shown.

better comparison, to include our data in Table 1. In all cases, the PdI' ligand adopts a η^5 -U coordination mode and the structural features of these complexes resemble those of **1**, except that two THF ligands are coordinated in the case of Ba. Whereas one THF ligand resides in the usual position at the open edge of one PdI' ligand, the second THF molecule is positioned at the backside of the second pentadienyl ligand. In $[(\eta^5\text{-2,4-Me}_2\text{C}_5\text{H}_5)_2\text{Zr}(\text{CO})_2]$ the two CO ligands feature a similar orientation with respect to the dienyl ligands.⁴³ The conformational angles χ range from 175° for **1** to 124.8° for **3** and the predominant driving force for these arrangements is the minimization of repulsive interactions between the PdI' and thf ligands. Furthermore, the C–C distances within the pentadienyl system show a distinct short–long–long–short–pattern. Previous studies on $[(\eta^5\text{-2,4-Me}_2\text{C}_5\text{H}_5)_3\text{Nd}]$, which also shows ionic bonding between the dienyl ligand and the metal cation, established that the M–C bonds to the formally



charged C1-, C3-, and C5-positions are shorter than those to the uncharged C2- and C4-positions.⁴⁴ For the complexes **1–3** the M–C distances vary significantly and the shortest is found to be the central carbon atom of the Pd^I ligand (C3-position) consistent with the observation on $[(\eta^5\text{-}2,4\text{-Me}_2\text{C}_5\text{H}_5)_3\text{Nd}]$. However, the average Ca–C1/5 distances (2.722(54) Å) in **1** are essentially identical to the average Ca–C3 distances (2.728(28) Å), a different trend is observed for the heavier homologues **2** and **3**, for which the average M–C2/4 and M–C1/5 bonds become progressively longer (Table 1). The increase in the average M–C distances of 2.738(40) Å in **1** to 3.100(68) Å in **3** nicely mirrors the increase in ionic radii for heptacoordinate Ca^{2+} (1.06 Å) and Sr^{2+} (1.21 Å) and octacoordinate Ba^{2+} (1.40 Å).⁴⁵ These observations can be compared to those in metal-allyl complexes, for which average M–C distances in $[(\eta^3\text{-}1,3\text{-(Me}_3\text{Si)}_2\text{C}_3\text{H}_3)_2\text{Ca}(\text{thf})_2]$ (2.654(4) Å),¹⁷ $[(\eta^3\text{-C}_3\text{H}_5)_2(\text{triglyme-}\kappa^4)]$ (2.727(72) Å),⁴⁶ and $[(\eta^3\text{-}1,3\text{-(Me}_3\text{Si)}_2\text{C}_3\text{H}_3)_2\text{Sr}(\text{thf})_2]$ (2.801 Å)²¹ are found. All attempts to prepare a monomeric allyl Ba analogue resulted in the formation of a heterometallic barium/potassium complex, $[\text{K}(\text{thf})\text{Ba}_2(1,3\text{-(Me}_3\text{Si)}_2\text{C}_3\text{H}_3)_5]$.²¹ This further supports the important features of the pentadienyl fragment in the stabilization of the heavy-alkaline earth metals by adopting an intermediate position between the allyl and cyclopentadienyl fragments. Furthermore, the average M–C (M = Ca, Sr, Ba) bond distances in **1–3** are longer than those in the related metallocenes, e.g. $[(\eta^5\text{-}1,3\text{-(Me}_3\text{Si)}_2\text{C}_5\text{H}_3)_2\text{-M}(\text{thf})]$ (M = Ca (2.678(14) Å),⁴⁷ Sr (2.82 Å)⁴⁸) and $[(\eta^5\text{-}1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2)_2\text{Sr}(\text{thf})]$ (2.87 Å).³⁵ This presumably indicates a more flexible and therefore weaker metal–ligand bonding in the pentadienyl systems, and therefore a hapticity switch should be relatively facile in the open group 2 metallocenes.

Conclusions

We have extended the series of group 2 open-metallocenes to Sr and Ba and established a reliable synthetic protocol that allows the preparation of synthetically useful quantities. In all cases the Pd^I ligand adopts a $\eta^5\text{-U}$ coordination mode in the solid state and in solution. It can be expected that the other group 2 open-metallocenes are also accessible and that they exhibit broad reactivity towards unsaturated molecules. These and related studies are ongoing and will be reported in due course.

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Notes and references

† Crystal data for $[(\text{thf})\text{K}(\mu\text{-}\eta^5\text{-}\eta^5\text{-PdI})_\infty]$: $\text{C}_{17}\text{H}_{31}\text{KO}$, $M = 290.52$, orthorhombic, $a = 10.1190(2)$ Å, $b = 10.7148(6)$ Å, $c = 16.4367(9)$ Å, $V = 1782.11(14)$ Å³, $T = 130(2)$

K, space group $P2_12_12_1$, $Z = 4$ (monomers), $\mu(\text{CuK}\alpha) = 2.5$ mm^{−1}, 18 651 reflections measured, 3697 independent reflections ($R_{\text{int}} = 0.108$). The final R_1 values were 0.0498 ($I > 2\sigma(I)$) and 0.0572 (all data). The final $wR(F^2)$ values were 0.1245 ($I > 2\sigma(I)$) and 0.1304 (all data). The goodness of fit on F^2 was 1.02.

Crystal data for **1**: $\text{C}_{30}\text{H}_{54}\text{OCa}$, $M = 470.81$, monoclinic, $a = 9.9014(2)$ Å, $b = 21.7075(4)$ Å, $c = 14.4003(3)$ Å, $\beta = 105.501(2)^\circ$, $V = 2982.56(10)$ Å³, $T = 100(2)$ K, space group $P2_1/n$, $Z = 4$, $\mu(\text{MoK}\alpha) = 1.9$ mm^{−1}, 78 853 reflections measured, 6171 independent reflections ($R_{\text{int}} = 0.048$). The final R_1 values were 0.0296 ($I > 2\sigma(I)$) and 0.0306 (all data). The final $wR(F^2)$ values were 0.0785 ($I > 2\sigma(I)$) and 0.0794 (all data). The goodness of fit on F^2 was 1.05.

Crystal data for **2**: $\text{C}_{30}\text{H}_{54}\text{OSr}$, $M = 518.35$, triclinic, $a = 9.7948(5)$ Å, $b = 14.1834(5)$ Å, $c = 23.3962(10)$ Å, $\alpha = 88.549(3)^\circ$, $\beta = 79.821(2)^\circ$, $\gamma = 71.131(2)^\circ$, $V = 3025.4(2)$ Å³, $T = 100(2)$ K, space group $P\bar{1}$, $Z = 4$, $\mu(\text{MoK}\alpha) = 1.8$ mm^{−1}, 132 306 reflections measured, 15 422 independent reflections ($R_{\text{int}} = 0.111$). The final R_1 values were 0.0544 ($I > 2\sigma(I)$) and 0.1022 (all data). The final $wR(F^2)$ values were 0.0724 ($I > 2\sigma(I)$) and 0.0825 (all data). The goodness of fit on F^2 was 1.04.

Crystal data for **3**: $\text{C}_{34}\text{H}_{62}\text{BaO}_2$, $M = 640.18$, triclinic, $a = 9.5411(3)$ Å, $b = 12.0829(3)$ Å, $c = 15.6171(5)$ Å, $\alpha = 96.320(2)^\circ$, $\beta = 97.530(3)^\circ$, $\gamma = 98.661(3)^\circ$, $V = 1748.97(9)$ Å³, $T = 100(2)$ K, space group $P\bar{1}$, $Z = 2$, $\mu(\text{MoK}\alpha) = 1.2$ mm^{−1}, 92 321 reflections measured, 10 431 independent reflections ($R_{\text{int}} = 0.031$). The final R_1 values were 0.0222 ($I > 2\sigma(I)$) and 0.0262 (all data). The final $wR(F^2)$ values were 0.0493 ($I > 2\sigma(I)$) and 0.0514 (all data). The goodness of fit on F^2 was 1.05.

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