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Synthesis and characterisation of divalent di(1,3-bis(diphenylphosphano)cyclopentadienyl)lanthanoid and alkaline earth complexes as potential platforms for heterometallic complexes

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Dedicated to Prof. Thomas Schleid on the occasion of his 65th birthday.

New divalent lanthanoid and alkaline earth metal complexes bearing the 1,3-bis(diphenylphosphano)cyclopentadienyl ligand have been synthesised using the redox-transmetallation protolysis (RTP) approach. From the reaction of the corresponding metal, diphenylmercury and the proligand C₅H₄(PPh₂)₂, the

compounds [M(η⁵-C₅H₃(PPh₂)₂-1,3)₂(S)] (with M = Yb, S = (thf)₂ or M = Yb, Eu, Ca, Sr, Ba, S = dme) were isolated and characterised by X-ray diffraction and multinuclear NMR spectroscopy. These compounds may provide a platform for early-late heterobimetallic complexes.

Introduction

Heterobimetallic complexes containing an early d-block or f-element and a late transition metal have been known for decades,^[1] but they are now increasingly studied for their applications in catalysis and small molecule activation,^[2] in medicinal chemistry^[3] or as single molecule magnets.^[4] Many of these complexes also feature intriguing structural aspects such as direct metal-metal bonding.^[5] Among various linkage units (CO, hydrides, amides, alkoxides, heteroaromatics, alkenes, carbyls, etc.),^[6] phosphines play an important role in accessing such heterobimetallic complexes.^[7] Within this context, a few examples with alkaline earth or lanthanoid metal complexes bearing anionic phospholyl or phosphine-containing cyclopentadienyl ligands have been reported (Figure 1).^[8]

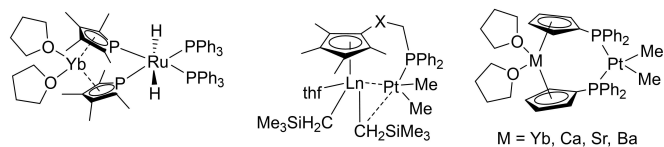


Figure 1. Selected examples of bimetallic lanthanoid or alkaline earth/late transition metal complexes bearing phosphine-containing cyclopentadienyl-type ligands.^[8]

Following our previous studies on the synthesis of bimetallic lanthanoid/Pt, Ni, W, Mo and alkaline earth/Pt complexes linked by the anionic CpPPh₂ ligand,^[8a,b,9] we herein report the synthesis of monometallic divalent metal complexes bearing the anionic 1,3-bis(diphenylphosphano)cyclopentadienyl ligand. This ligand has so far only been investigated in ferrocene complexes,^[10] for example, in the synthesis of the bimetallic structurally characterised Pd/Fe complex [Fe(η⁵-C₅H₃(PPh₂)₂-1,3)₂(PdCl(CH₂Cl))₂]. Furthermore, the combination of [Fe(η⁵-C₅H₃(PPh₂)₂-1,3)₂] with [PdCl(η⁵-C₃H₅)₂] successfully catalysed the reaction of haloarenes with thiophenols.^[10b]

Results and Discussion

Lithium (diphenylphosphano)cyclopentadienide was synthesised from 1-(diphenylphosphano)cyclopentadiene (Scheme 1) using a literature procedure.^[11] The lithiated cyclopentadienyl ligand was then mixed with a stoichiometric amount of chlorodiphenylphosphane in Et₂O providing a solution of 1,3-bis(diphenylphosphano)cyclopentadiene after removal of LiCl. In a typical redox-transmetallation protolysis procedure,^[12] the Et₂O solution of the proligand was added to a mixture of freshly filed ytterbium metal and HgPh₂ in thf. Sonication for 48 h

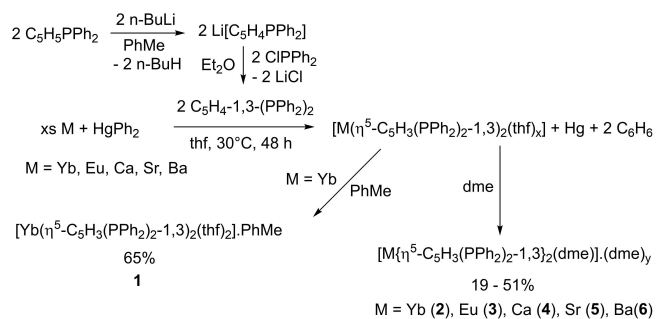
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Scheme 1. Synthesis of complexes 1–6 by redox-transmetalation protolysis.

yielded the new complexes, $[\text{Yb}(\eta^5\text{-C}_5\text{H}_3(\text{PPh}_2)_2\text{-1,3})_2(\text{thf})_2]$ (**1**) and $[\text{Yb}(\eta^5\text{-C}_5\text{H}_3(\text{PPh}_2)_2\text{-1,3})_2(\text{dme})]$ (**2**), in good yields after recrystallisation from either toluene or dme. The ^{31}P NMR spectrum of the crude reaction mixture showed some minor impurities including PPh_3 and PPh_2H , which may arise from some C–P bond activation processes.^[13] The Eu analogue $[\text{Eu}(\eta^5\text{-C}_5\text{H}_3(\text{PPh}_2)_2\text{-1,3})_2(\text{dme})]$ (**3**) and the alkaline earth metal complexes $[\text{M}(\eta^5\text{-C}_5\text{H}_3(\text{PPh}_2)_2\text{-1,3})_2(\text{dme})]$ ($\text{M} = \text{Ca}$ (**4**), Sr (**5**), Ba (**6**)) were synthesised in the same way, albeit in lower yields.

Air and moisture sensitive complexes 1–6 were characterised by infrared spectroscopy, and the representative complex **2** was characterised by multinuclear NMR spectroscopy in detail. Furthermore, single crystals of complexes 1–6 suitable for X-ray diffraction were obtained. The presence of some disordered solvent molecules in the crystal structures required the application of the Platon program SQUEEZE and hence prevented the determination of the exact complex composition which was however further studied by metal and elemental analysis (see Experimental Section, SI, Table T1 and T2).

A singlet peak in the $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra of 1–6 (not observed for the paramagnetic Eu^{2+} complex **3**) was observed in the range of -19 to -23 ppm. This phosphorus resonance is similar to that of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_3(\text{PPh}_2)_2\text{-1,3})_2]$ ^[10a] (-22.46 ppm in benzene- d_6) but is significantly different from the Li salt (-15.83 ppm in thf- d_8). The previously synthesised ytterbocene complex, $[\text{Yb}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2(\text{thf})]$ ^[8a] showed a phosphorus resonance at -20.01 ppm, indicative of equivalent and uncoordinated phosphane groups.

The ^1H and ^{13}C NMR spectra of complex **2** were studied in detail and compared to the previously reported ferrocene complex $[\text{Fe}(\eta^5\text{-C}_5\text{H}_3(\text{PPh}_2)_2\text{-1,3})_2]$ (Table 1 and SI).^[10a] The ^1H

NMR spectrum of **2** showed two signals for the Cp protons at 6.11 and 6.58 ppm in a 1:2 ratio. In contrast, in the linear ferrocene complex, these protons were reported at 3.97 and 4.40 ppm in a 2:1 ratio.^[10a] In the ^{13}C NMR spectrum of **2**, three signals corresponding to the Cp ring carbons are observed at 116.1, 118.3 and 120.6 ppm, which are again significantly shifted to higher frequencies compared to the related ferrocene complex $[\text{Fe}(\eta^5\text{-C}_5\text{H}_3(\text{PPh}_2)_2\text{-1,3})_2]$ (76.2, 81.0 and 83.0 ppm).^[10a] A possible explanation for these remarkable differences in the chemical shifts may stem from the complex geometries (linear vs. bent) and the highly ionic bonding character in the lanthanoid complex compared to the covalent bonding in the ferrocene complex. Finally, an intriguing feature of the ^{13}C NMR signals of **2** is their multiplicity, which suggests that the phosphane groups are not fully equivalent. A similar observation was made for the ferrocene complex but no explanation has been put forward.

The room-temperature ^{171}Yb NMR chemical shift for **2** ($+308$ ppm in benzene- d_6) is in the region observed for an eight-coordinate complex such as $[\text{Yb}(\rho\text{-HC}_6\text{F}_4\text{NC}_2\text{H}_4\text{NET}_2)_2(\text{dme})]$ ($+389$ ppm in benzene- d_6).^[14] Interestingly, this value is quite close to the value observed for the seven-coordinate Yb–F half-sandwich complex $[\text{Yb}(\eta^5\text{-C}_5\text{Ph}_4\text{H})(\mu\text{-F})(\text{thf})_2]$ ($+376$ ppm in thf/benzene), whereas the structurally much closer seven-coordinated sandwich complex $[\text{Yb}(\eta^5\text{-C}_5\text{Ph}_4\text{H})_2(\text{thf})]$ shows a signal at $+116$ ppm in thf/benzene.^[15] Further coordination of thf in the donor medium may account for the differences.

The infrared spectra of complexes 1–6 are very similar to those of $[\text{Ae}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2(\text{S})_2]$ ($\text{Ae} = \text{Ca}, \text{Sr}, \text{Ba}; \text{S} = \text{thf}$ or dme) complexes reported previously.^[8b] The C–O stretching frequency of dme in the spectra is shifted from that of the free ligand (1105 cm^{-1}) to $1057\text{--}1069\text{ cm}^{-1}$ as previously observed for $[\text{Yb}(\eta^5\text{-C}_5\text{H}_4\text{R})_2(\text{dme})]$ ($\text{R} = \text{H}$ or Me).^[16] For complex **1**, ring stretching modes of thf were observed at 1039 and 874 cm^{-1} and were displaced from the free ligand values (1072 and 912 cm^{-1}) as expected on complexation.^[17]

Complexes 1–6 contain eight-coordinate metal atoms interacting with two $\eta^5\text{-C}_5\text{H}_3(\text{PPh}_2)_2$ donors and two oxygen atoms (from either dme or thf). The coordination geometries of complexes 1–6 are distorted tetrahedral, if the centroids (Ct) of the Cp rings are considered as donor points. The crystal structure of complex **1** has two thf ligands bound to the metal (Figure 2). Complexes 2–6 have two independent molecules in the asymmetric unit. In each case, the bond lengths and distances are similar with only slight differences. Thus, only one of the two molecules in the asymmetric unit is used as representative. The bond distances and angles in Table 2 describe only one of the two molecules in the asymmetric unit (for bond distances and angles of the second molecule for complexes 2–6 refer to Table T3 in SI). X-ray crystallographic data is shown in Table T4 (see SI). These complexes are isotopic, hence complex **2** (molecule 1) is shown as a representative molecule (Figure 3) (for X-ray structures of the second molecule for complexes 2–6 refer to Figures F1 and F2 in SI).

The Yb–C bond lengths of **2** (ranging from $2.677(5)\text{--}2.771(5)$ Å with a mean distance of 2.73 Å) compare well with **1** ($2.705\text{--}2.789(3)$ Å with a mean distance of 2.74 Å). These are near to

Table 1. ^1H , ^{13}C and ^{31}P NMR chemical shifts (in ppm) of complex **2** and $[\text{Fe}(\eta^5\text{-C}_5\text{H}_3(\text{PPh}_2)_2\text{-1,3})_2]$ ^[10a] in C_6D_6 .

Complex	Cp (^1H)	Cp (^{13}C)	^{31}P
2	6.11 (s, 1H)	116.1 (pt)	-21.30 (s)
	6.58 (s, 2H)	118.3 (dd)	
		120.6 (pt)	
Fe	3.97 (s, 2H)	76.2 (m)	-22.46 (s)
	4.40 (s, 1H)	81.0 (m)	
		83.0 (m)	

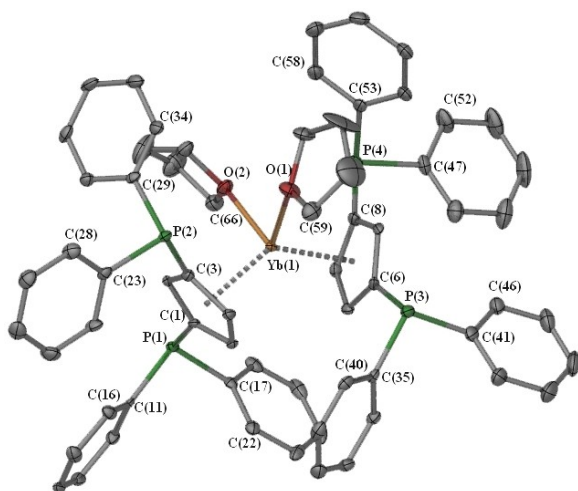


Figure 2. X-ray crystal structure of $[\text{Yb}(\eta^5\text{-C}_5\text{H}_3(\text{PPh}_2)_2)_{1,3}]_2(\text{thf})_2 \cdot \text{PhMe}$ (**1**). Hydrogen atoms and solvent of crystallisation have been omitted for clarity.

values for other structurally characterised divalent ytterbium bis-cyclopentadienyl complexes: $[\text{Yb}(\eta^5\text{-C}_5\text{H}_5)_2(\text{dme})]$ (mean 2.74 Å),^[18] $[\text{Yb}(\eta^5\text{-Bu}^t\text{-C}_5\text{H}_4)_2(\text{thf})_2]$ (mean 2.75 Å),^[19] $[\text{Yb}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2(\text{dme})]$ (mean 2.71 Å),^[8a] $[\text{Yb}(\eta^5\text{-1,3-Bu}^t_2\text{C}_5\text{H}_3)_2(\text{dme})]$ (mean 2.70 Å).^[20] The average Yb–C distance of **2** is also similar to that of $[\text{Yb}(\text{thf})_2(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2\text{Pt}(\text{Me})_2] \cdot \text{thf}^{[8a]}$ (mean Yb–C: 2.71 Å). The Ct1–Yb–Ct2 angle of 133.8° for **2** is also concordant with **1** (133.0°). These values are also quite similar to those of $[\text{Yb}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2(\text{dme})]^{[8a]}$ (Ct1–Yb–Ct2 angle: 133.8°). There is

slight disorder associated with one of the thf groups in **1** but this does not affect the Yb–O bond metrics. The Yb–O distances (**1**: mean 2.40 Å; **2**: mean 2.42 Å) (Table 2) are close to those of $[\text{Yb}(\text{thf})_2(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2\text{Pt}(\text{Me})_2] \cdot \text{thf}^{[8]}$ (mean 2.40 Å) but are much smaller than in $[\text{Yb}(\eta^5\text{-Pr}^i\text{-indenyl})_2(\text{thf})_2]^{[21]}$ (mean 2.62 Å) (may be due to the larger steric bulk of the Prⁱ-indenyl groups) but slightly longer than that observed for the bis(indenyl)ytterbium *ansa* complex $\text{rac-}[\text{Yb}(\eta^5\text{-}(\text{CH}_2)_2\text{C}_9\text{H}_6)_2(\text{thf})_2]^{[22]}$ (mean 2.37 Å).

The mean Eu–C bond length for **3** of 2.85 Å (distance ranging from 2.797(5)–2.938(6) Å) and mean Eu–O distance of 2.55 Å (Eu–O(1): 2.539(4) and Eu–O(2): 2.576(4) Å) are slightly shorter compared with the previously synthesised nine-coordinate, $[\text{Eu}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2(\text{diglyme})]^{[9]}$ complex (Eu–C: 2.83–2.94 Å; (mean 2.89 Å)) and Eu–O: 2.60–2.63 Å (mean 2.62 Å), as expected for the coordination number changes. These bond lengths in **3** are longer than those of Yb–C and Yb–O of complexes **1** (mean Yb–C: 2.74 Å; Yb–O: 2.40 Å) and **2** (mean Yb–C: 2.73 Å; Yb–O: 2.42 Å) in accordance with the “lanthanoid contraction” (ionic radii of eight-coordinate Eu^{2+} and Yb^{2+} are 1.25 Å and 1.14 Å, respectively^[23]). However, the Ct1–Eu–Ct2 angle of **3** (127.9°) is smaller than that of the Ct1–Yb–Ct2 angle of **1** (133.0°) and **2** (133.8°), which is presumably due to the greater steric crowding around Yb^{2+} than Eu^{2+} because of the relatively smaller size of Yb^{2+} .

The average Ca–C and Ca–O average bond distances for **4** are 2.73 Å (ranging from 2.680(2)–2.828(2) Å) and 2.39 Å respectively. For complex **5**, (Sr–C: mean 2.86 Å ranging from 2.825(4)–2.946(5) Å; Sr–O: 2.54 Å) and **6** (Ba–C: 3.03 Å ranging from 2.963(5)–3.093(5) Å; Ba–O: 2.73 Å), the differences in bond distances are expected due to the increasing ionic radii from Ca^{2+} to Ba^{2+} (ionic radii of eight-coordinate Ca^{2+} , Sr^{2+} and Ba^{2+}

Table 2. Selected bond lengths (in Å) and angles (in °) of complexes **1**–**6**.

	1	2	3	4	5	6
Average M(1)–C	2.74	2.73	2.85	2.73	2.86	3.03
M(1)–C	2.705(3)– 2.789(4)	2.677(5)– 2.771(5)	2.797(5)– 2.938(6)	2.680(2)– 2.828(2)	2.825(4)– 2.946(5)	2.963(5)– 3.093(5)
M–O(1)	2.401(3)	2.425(5)	2.539(4)	2.386(2)	2.560(3)	2.739(4)
M–O(2)	2.402(3)	2.410(4)	2.576(4)	2.406(2)	2.525(3)	2.729(4)
P(1)–C(1)	1.809(3)	1.799(5)	1.791(6)	1.808(2)	1.799(5)	1.787(5)
P(2)–C(3)	1.805(4)	1.800(5)	1.797(6)	1.800(2)	1.809(5)	1.807(5)
P(3)–C(6)	1.808(4)	1.808(6)	1.810(6)	1.811(2)	1.791(5)	1.794(5)
P(4)–C(8)	1.805(4)	1.800(5)	1.808(6)	1.808(2)	1.799(5)	1.805(5)
C(1)–C(2)	1.418(5)	1.419(7)	1.390(8)	1.417(3)	1.404(6)	1.420(7)
C(2)–C(3)	1.409(5)	1.413(7)	1.426(8)	1.422(3)	1.405(6)	1.407(6)
C(3)–C(4)	1.429(5)	1.415(7)	1.410(8)	1.430(3)	1.415(6)	1.422(6)
C(4)–C(5)	1.399(5)	1.405(7)	1.380(8)	1.393(3)	1.384(6)	1.400(7)
C(1)–C(5)	1.429(5)	1.437(6)	1.427(8)	1.425(3)	1.417(6)	1.429(7)
C(6)–C(7)	1.422(5)	1.424(7)	1.412(8)	1.417(3)	1.421(6)	1.414(7)
C(7)–C(8)	1.412(5)	1.416(7)	1.414(7)	1.422(3)	1.399(6)	1.405(7)
C(8)–C(9)	1.433(5)	1.424(7)	1.417(8)	1.419(3)	1.422(6)	1.415(6)
C(9)–C(10)	1.394(5)	1.392(7)	1.387(8)	1.403(3)	1.399(6)	1.399(7)
C(6)–C(10)	1.432(5)	1.419(7)	1.433(8)	1.420(3)	1.430(6)	1.422(6)
O(1)–M(1)–O(2)	102.48(1)	68.99(2)	65.20(2)	68.84(7)	65.56(1)	60.76(1)
Ct1–M–Ct2	133.0*	133.8*	127.9*	128.8*	127.7*	130.1*
Tilt of C ₅ planes	49.73	52.78	54.52	54.95	55.14	51.53

Ct = centroid; M = Yb (1) and (2); Eu (3); Ca (4); Sr (5); Ba (6)
* = Ct not refined in calculated positions.

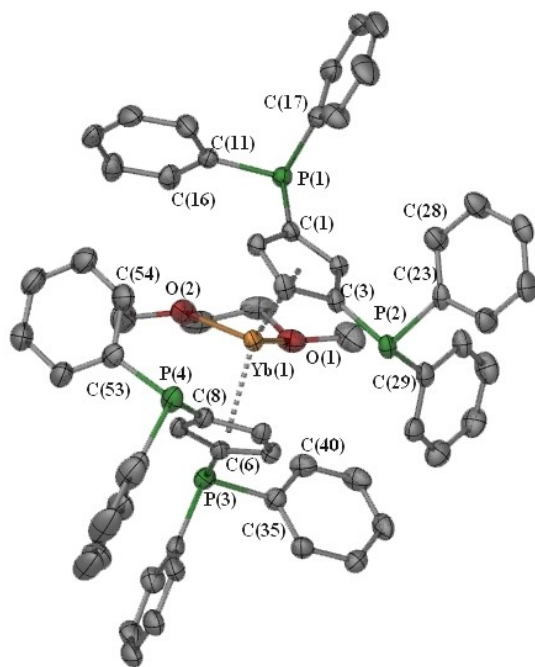


Figure 3. X-ray crystal structure of $[\text{Yb}(\eta^5\text{-C}_5\text{H}_3(\text{PPh}_2)_2\text{-1,3})_2(\text{dme})]$ (**2**) (molecule 1). Hydrogen atoms are omitted for clarity.

are 1.12 Å, 1.26 Å and 1.42 Å, respectively^[23]. The Ct1–M–Ct2 angle of **4** (128.8°) and **5** (127.7°) are also smaller than for **6** (130.1°). The Ca–C, Ca–O distances and Ct1–Ca–Ct2 angle are quite close to **2** (Yb–C: mean 2.73 Å; Yb–O: 2.42 Å; Ct1–Yb–Ct2: 133.8°) and the Sr–C, Sr–O distances and Ct1–Sr–Ct2 angle compare well with complex **3** (Eu–C: mean 2.85 Å; Eu–O: mean 2.55 Å; Ct1–Eu–Ct2: 127.9°) owing to the similar ionic radii between Ca^{2+} and Yb^{2+} and between Sr^{2+} and Eu^{2+} . The mean Ba–C distance (3.03 Å) of **6** agrees with a number of eight-coordinate Ba^{2+} complexes such as the bis(diisopropylindenyl)barium complex $[\text{Ba}(\eta^5\text{-1,3-Pr}^i\text{-C}_9\text{H}_5)_2(\text{thf})_2]$ ^[24] (mean 3.03 Å); the triisopropylcyclopentadienyl barium complex, $[\text{Ba}[\eta^5\text{-C}_5\text{H}_2(\text{C}_3\text{H}_7)_3]_2(\text{thf})_2]$ ^[25] (mean 3.03 Å) and $[\text{Ba}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{thf})_2]$ ^[26] (mean 3.03 Å). The Ct1–Ba–Ct2 angle of **6** (130.1°) is close to $[\text{Ba}[\eta^5\text{-C}_5\text{H}_2(\text{C}_3\text{H}_7)_3]_2(\text{thf})_2]$ ^[25] (131.7°) but smaller than that for $[\text{Ba}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{thf})_2]$ ^[26] (137.4°) and $[\text{Ba}(\eta^5\text{-1,3-Pr}^i\text{-C}_9\text{H}_5)_2(\text{thf})_2]$ ^[24] (140.2°).

The O–M–O angles (M=Yb (**2**): 68.99(15)°; M=Eu (**3**): 65.20(15)°; M=Ca (**4**): 68.84(7)°; M=Sr (**5**): 65.56(12)° and M=Ba (**6**): 60.76(12)°) are distorted from the ideal tetrahedral angle due to the geometrical constraint of the chelating dme ligand, and the O–Yb–O angle for **2** is similar to those in most dme solvated ytterbocenes.^[20,22]

The tilt of the two C_5 planes of the substituted cyclopentadienyl ligands in complexes **1–6** show that they are not parallel to each other with angles ranging from 49.73(0.13)° to 55.14(0.47)° in contrast to $[\text{Fe}(\eta^5\text{-C}_5\text{H}_3(\text{PPh}_2)_2\text{-1,3})(\eta^5\text{-C}_5\text{H}_5)]$ ^[10a] which has a tilt angle of 0.67° and confirms the inclined nature of the cyclopentadienyl rings in complexes **1–6**. Broussier *et al.* have shown that the tilt angle clearly increases with degree of substitution ($[\text{Fe}(\eta^5\text{-C}_5\text{H}_3(\text{PPh}_2)_2\text{-1,3})(\eta^5\text{-C}_5\text{H}_5)] < [\text{Fe}(\eta^5\text{-C}_5\text{H}_2\text{-1,2-$

$(\text{PPh}_2)_2\text{-4-Bu}^i)(\eta^5\text{-C}_5\text{H}_5)] < [\text{Fe}(\eta^5\text{-C}_5\text{H}_3\text{-1-PPh}_2\text{-3-Bu}^i)_2]$ ^[10a]). A similar observation can be made in complexes **4** (54.95(0.09)°) and $[\text{Ca}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2(\text{thf})]$ (51.77(0.07)°)^[8b] where the bulkiness of the extra diphenylphosphano group causes an increased tilt angle in **4**.

Preliminary studies on the formation of bimetallic early-late complexes were conducted. The reaction of $[\text{Ca}(\eta^5\text{-C}_5\text{H}_3(\text{PPh}_2)_2\text{-1,3})_2(\text{dme})] \cdot 0.75\text{dme}$ (**4**) or $[\text{Sr}(\eta^5\text{-C}_5\text{H}_3(\text{PPh}_2)_2\text{-1,3})_2(\text{dme})] \cdot 1.6\text{dme}$ (**5**) with NiCl_2 in refluxing acetonitrile showed several peaks in the ^{31}P NMR spectrum indicating possible metal coordination, but no pure product could be isolated or characterised. When complex **4** was treated with $[\text{Pt}(\text{cod})(\text{Me})_2]$ in toluene and stirred at room temperature for 24 hours a yellow precipitate formed. ^{31}P NMR studies showed several signals, including a resonance at +18.91 ppm with platinum satellites ($J_{\text{Pt,P}} = 1800$ Hz). This shift and the $J_{\text{Pt,P}}$ coupling value are similar to the values observed for the bimetallic complex $[\text{Ca}(\text{thf})_2(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2\text{Pt}(\text{Me})_2] \cdot 1.5\text{thf}$ (+18.13 ppm; 1800 Hz)^[8b] hence suggesting the formation of a bimetallic compound. Unfortunately, no pure product could be isolated from these reactions.

Conclusions

We have prepared a series of unprecedented lanthanoid and alkaline earth metallocene complexes carrying 1,3-bis(diphenylphosphano)cyclopentadienyl ligands by redox transmetalation/protolysis reactions. The complexes $[\text{M}(\eta^5\text{-C}_5\text{H}_3(\text{PPh}_2)_2\text{-1,3})_2(\text{S})] \cdot (\text{solvent})_y$ (M=Yb, S=(thf)₂, solv=PhMe, y=1 (**1**); M=Yb, S=dme, solv=dme, y=0.8 (**2**); M=Eu, S=dme, solv=dme, y=1.8 (**3**); M=Ca, S=dme, solv=dme, y=0.75 (**4**); M=Sr, S=dme, solv=dme, y=1.6 (**5**); M=Ba, S=dme, solv=dme, y=1.4 (**6**)) were characterised by X-ray diffraction showing good correlation between metal size and structural parameters. Attempts to synthesise bimetallic complexes have not been successful so far but are under further investigation.

Experimental Section

General considerations: Both the synthesis and subsequent manipulations of compounds were conducted under purified nitrogen using greaseless Schlenk assemblies and vacuum/inert gas lines. Isolated compounds were handled in a recirculating atmosphere dry-box. 1,2-Dimethoxyethane (dme), diethylether (Et_2O) and tetrahydrofuran (thf) were freshly distilled from sodium/benzophenone under nitrogen. Toluene was distilled from sodium under nitrogen. Infrared spectra (4000–650 cm^{-1}) were recorded as Nujol mulls under inert atmosphere and recorded again with plates open (compound exposed to air) for comparison with a Perkin Elmer 1600 FTIR spectrophotometer. ^1H , $^{13}\text{C}\{-^1\text{H}\}$, $^{31}\text{P}\{-^1\text{H}\}$ and $^{171}\text{Yb}\{-^1\text{H}\}$ NMR spectra were recorded with a Bruker DPX 300 MHz or 400 MHz spectrometer with dry degassed *perdeutero*-toluene, *perdeutero*-benzene and *perdeutero*-tetrahydrofuran as solvents (dried over sodium). For ^1H and $^{13}\text{C}\{-^1\text{H}\}$ NMR measurements, resonances were referenced to residual hydrogen from the solvent. For $^{31}\text{P}\{-^1\text{H}\}$ and $^{171}\text{Yb}\{-^1\text{H}\}$ NMR measurements, external 85% H_3PO_4 ($\delta=0$) and $[\text{Yb}(\text{thf})_2(\eta^5\text{-C}_5\text{Me}_5)_2]$ (0.16 M in thf/10% benzene- d_6) ($\delta=0$) respectively, were used as references. ^1H NMR measurements were also

recorded on hydrolysed samples by dissolving the complex in benzene- d_6 (or CD_3CN) and cooling the NMR tube in ice for 5 mins. Then 1–2 drops of trifluoroacetic acid (Aldrich) was added to the solution and mixed. Microanalysis samples were sealed in glass ampoules under purified nitrogen and analyses were determined by the Campbell Microanalytical Service, University of Otago, New Zealand. For metal analyses, samples of the compounds were accurately (± 0.0001 g) weighed and were decomposed by dilute HCl and made up to a standard volume (100 ml). For the lanthanoid complexes (**1**, **2** and **3**), aliquots, buffered with hexamethylenetetraamine, were titrated with disodium ethylenediamine- N,N,N',N' -tetraacetate (Na_2H_2EDTA) using Xylenol Orange indicator.^[27] For alkaline earth metal complexes (**4**, **5** and **6**), aliquots, buffered with ammonia-ammonium chloride solution with added disodium magnesium ethylenediamine- N,N,N',N' -tetraacetate, were titrated with disodium ethylenediamine- N,N,N',N' -tetraacetate (Na_2H_2EDTA) using Solochrome Black indicator.^[28] Blank analyses on known compounds ($BaCl_2$ and $CaCO_3$) gave satisfactory results. Lithium (diphenylphosphano)cyclopentadienide was synthesised according to a literature procedure.^[11] Sodium cyclopentadienide was synthesised according to a literature procedure.^[29] A steady nitrogen flow was introduced into chlorodiphenylphosphane (Aldrich) via a syringe prior to use. Diphenylmercury (Aldrich) was stored in the dry box.

General procedure for the synthesis of di(1,3-bis(diphenylphosphano)cyclopentadienyl)lanthanoid and alkaline earth complexes (1–6)

Lithium (diphenylphosphano)cyclopentadienide was suspended in dry ether and cooled to $-78^\circ C$. Chlorodiphenylphosphane was added and the solution was warmed to and stirred for 2 h at room temperature. LiCl was filtered off and the solution was added to a Schlenk flask containing excess metal and a stoichiometric amount of $HgPh_2$ in thf (30 mL). The reaction mixture was placed in a sonic bath at $30^\circ C$ for 48 h or until the appearance of black mercury. The mixture was allowed to stand at room temperature until the excess metal and mercury product had settled to the bottom of the reaction vessel. The supernatant solution was separated by filtration through a filter cannula under an atmosphere of nitrogen. The thf was then evaporated giving a honeycomb-like semi-solid. Dme (except for complex **1** where toluene was added) was then added to the Schlenk flask and the solution was concentrated and placed in a freezer at $-30^\circ C$. After 3–4 days, crystals were observed. For further characterisation, the remaining solution in the Schlenk flask was removed using a filter cannula and the crystals were washed with hexane and dried under vacuum for 1–2 h.

[Yb($\eta^5-C_5H_3(PPh_2)_2-1,3$)(thf) $_2$] $\cdot PhMe$ (1**).** Li[C₅H₄PPh₂] (0.490 g, 3.85 mmol), ClPPh₂ (0.850 g, 3.85 mmol), Yb (1.00 g, 5.78 mmol), HgPh₂ (0.680 g, 1.93 mmol) gave a deep red solution which was filtered and concentrated to 10 mL and deposited red needle-like single crystals of **1** upon storage at $-30^\circ C$: (1.53 g, 65%); m.p. 115–122 °C. Found: Yb, 14.01; (C₇₃H₇₀O₂P₄Yb) requires: Yb, 13.56%; IR (Nujol, cm⁻¹): 1583 m, 1305 m, 1264w, 1177 m, 1155 m, 1119 m, 1091 s, 1085 s, 1039 s, 1026vs, 998 m, 915 m, 874 s, 850 m, 819 s, 804 s, 740vs, 695vs, 644 m. ³¹P-{¹H} NMR (121.5 MHz, toluene- d_8 , 296 K): δ -21.95 (s).

[Yb($\eta^5-C_5H_3(PPh_2)_2-1,3$)(dme) $_2$] $\cdot 0.8$ dme (2**):** Li[C₅H₄PPh₂] (0.490 g, 3.85 mmol), ClPPh₂ (0.850 g, 3.85 mmol), Yb (1.00 g, 5.78 mmol), HgPh₂ (0.680 g, 1.93 mmol) gave a deep green solution which was filtered and concentrated to 10 mL and deposited dark green block-shaped single crystals of **2** upon storage at $-30^\circ C$: (1.23 g, 51%); m.p. 199–209 °C. Found: C, 64.99; H, 5.18; Yb, 13.20; (C₆₂H₅₆O₂P₄Yb) (Loss of 0.8 molecules of lattice dme) requires: C,

65.89; H, 4.99; Yb, 13.67%; IR (Nujol, cm⁻¹): 1538w, 1305 m, 1260 m, 1170 m, 1145 m, 1120 m, 1089 s, 1087 m, 1067 s, 1057vs, 1025 s, 999w, 920 m, 856 m, 825 m, 800s, 739vs, 697vs, 648 m; ¹H NMR (400 MHz, C₆D₆, 298 K): δ 3.15 (s, CH₃, dme); 3.33 (s, CH₂, dme); 6.11 (br s, 2H, C₅H₃); 6.58 (br s, 4H, C₅H₃); 6.96–7.16 (m, 24H; *m*-H and *p*-H of Ph₂P); 7.50; (m, 16H; *o*-H of Ph₂P); ¹³C NMR (100 MHz, C₆D₆, 298 K): δ 58.8 (s, dme), 72.1 (s, dme), 116.1 (pt, ¹J_{CP} = 5.7 Hz, C1/C3), 118.3 (dd, ²J_{CP} = 15.9 Hz, ³J_{CP} = 5.9 Hz, C4/C5), 120.6 (pt, ²J_{CP} = 16.4 Hz, C2), 128.6–128.9 (m, *m*-C + *p*-C of Ph₂P), 134.1 (d, ²J_{CP} = 19.9 Hz, *o*-C of Ph₂P), 134.2 (d, ²J_{CP} = 19.6 Hz, *o*-C of Ph₂P), 141.8 (d, ¹J_{CP} = 10.8 Hz, *i*-C of Ph₂P), 142.6 (d, ¹J_{CP} = 12.0 Hz, *i*-C of Ph₂P); ³¹P-{¹H} NMR (162 MHz, C₆D₆, 298 K): δ -21.30 (s); ¹⁷¹Yb-{¹H} NMR (121.5 MHz, C₆D₆, 296 K): δ +308 (s).

[Eu($\eta^5-C_5H_3(PPh_2)_2-1,3$)(dme) $_2$] $\cdot 1.8$ dme (3**).** Li[C₅H₄PPh₂] (0.560 g, 2.19 mmol), ClPPh₂ (0.480 g, 2.19 mmol), Eu (0.500 g, 3.29 mmol), HgPh₂ (0.390 g, 1.09 mmol) gave a deep orange solution which was filtered and concentrated to 10 mL and deposited orange needle-like single crystals of **3** upon storage at $-30^\circ C$: (0.601 g, 49%); m.p. 168–174 °C. Found: C, 65.47; H, 5.30; Eu, 12.02; (C₆₈H₇₁O₅P₄Eu) (loss of 0.3 molecules of lattice dme) requires: C, 65.64; H, 5.75; Eu, 12.21%; IR (Nujol, cm⁻¹): 1583 m, 1305 m, 1282 m, 1260 m, 1168 m, 1145w, 1155 m, 1090 s, 1061vs, 1051 s, 1021vs, 998 m, 915w, 854vs, 815vs, 800s, 745vs, 697vs, 648 s; The ¹H NMR of a hydrolysed sample of wet crystals taken out of the dme solution without drying recorded the presence of 3 dme molecules in complex **3**.

[Ca($\eta^5-C_5H_3(PPh_2)_2-1,3$)(dme) $_2$] $\cdot 0.75$ dme (4**).** Li[C₅H₄PPh₂] (0.930 g, 3.62 mmol), ClPPh₂ (0.800 g, 3.62 mmol), Ca (0.210 g, 5.44 mmol), HgPh₂ (0.640 g, 1.81 mmol) gave a pale yellow solution which was filtered and concentrated to 10 mL and deposited colourless block-shaped single crystals of **4** upon storage at $-30^\circ C$: (0.500 g, 29%); m.p. 188–194 °C. Found: C, 73.25; H, 6.27; Ca, 3.66; (C₆₅H_{63.5}O_{3.5}P₄Ca) requires: C, 73.33; H, 6.01; Ca, 3.75%; IR (Nujol, cm⁻¹): 1582w, 1310 m, 1289 m, 1258 m, 1172 m, 1153w, 1095 m, 1057vs, 1024 s, 999 m, 920w, 858vs, 817vs, 798 s, 738vs, 696vs, 649 m; ³¹P-{¹H} NMR (121.5 MHz, toluene- d_8 , 296 K): δ -22.09 (s).

[Sr($\eta^5-C_5H_3(PPh_2)_2-1,3$)(dme) $_2$] $\cdot 1.6$ dme (5**).** Li[C₅H₄PPh₂] (0.970 g, 3.80 mmol), ClPPh₂ (0.830 g, 3.80 mmol), Sr (0.500 g, 5.70 mmol), HgPh₂ (0.670 g, 1.90 mmol) gave a pale yellow solution which was filtered and concentrated to 10 mL and deposited colourless needle-like single crystals of **5** upon storage at $-30^\circ C$: (0.490 g, 19%); m.p. 163–170 °C. Found: C, 68.66; H, 5.87; Sr, 7.68; (C_{68.4}H₇₂O_{5.2}P₄Sr) requires: C, 69.11; H, 6.10; Sr, 7.37%; IR (Nujol, cm⁻¹): 1583 s, 1306 m, 1246 m, 1170vs, 1150 m, 1118 m, 1090 s, 1070w, 1059vs, 1020 s, 997w, 910 m, 855vs, 813vs, 796 s, 741vs, 697vs, 650s; ³¹P-{¹H} NMR (121.5 MHz, toluene- d_8 , 296 K): δ -18.74 (s).

[Ba($\eta^5-C_5H_3(PPh_2)_2-1,3$)(dme) $_2$] $\cdot 1.4$ dme (6**).** Li[C₅H₄PPh₂] (1.24 g, 4.85 mmol), ClPPh₂ (1.07 g, 4.85 mmol), Ba (1.00 g, 7.28 mmol), HgPh₂ (0.860 g, 2.43 mmol) gave a pale orange solution which was filtered and concentrated to 10 mL and deposited colourless block-shaped single crystals of **6** upon storage at $-30^\circ C$: (0.730 g, 27%); m.p. 188–194 °C. Found: C, 66.06; H, 5.11; Ba, 12.42; (C₆₆H₆₆BaO₄P₄) (loss of 0.4 molecules of lattice dme) requires: C, 66.92; H, 5.61; Ba, 11.59%; IR (Nujol, cm⁻¹): 1583 s, 1305 m, 1263 m, 1191 m, 1156w, 1120 m, 1090 s, 1067vs, 1056vs, 1020 s, 998w, 915vw, 852 s, 820 m, 809 m, 743vs, 697vs, 647 m; ³¹P-{¹H} NMR (121.5 MHz, toluene- d_8 , 296 K): δ -22.63 (s).

X-ray crystal refinement data

Crystals were mounted on a fine glass fibre using viscous hydrocarbon oil and data collections were maintained at 123 K using an open-flow N₂ Oxford Cryosystems cryostream. Data were collected using a Bruker X8 Apex II diffractometer (complexes **3**, **5**, **6**)

equipped with graphite monochromated Mo K α radiation ($\lambda = 0.71013 \text{ \AA}$). Data were initially processed with the SAINT program.^[30] Crystals of complexes **1**, **2** and **4** were collected using the MX1 beamline at the Australian Synchrotron, Victoria, Australia. For these compounds, a very small crystal was mounted on a cryoloop and then flash cooled to 100 K. The crystal dimensions could not be measured due to the small size. Data were collected using a single wavelength ($\lambda = 0.712 \text{ \AA}$). The MX1 end station comprised a phi goniostat and ADSC Quantum 210r 210 \times 210 mm large area detector. Due to hardware constraints (fixed detector angle), the maximum available data resolution on MX1 was limited to approximately 0.80 \AA at the detector edges. Data were collected using the Blue Ice^[31] GUI and processed with the XDS^[32] software package. All structures were solved using direct methods with SHELXS-97^[33] and refined using conventional alternating least squares methods with SHELXL-97.^[33] The program X-Seed^[33] was used as a graphical interface. All non-hydrogen atoms in the structures were refined anisotropically, and hydrogen atoms attached to carbon were placed in idealised positions and allowed to ride on the atom to which they are attached. All CIF files were checked at <http://www.iucr.org/>. Complexes **2**, **3**, **5**, **6** are isotopic and contained molecules of disordered dme in the lattice (verified by ^1H NMR and/or microanalysis) (see SI). The Platon program "SQUEEZE" was therefore used to determine the number of disordered solvents using electron density calculations. Therefore the crystallography data below do not include the lattice solvents (except for **1** and **4**). CCDC, 2184252 for **1**, 2184253 for **2**, 2184254 for **3**, 2184255 for **4**, 2184256 for **5**, 2184257 for **6**, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Crystal data for [Yb($\eta^5\text{-C}_5\text{H}_3(\text{PPh}_2)_2\text{-1,3})_2(\text{thf})_2\text{]}\cdot\text{PhMe}$ **1**. $\text{C}_{73}\text{H}_{70}\text{O}_2\text{P}_4\text{Yb}$, $M = 1276.21$, red needles, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.285(2)$, $b = 12.989(3)$, $c = 23.115(5) \text{ \AA}$, $\alpha = 84.42(3)$, $\beta = 85.60(3)$, $\gamma = 84.57(3)^\circ$, $V = 3052.4(11) \text{ \AA}^3$, $Z = 2$, $D_c = 1.389 \text{ g/cm}^3$, $F_{000} = 1308$, ADSC Quantum 210r, Synchrotron radiation, $\lambda = 0.712 \text{ \AA}$, $T = 100 \text{ K}$, $2\theta_{\text{max}} = 50.0^\circ$, 39523 reflections collected, 10084 unique ($R_{\text{int}} = 0.0213$). Final $\text{Goof} = 1.024$, $R1 = 0.0331$, $wR2 = 0.0840$, R indices based on 9444 reflections with $I > 2\sigma(I)$ (refinement on F^2), 722 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 1.683 \text{ mm}^{-1}$.

Crystal data for [Yb($\eta^5\text{-C}_5\text{H}_3(\text{PPh}_2)_2\text{-1,3})_2(\text{dme})]$ **2**. $\text{C}_{62}\text{H}_{56}\text{O}_2\text{P}_4\text{Yb}$, $M = 1130.04$, green blocks, monoclinic, space group $P2_1/c$ (No. 14), $a = 25.150(5)$, $b = 24.483(5)$, $c = 18.369(4) \text{ \AA}$, $\beta = 91.55(3)^\circ$, $V = 11307(4) \text{ \AA}^3$, $Z = 8$, $D_c = 1.328 \text{ g/cm}^3$, $F_{000} = 4592$, ADSC Quantum 210r, Synchrotron radiation, $\lambda = 0.712 \text{ \AA}$, $T = 100 \text{ K}$, $2\theta_{\text{max}} = 53.9^\circ$, 165066 reflections collected, 23781 unique ($R_{\text{int}} = 0.0751$). Final $\text{Goof} = 1.031$, $R1 = 0.0522$, $wR2 = 0.1259$, R indices based on 18953 reflections with $I > 2\sigma(I)$ (refinement on F^2), 1243 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 1.808 \text{ mm}^{-1}$.

Crystal data for [Eu($\eta^5\text{-C}_5\text{H}_3(\text{PPh}_2)_2\text{-1,3})_2(\text{dme})]$ **3**. $\text{C}_{62}\text{H}_{56}\text{EuO}_2\text{P}_4$, $M = 1108.97$, orange needles, $0.12 \times 0.1 \times 0.1 \text{ mm}^3$, monoclinic, space group $P2_1/c$ (No. 14), $a = 25.307(3)$, $b = 24.493(3)$, $c = 18.496(2) \text{ \AA}$, $\beta = 91.856(3)^\circ$, $V = 11459(2) \text{ \AA}^3$, $Z = 8$, $D_c = 1.286 \text{ g/cm}^3$, $F_{000} = 4536$, Bruker X8 Apex II CCD, MoK α radiation, $\lambda = 0.71013 \text{ \AA}$, $T = 123(1) \text{ K}$, $2\theta_{\text{max}} = 55.0^\circ$, 57815 reflections collected, 25064 unique ($R_{\text{int}} = 0.1030$). Final $\text{Goof} = 0.981$, $R1 = 0.0790$, $wR2 = 0.2001$, R indices based on 12415 reflections with $I > 2\sigma(I)$ (refinement on F^2), 1243 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 1.246 \text{ mm}^{-1}$.

Crystal data for [Ca($\eta^5\text{-C}_5\text{H}_3(\text{PPh}_2)_2\text{-1,3})_2(\text{dme})]\cdot 0.75 \text{ dme}$ **4**. $\text{C}_{65}\text{H}_{63.50}\text{CaO}_{3.50}\text{P}_4$, $M = 1064.62$, colourless block, monoclinic, space group $P2_1/c$ (No. 14), $a = 25.167(5)$, $b = 24.493(5)$, $c = 18.348(4) \text{ \AA}$, $\beta = 91.89(3)^\circ$, $V = 11304(4) \text{ \AA}^3$, $Z = 8$, $D_c = 1.251 \text{ g/cm}^3$, $F_{000} = 4492$,

ADSC Quantum 210r, Synchrotron radiation, $\lambda = 0.712 \text{ \AA}$, $T = 100 \text{ K}$, $2\theta_{\text{max}} = 59.0^\circ$, 217734 reflections collected, 29968 unique ($R_{\text{int}} = 0.0471$). Final $\text{Goof} = 1.034$, $R1 = 0.0580$, $wR2 = 0.1579$, R indices based on 25957 reflections with $I > 2\sigma(I)$ (refinement on F^2), 1358 parameters, 14 restraints. Lp and absorption corrections applied, $\mu = 0.271 \text{ mm}^{-1}$. Variata: 0.75 molecules of dme were found in the lattice and were highly disordered. Thus the DANG and DFIX commands were placed on these atoms.

Crystal data for [Sr($\eta^5\text{-C}_5\text{H}_3(\text{PPh}_2)_2\text{-1,3})_2(\text{dme})]$ **5**. $\text{C}_{62}\text{H}_{56}\text{O}_2\text{P}_4\text{Sr}$, $M = 1044.62$, colourless needles, $0.12 \times 0.1 \times 0.1 \text{ mm}^3$, monoclinic, space group $P2_1/c$ (No. 14), $a = 25.340(2)$, $b = 24.462(2)$, $c = 18.4190(15) \text{ \AA}$, $\beta = 91.902(3)^\circ$, $V = 11411.0(16) \text{ \AA}^3$, $Z = 8$, $D_c = 1.216 \text{ g/cm}^3$, $F_{000} = 4336$, Bruker X8 Apex II CCD, MoK α radiation, $\lambda = 0.71013 \text{ \AA}$, $T = 123(1) \text{ K}$, $2\theta_{\text{max}} = 55.0^\circ$, 76352 reflections collected, 26086 unique ($R_{\text{int}} = 0.1189$). Final $\text{Goof} = 0.826$, $R1 = 0.0646$, $wR2 = 0.1422$, R indices based on 11062 reflections with $I > 2\sigma(I)$ (refinement on F^2), 1243 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 1.097 \text{ mm}^{-1}$.

Crystal data for [Ba($\eta^5\text{-C}_5\text{H}_3(\text{PPh}_2)_2\text{-1,3})_2(\text{dme})]$ **6**. $\text{C}_{62}\text{H}_{56}\text{BaO}_2\text{P}_4$, $M = 1094.33$, colourless block, $0.15 \times 0.12 \times 0.12 \text{ mm}^3$, monoclinic, space group $P2_1/c$ (No. 14), $a = 25.4628(5)$, $b = 24.3793(6)$, $c = 18.5474(4) \text{ \AA}$, $\beta = 91.3570(10)^\circ$, $V = 11510.4(4) \text{ \AA}^3$, $Z = 8$, $D_c = 1.263 \text{ g/cm}^3$, $F_{000} = 4480$, Bruker X8 Apex II CCD, MoK α radiation, $\lambda = 0.71013 \text{ \AA}$, $T = 123(1) \text{ K}$, $2\theta_{\text{max}} = 55.0^\circ$, 114440 reflections collected, 26373 unique ($R_{\text{int}} = 0.0845$). Final $\text{Goof} = 0.998$, $R1 = 0.0719$, $wR2 = 0.1519$, R indices based on 19482 reflections with $I > 2\sigma(I)$ (refinement on F^2), 1238 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.841 \text{ mm}^{-1}$.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: phosphine · cyclopentadienyl · lanthanide · alkaline earth · bimetallic complexes

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