

Redox reactions of low-valent Group 4 organometallics with 9,10-phenanthrenequinone (PQ). Crystal and molecular structure of a 10-membered tetraoxametallacycle of bis(cyclopentadienyl)zirconium(IV)

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Abstract

The bis(arene) derivative of titanium(0), $\text{Ti}(\eta^6\text{-toluene})_2$, reacts with 9,10-phenanthrenequinone (PQ) with release of the arene ligands and formation of a diamagnetic brown compound best formulated as a dinuclear titanium(IV) derivative containing both 9,10-phenanthrenesemiquinone (PSQ) and 9,10-phenanthrenediolato (PDA) ligands. $\text{MCp}_2(\text{CO})_2$ ($M = \text{Zr, Hf}$) react with PQ to give MCp_2PDA which has been characterized by single crystal X-ray diffractometry for $M = \text{Zr}$. Crystal data: $\text{C}_{48}\text{H}_{36}\text{O}_4\text{Zr}_2$, $M = 859.26 \text{ g mol}^{-1}$, monoclinic, space group $P2_1/n$ (No. 14), $a = 11.647(8)$, $b = 17.07(1)$, $c = 18.80(1) \text{ \AA}$, $\beta = 97.17(6)^\circ$, $V = 3709(7) \text{ \AA}^3$, $Z = 4$, $d_{\text{calc}} = 1.539 \text{ g cm}^{-3}$, $\mu = 5.97 \text{ cm}^{-1}$, $F(000) = 1744$. The structure consists of dinuclear $[\text{ZrCp}_2\text{PDA}]_2$ units, the two ZrCp_2 groups being bridged by the PDA ligands to give a 10-membered tetraoxazirconacycle. © 1997 Elsevier Science S.A.

1. Introduction

1,2-Quinones occupy a special position in coordination chemistry due to the fact that they can coordinate to a metal either as neutral or as charged ligands (semiquinone radical anion or diolate dianion) [1,2].

Complexes derived from 1,2-benzoquinones have been studied for their relevance to metal-assisted biological redox reactions such as the photosynthetic electron-transport chain; the viability of a manganese-quinone complex as a model for the manganese cofactor has been considered [3].

Many examples are reported in the literature of 1,2-quinones as prepared from compounds of low-valent transition elements, mainly metal carbonyls from Groups 5 to 9 [1,2]. In general, in the reactions between organometallics and quinones, the organometallic compound is used as a carrier of the metal and the neutral carbon-containing ligands are totally released under the action of the quinone. Nevertheless, compounds con-

taining other ligands in addition to quinones have been prepared, namely iron-, cobalt-, nickel- and platinum-olefin or platinum-phosphino derivatives (for selected examples see Ref. [4]).

As far as the interaction between quinones and low-valent, transition metal complexes of Group 4 is concerned, it is known that the reaction of $\text{Ti}(\eta^6\text{-toluene})_2$ with 1,4-quinones [5] affords insoluble materials of probable polynuclear nature. Moreover, it is known that titanocene dicarbonyl, $\text{TiCp}_2(\text{CO})_2$, gives $\text{Cp}_2\text{Ti}(\text{C}_{14}\text{H}_8\text{O}_2)$ by treatment with 9,10-phenanthrenequinone [6], and that the bis-trimethylphosphine, or the ethylene/phosphine adducts of zirconium(II), ZrCp_2L_2 , react with 1,2- or 1,3-dihydroxybenzene to give dinuclear zirconocene derivatives containing bridging catecholato ligands with a zirconium/catecholato molar ratio of 2 [7].

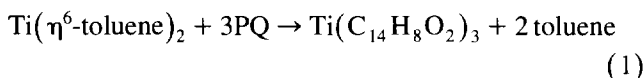
In this paper we report new examples of quinone derivatives of titanium, zirconium and hafnium as obtained by oxidation of reduced organometallic precursors with 9,10-phenanthrenequinone and the first crystallographically characterized example of a compound containing a 10-membered tetraoxa-zirconacycle derived from 9,10-phenanthrenequinone.

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2. Results and discussion

2.1. Synthesis and crystal structure

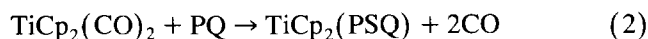
When $\text{Ti}(\eta^6\text{-toluene})_2$ is treated with PQ in toluene, an instantaneous reaction is observed with formation of $\text{Ti}(\text{C}_{14}\text{H}_8\text{O}_2)_3$, according to Eq. (1).



The diamagnetic dark brown solid has been characterized by elemental analysis and NMR and IR spectroscopy. The infrared spectra show absorptions typical of 9,10-phenanthrenesemiquinone (1498 cm^{-1}) and 9,10-phenanthrenediolate ($1572, 1116, 1079, 1038, 756, 731, 723 \text{ cm}^{-1}$), suggesting the presence of two quinone ligands differing in the formal charge, namely -1 and -2 . By taking into consideration the structural results obtained on hexakis(tetrachloro-1,2-benzenedialcoholato)dimetal, $\text{M}_2(\mu\text{-O}_2\text{C}_6\text{Cl}_4)_2(\text{O}_2\text{C}_6\text{Cl}_4)_4$ ($\text{M} = \text{Mo}$ [8], W [9]), and on the zirconocene system $[\text{ZrCp}_2(\text{PDA})]_2$ (vide infra), a possible structure for this titanium(IV) derivative is that of a dinuclear compound containing two 9,10-phenanthrenediolate bridges and two 9,10-phenanthrenesemiquinone for each titanium(IV) centre, i.e. $\text{Ti}_2(\mu\text{-PDA})_2(\text{PSQ})_4$. The diamagnetism of $\text{Ti}(\text{C}_{14}\text{H}_8\text{O}_2)_3$ can be explained by considering an intramolecular spin coupling mechanism [1,10,11] between the two semiquinone ligands.

An attempt was made to obtain $\text{Ti}(\text{C}_{14}\text{H}_8\text{O}_2)_3$ by an alternative route. $\text{TiCl}_3(\text{THF})_3$ was treated with three equivalents of NaPSQ and rapidly gave a dark coloured suspension, which was washed with water to give the pure titanium derivative in high yields.

Some years ago, $\text{TiCp}_2(\text{CO})_2$ was reacted [6] with PQ according to Eq. (2): the infrared spectrum of the diamagnetic solid showed a strong absorption in the $1490\text{--}1440 \text{ cm}^{-1}$ region, thus suggesting the presence of 9,10-phenanthrenesemiquinone ligand for titanium in the formal oxidation state III.



We have now found that $\text{MCp}_2(\text{CO})_2$ ($\text{M} = \text{Zr}, \text{Hf}$) react, Eq. (3), with PQ in toluene affording high yields of the diamagnetic $[\text{MCp}_2(\text{C}_{14}\text{H}_8\text{O}_2)]_2$ ($\text{M} = \text{Zr}, \text{Hf}$) (the dinuclear nature of the compound will be demonstrated in the course of the discussion). The air-sensitive pale brown zirconium derivative was also obtained by the reaction of ZrCp_2Cl_2 with Na_2PDA , see Eq. (4).

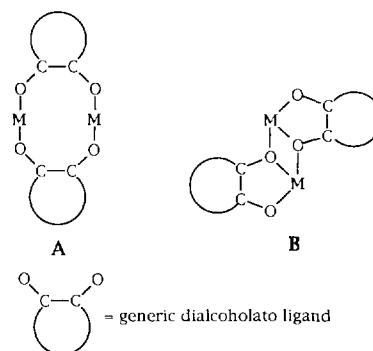
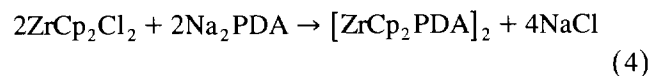
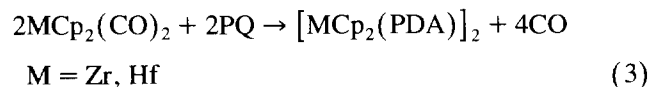


Fig. 1. Schematic representation of 10-membered tetraoxametallacyclic (A) and metallatricyclic (B) systems containing bridging alcoholate ligands.

As compounds of zirconium(III) or hafnium(III) are still rather rare [12] and no strong absorptions in the region $1490\text{--}1440 \text{ cm}^{-1}$ (typical of semiquinone ligands) are observed in the solid state infrared spectrum, we had assumed that $[\text{MCp}_2(\text{C}_{14}\text{H}_8\text{O}_2)]_2$ ($\text{M} = \text{Zr}, \text{Hf}$) should contain the 9,10-phenanthrenediolate ligand.

Zirconocene derivatives of general formula $\text{ZrCp}_2(\text{catecholato})$ are known but their nature is still a matter of debate. They were initially proposed to be mononuclear and air-stable compounds at least in the solid state [13]; later, on the basis of their chemical and physical properties, a polynuclear structure was proposed [14].

A recent structural study on titanium(IV) and zirconium(IV) 1,4-catecholato derivatives of general formula $[\text{M}(\text{C}_5\text{R}_5)_2\text{Cl}]_2(\mu\text{-O}_2\text{C}_6\text{H}_4)$ ($\text{M} = \text{Ti}, \text{C}_5\text{R}_5 = \text{C}_5\text{Me}_5$; $\text{M} = \text{Zr}, \text{C}_5\text{R}_5 = \text{C}_5\text{Me}_4\text{Et}$) has shown their dinuclear structure [15].

In a recent NMR study on the solution behaviour of $\text{ZrCp}_2(\text{catecholato})$ complexes (catecholato = conjugate base of 1,2-dihydroxybenzene or 4-*t*-butyl-1,2-dihydroxybenzene), Erker and coworker [16] have suggested that 10-membered tetraoxametallacycles, Fig. 1(A) (vide infra) should not be stable in solution with respect to dimetallatricyclic structures, as reported in Fig. 1(B).

As far as the formal charge accepted by the quinone is concerned, it is worth noting that metal–oxygen bond lengths and carbon–oxygen bond distances may be indicative of the charge on the ligand [1,2,17]. Although the number of structural studies on phenanthrenequinone complexes is small, the data collected in Table 1 indicate that a long C–O distance ($\geq 1.31 \text{ \AA}$) and a short C–C bond distance ($\leq 1.4 \text{ \AA}$) are typical of a PDA ligand. Metrical data are therefore available in the literature for useful comparisons and for bonding considerations.

We therefore decided to investigate the solid-state structure of $[\text{ZrCp}_2(\text{PDA})]_2$ by X-ray crystallography. Fig. 2 reports a view of the molecule and Table 2 is a list of selected bond distances and angles. As can be

Table 1
Representative bond distances in 9,10-phenanthrenesemiquinone (PSQ) and 9,10-phenanthrenediolato (PDA) transition metal derivatives

Compound	C–C (Å)	C–O (Å)	M–O (Å)	Reference
Mo(PDA) ₂ (PSQ)	1.348 (av.)	1.346 (av.)	1.952 (av.)	[18]
	PSQ 1.427(10)	1.312 (av.)	1.978 (av.)	
Fe(PSQ) ₃	1.435(6)	1.283(3)	2.027(4)	[11]
NiPy ₂ (PSQ) ₂	1.442(14)	1.272(11)	2.058(7)	[19]
Mo ₂ O ₂ (PSQ) ₂	1.426(9)	1.312(7)	2.141(4)	[20]
[ZrCp ₂ (PDA) ₂]	1.372 (av.)	1.34 (av.)	2.002 (av.)	this work

seen from Fig. 2, in the dinuclear [ZrCp₂(PDA)₂]₂ the two ZrCp₂ units are bridged by two oxygen-donor ligands to give a 10-membered tetraoxazirconacycle with a Zr···Zr non-bonding distance of 4.71 Å. The zirconium atoms are tetrahedrally coordinated to the Cp groups (average Zr–centroid distance 2.22 Å) and to two oxygen atoms of the bridging ligands. As is shown in Table 1, the average Zr–O distance, 2.002 Å, the average C–O distance, 1.34 Å, and the average C–C distance, 1.37 Å, are in agreement with the presence of a phenanthrenediolato ligand. The coordination geometry at the zirconium centre is that of a typical bent metallocene (the average bond angle at zirconium is 128.5°). The dihedral angle between planes of bridging ligands is 70.8° compared with 70.6° and 78.7° observed for M₂(μ-O₂C₆Cl₄)₂(O₂C₆Cl₄)₄ (M = Mo [8], W [9] respectively). The dihedral angle between the two planes defined by Zr1 and its centroids and by Zr2 and its centroids is 51.3°.

Examples are known of 1,2-diolato ligands bridging two metal atoms, of type A or B (Fig. 1).

The latter type of coordination is observed in [VO(3,5-DBSQ)(3,5-DBDA)]₂ [22], Mn₂(3,5-DBDA)₂(C₅H₅N)₆ [23], Re₂(CO)₇(PSQ)₂ [24], Fe₄(3,5-DBSQ)₄(DBDA)₄ [25], Co₄(3,5-DBSQ)₈ [26],

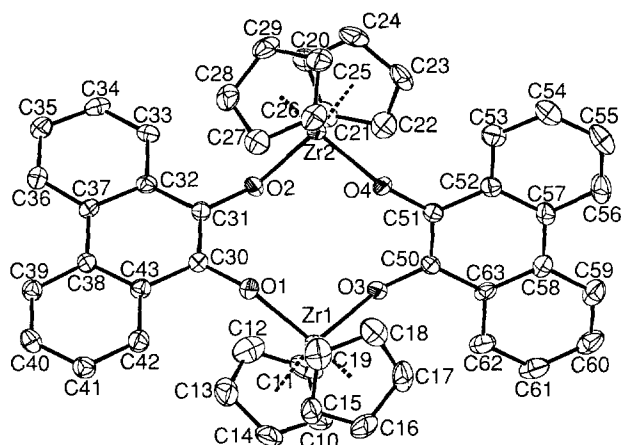


Fig. 2. PLATON [21] plot of the molecular structure of [ZrCp₂(PDA)₂]₂ with the atom numbering used. Ellipsoids are drawn at 30% probability.

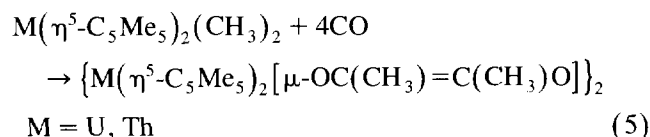
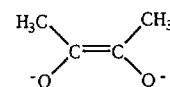
Table 2
Selected bond distances (Å) and angles (deg) of [ZrCp₂(PDA)₂]₂. Estimated standard deviations in parentheses refer to the least significant digit

Zr1	O1	1.992(3)	O1	C30	1.345(4)		
Zr1	O3	2.009(3)	O2	C31	1.338(5)		
Zr2	O2	2.007(3)	O3	C50	1.333(5)		
Zr2	O4	2.002(2)	O4	C51	1.343(5)		
C30	C31	1.368(5)	C50	C51	1.374(5)		
O1	Zr1	O3	106.3(1)	Zr1	O1	C30	139.0(3)
O2	Zr2	O4	105.2(1)	Zr1	O3	C50	140.6(3)
O1	C30	C31	120.0(4)	Zr2	O4	C51	140.1(3)
O1	C30	C43	119.3(3)	C30	C31	C32	120.0(4)
O2	C31	C30	120.9(3)	C31	C30	C43	120.7(3)
O2	C31	C32	119.1(4)	C51	C50	C63	120.0(4)
O3	C50	C63	119.3(4)	C50	C51	C52	120.4(4)
O3	C50	C51	120.7(4)				
O4	C51	C50	120.3(4)				
O4	C51	C52	119.3(4)				

[Cu(3,5-DBDA)(C₅H₅N)]₄ · 2CH₃CN [27] (3,5-DBSQ = 3,5-di-*t*-butylbenzenesemiquinone, 3,5-DBDA = 3,5-di-*t*-butylbenzenediololate) in the substituted cyclopentadienyl derivative of niobium(V) {[Nb(η⁵-C₅H₄SiMe₃)Cl]₂(μ-O)(μ-O₂C₆H₄)₂} [28]} and in a zirconocene–methyltartrato complex [29].

The type A coordination is observed in hexakis(tetrachloro-1,2-benzenediololate)dimetal, M₂(μ-O₂C₆Cl₄)₂(O₂C₆Cl₄)₄ (M = Mo [8], W [9]) and in a derivative of copper(II) containing an N,O-macrocycle and a tetrachloro-1,2-benzenediololate as ligands [30]. 10-Membered metallacycles containing titanocene or zirconocene fragments are known with pinacolato [31] or dimethyltartrato [29] bridging ligands respectively.

It is noteworthy that two derivatives of uranium(IV) and thorium(IV) of general formula {M(C₅Me₅)₂[μ-OC(CH₃)=C(CH₃)O]}₂ (M = U, Th) [32] reported some years ago by Marks and coworkers as a result of the reaction of uranocene or thoriocene dimethyls with CO, Eq. (5), have been shown by X-ray crystallography to contain a 2-butene-2,3-diolato fragment as bridging ligand and to give a 10-atom two-thorium metallacycle



Due to the lower steric hindrance of the ene-diolate ligand with respect to PDA, the eight non-metallic

atoms of the 10-atom thorium metallacycle are coplanar [32].

In the field of zirconocene complexes, it is worth mentioning that also other binuclear metallacycles with 14 [33] and 16 [33] members are known.

2.2. Electrochemistry

The mononuclear [6] titanium derivative $\text{TiCp}_2(\text{PSQ})$ and the dinuclear zirconium derivatives $[\text{ZrCp}_2(\text{PDA})]_2$ have been studied by cyclic voltammetry. The titanium compound shows an irreversible oxidation at +0.43 V with a cathodic follow-up peak corresponding to the first reduction of 9,10-phenanthrenequinone (−0.64 V under the same experimental conditions). This suggests that the titanium derivative dissociates the quinone on oxidation. The cathodic part of the voltammogram is characterized by a reversible couple at $E_{1/2} = -1.11$ V which is assigned to a quinone-based reduction. Though the potential is near to that of free quinone, the reduction behaviour of 9,10-phenanthrenequinone under identical conditions is quite different. The observed reduction must therefore be associated with the metal complex.

The zirconium derivative does not show a reduction peak, but a reversible oxidation is observed at +0.51 V assigned to a PDA/PSQ oxidation in accordance with the redox behaviour observed for $\text{Cr}(\text{PSQ})_3$ [34].

According to these results, it appears that the quinone ligand in the titanium derivative is less reduced than in the zirconium compound, thus confirming the results obtained by other techniques (infrared spectroscopy in the case of titanium and infrared spectroscopy and X-ray crystallography for zirconium).

2.3. Conclusions

9,10-Phenanthrenequinone complexes have been prepared starting from low-valent compounds of Group 4 metals. The solid-state structure of $[\text{ZrCp}_2(\text{PDA})]_2$ and the electrochemical measurements of both this compound and the titanium analogue $\text{TiCp}_2(\text{PSQ})$ strongly suggest that the quinone-based ligand behaves as a formal single charged anion in the titanium derivative and as a doubly charged anion in the zirconium system; this implies that we are dealing with titanium(III) and zirconium(IV) compounds respectively. Thus, the observed experimental results confirm the higher stability of high oxidation states in descending a group of transition elements.

We have shown that, as proposed by Erker and coworker [16], 10-membered tetraoxabis(cyclopentadienyl)zirconacycles (Fig. 1(B)) can be stabilized with respect to compounds characterized by a metallatri-cyclic framework (Fig. 1(A)) when the proper quinone ligand is used.

Because of the close similarities in the chemistry (including structural chemistry, ZrCl_4 and HfCl_4 are isotopic [35]) of zirconium and hafnium derivatives in the oxidation state IV, and on the basis of the substantially identical infrared data for $[\text{MCp}_2(\text{PDA})]_2$ ($M = \text{Zr}, \text{Hf}$), it can be anticipated that the hafnium compound has a dinuclear structure similar to the zirconium derivative. Work is in progress in order to definitely characterize other catecholato derivatives of zirconium and hafnium.

3. Experimental

Unless otherwise stated, all of the operations were carried out under an atmosphere of pre-purified argon. Solvents were dried by conventional methods prior to use.

IR spectra were measured with an FT-1725X instrument on solutions or on Nujol and/or polychlorotrifluoroethylene (PCTFE) mulls prepared under rigorous exclusion of moisture and air.

^1H NMR spectra were measured with a Varian Gemini 200 instrument.

Magnetic susceptibility measurements were performed (in the temperature range 290–70 K) with a Faraday balance using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as standard, with Pascal contributions for the diamagnetic correction (the diamagnetic contributions are from Ref. [36]).

An EG&G/PAR electrochemical equipment as described previously [37] was used for recording cyclic voltammograms. Rapid scan ($v > 1 \text{ V s}^{-1}$) voltammograms were sampled with a Nicolet 3091 digital storage oscilloscope and transferred to a PC. The electrochemical measurements have been performed at a platinum electrode in acetonitrile using Bu_4NPF_6 as supporting electrolyte; potentials are referred to ferrocene at 0.4 V vs. SCE.

The metal content of the complexes was determined as follows. Titanium: dissolution of the sample in dilute sulphuric acid and measurement of the absorbance at 410 nm of the resulting solution after addition of a 30% hydrogen peroxide solution. Zirconium and hafnium: as MO_2 after decomposition of the sample with dilute nitric acid and calcination in a platinum crucible at ca. 1000 °C. The chloride content of the complexes was determined by the Volhardt method after treatment of the sample with a KOH aqueous solution at the reflux temperature.

9,10-Phenanthrenequinone (Fluka) (PQ) was purified by sublimation. ZrCp_2Cl_2 was a commercial product used without purification. Disodium phenanthrenediolate (Na_2PDA) [38], $\text{TiCp}_2(\text{PSQ})$ [6], and $\text{ZrCp}_2(\text{CO})_2$ [39] were prepared according to the literature. $\text{Ti}(\eta^6\text{-toluene})_2$ was prepared from $\text{Ti}_{(g)}$ and toluene vapours

according to the metal–ligand co-condensation technique [40]¹.

3.1. Preparation of $Ti(C_{14}H_8O_2)_3$

(A) From $Ti(\eta^6\text{-toluene})_2$ and PQ. A solution of $Ti(\eta^6\text{-toluene})_2$ (0.24 g, 1.03 mmol) in toluene (50 ml) was treated with PQ (0.65 g, 3.12 mmol). An instantaneous precipitation of a brown solid was observed and the colour of the solution changed from ruby red to brown. After 6 h stirring at room temperature, the suspension was filtered and the brown solid was dried in vacuo and identified as $Ti(C_{14}H_8O_2)_3$ (0.59 g, 85% yield). Anal. Found: C, 75.2; H, 4.2; Ti, 7.3. $C_{42}H_{24}O_6Ti$ Calc.: C, 75.0; H, 3.6; Ti, 7.1%. IR (Nujol and PCTFE): $\tilde{\nu} = 3068w, 3025w, 1598m, 1572m, 1557m, 1516s, 1503s, 1488vs, 1468s, 1459s, 1452s, 1428s, 1395s, 1373vs, 1351s, 1342s, 1307s, 1273ms, 1239w, 1201w, 1180vw, 1163w, 1116m, 1079ms, 1038m, 941w, 929w, 811m, 791m, 756ms, 731m, 723ms, 697mw, 688m, 674w, 599m, 549s, 520m, 445w\text{ cm}^{-1}$. ¹H NMR (200 MHz, CD_3CN , 25 °C): $\delta = 7.52$ (t, 2H), 7.78 (t, 2H), 8.10 (d, 2H), 8.18 (d, 2H). The compound has a limited solubility in THF and aromatic hydrocarbons and is almost insoluble in aliphatic media.

(B) From $TiCl_3(THF)_3$ and NaPSQ. A suspension of sodium (0.097 g, 4.22 mmol) in THF was stirred for 15 h at room temperature with PQ (0.887 g, 4.25 mmol). The green suspension was treated with $TiCl_3(THF)_3$ (0.526 g, 1.42 mmol) to obtain a deeply coloured suspension within mixing of the reagents. After 10 h stirring at room temperature, the solvent was removed in vacuo and the residue was treated with toluene (50 ml). The suspension was filtered, the solid was dried in vacuo at room temperature and washed on the frit with water (3×10 ml) until the washings were free of chloride ion. The deep brown solid was dried in vacuo at room temperature over P_4O_{10} for 10 h and identified as $Ti(C_{14}H_8O_2)_3$ (0.764 g, 80% yield) from analytical and spectroscopic (IR, ¹H NMR) data.

3.2. Synthesis of $[MCp_2(PDA)]_2$ ($M = Zr, Hf$)

(A) From $MCp_2(CO)_2$ and PQ. Only the procedure for zirconium is described in detail, the hafnium compound being obtained by a similar procedure. A solution of $ZrCp_2(CO)_2$ (1.87 g, 6.75 mmol) in toluene (200 ml) was treated with PQ (1.41 g, 6.78 mmol). Fast gas evolution and precipitation of a yellow–brown solid were observed. After 12 h, the yellow–red suspension was filtered and the solid dried in vacuo (0.20 g). The solution was concentrated in vacuo to ca. 100 ml and heptane was added (100 ml). After two days, large crystals

of $[ZrCp_2(PDA)]_2$ were recovered by decantation (0.67 g). The solution was evaporated to dryness under reduced pressure at room temperature and heptane (100 ml) was added; the resulting suspension was filtered and the yellow solid, dried in vacuo, was identified as $[ZrCp_2(PDA)]_2$ (1.56 g, 77% total yield). Anal. Found: C, 67.8; H, 4.4; Zr, 21.4. $C_{48}H_{36}O_4Zr_2$ Calc.: C, 67.3; H, 4.2; Zr, 21.0%. IR (Nujol and PCTFE): $\tilde{\nu} = 3111w, 3063m, 3025w, 1603m, 1583s, 1571m, 1518m, 1484s, 1446vs, 1417s, 1371vs, 1342s, 1281m, 1262w, 1249w, 1225w, 1195ms, 1161w, 1120m, 1109m, 1064m, 1031m, 923mw, 802vs, 756s, 725s, 698ms, 682m, 652m, 600w, 550m, 441m\text{ cm}^{-1}$. ¹H NMR (200 MHz, C_6D_6 , 25 °C): $\delta = 6.02$ (s, 5H, Cp), 7.52 (t, 2H), 7.71 (t, 2H), 8.21 (d, 2H), 8.71 (d, 2H). When the reaction was carried out in a gas–volumetric apparatus the gas evolved (CO) was found to correspond to a $CO/ZrCp_2(CO)_2$ molar ratio of 1.8.

$[HfCp_2(PDA)]_2$. Yield 77%. Anal. Found: C, 54.6; H, 3.4. $C_{48}H_{36}O_4Hf_2$ Calc.: C, 55.8; H, 3.5%. IR (Nujol and PCTFE): $\tilde{\nu} = 3111w, 3069m, 3025w, 1604m, 1586vs, 1572m, 1519m, 1485m, 1448vs, 1418s, 1375vs, 1342s, 1281m, 1262w, 1250w, 1225w, 1197m, 1161w, 1121m, 1108m, 1063m, 1024s, 924m, 809vs, 753s, 723s, 697ms, 687m, 651w, 555m, 442w\text{ cm}^{-1}$. ¹H NMR (200 MHz, C_6D_6 , 25 °C): $\delta = 5.91$ (s, 5H, Cp), 7.51 (t, 2H), 7.72 (t, 2H), 8.22 (d, 2H), 8.72 (d, 2H).

(B) From $ZrCp_2Cl_2$ and Na_2PDA . A suspension of Na (0.22 g, 9.96 mmol) in THF (250 ml) was treated with PQ (0.62 g, 2.98 mmol). After about 12 h, a suspension of the excess sodium in a red solution was obtained. After filtration, the solution was added of $ZrCp_2Cl_2$ (0.86 g, 2.94 mmol). The colour of the mixture promptly turned yellow and precipitation of a solid was observed. After 12 h, the yellow–red suspension was filtered and the solid dried in vacuo (0.49 g) was analytically identified as a mixture of $[ZrCp_2(PDA)]_2$ and NaCl in the approximate molar ratio of 1:3. The solution was evaporated to dryness under reduced pressure at room temperature and toluene (200 ml) was added; the resulting suspension was filtered and the yellow solid, dried in vacuo, (0.12 g) was analytically identified as a mixture of $[ZrCp_2(PDA)]_2$ and NaCl in the approximate molar ratio of 4:1. The solution was evaporated to dryness under reduced pressure at room temperature and heptane (50 ml) was added; the resulting suspension was filtered and the yellow solid, dried in vacuo, was identified as pure $[ZrCp_2(PDA)]_2$ (0.55 g, 44% yield). ¹H NMR (200 MHz, CD_3CN , 25 °C): $\delta = 6.02$ (s, 5CH), 7.52 (t, 2CH), 7.71 (t, 2CH), 8.21 (d, 2CH), 8.71 (d, 2CH).

3.3. Crystal structure solution and refinement of $[ZrCp_2(PDA)]_2$

A complete list of all atomic coordinates, anisotropic displacement parameters, and interatomic distances are

¹ We thank Dr. Isabella Ferri who provided a sample of $Ti(\eta^6\text{-toluene})_2$ prepared during her stay at the Inorganic Chemistry Laboratories, University of Oxford, UK.

Table 3

Atomic coordinates and equivalent isotropic displacement parameters for $[\text{ZrCp}_2(\text{PDA})_2]$. Estimated standard deviations in parentheses refer to the least significant digit

Atom	x	y	z	B_{eq} (\AA^2)
Zr1	0.03515(4)	0.79407(3)	0.93903(2)	2.627(9)
Zr2	-0.34560(4)	0.86091(3)	0.84465(2)	2.456(9)
O1	-0.1069(3)	0.7309(2)	0.9459(2)	2.90(7)
O2	-0.2856(3)	0.8340(2)	0.9465(2)	2.78(7)
O3	-0.0180(3)	0.8949(2)	0.8906(2)	2.87(7)
O4	-0.2057(2)	0.8629(2)	0.7927(2)	2.68(7)
C10	0.1820(4)	0.8581(4)	1.0279(3)	4.3(1)
C11	0.0796(5)	0.8949(4)	1.0376(3)	5.0(1)
C12	0.0088(5)	0.8399(4)	1.0650(3)	5.7(2)
C13	0.0691(5)	0.7691(4)	1.0721(3)	5.4(2)
C14	0.1758(5)	0.7799(4)	1.0500(3)	4.8(1)
C15	0.1525(5)	0.6797(4)	0.9049(3)	4.4(1)
C16	0.2155(5)	0.7458(4)	0.8909(3)	5.6(2)
C17	0.1505(5)	0.7868(4)	0.8351(3)	5.7(1)
C18	0.0488(5)	0.7441(4)	0.8151(3)	5.4(1)
C19	0.0520(5)	0.6767(4)	0.8567(3)	5.0(1)
C20	-0.4770(5)	0.9633(3)	0.8865(3)	4.3(1)
C21	-0.3651(5)	0.9874(3)	0.9124(3)	3.7(1)
C22	-0.3087(5)	1.0068(3)	0.8535(3)	4.3(1)
C23	-0.3851(5)	0.9967(3)	0.7916(3)	4.2(1)
C24	-0.4903(5)	0.9704(3)	0.8114(3)	4.7(1)
C25	-0.4767(4)	0.7939(4)	0.7470(3)	4.1(1)
C26	-0.3772(5)	0.7470(3)	0.7579(3)	4.0(1)
C27	-0.3696(5)	0.7152(3)	0.8273(3)	4.0(1)
C28	-0.4667(5)	0.7410(3)	0.8576(3)	4.2(1)
C29	-0.5326(4)	0.7900(4)	0.8081(3)	4.4(1)
C30	-0.1865(4)	0.7206(3)	0.9910(2)	2.7(1)
C31	-0.2754(4)	0.7730(3)	0.9914(2)	2.5(1)
C32	-0.3591(4)	0.7629(3)	1.0403(2)	2.49(9)
C33	-0.4472(4)	0.8192(3)	1.0448(3)	2.8(1)
C34	-0.5267(4)	0.8099(3)	1.0900(3)	3.6(1)
C35	-0.5265(4)	0.7432(3)	1.1318(3)	3.6(1)
C36	-0.4409(4)	0.6884(3)	1.1313(3)	3.3(1)
C37	-0.3532(4)	0.6972(3)	1.0866(2)	2.52(9)
C38	-0.2588(4)	0.6424(3)	1.0865(2)	2.53(9)
C39	-0.2450(4)	0.5773(3)	1.1323(3)	2.9(1)
C40	-0.1563(4)	0.5255(3)	1.1304(3)	3.3(1)
C41	-0.0748(4)	0.5372(3)	1.0827(3)	3.5(1)
C42	-0.0858(4)	0.6005(3)	1.0374(3)	3.3(1)
C43	-0.1773(4)	0.6541(3)	1.0385(2)	2.6(1)
C50	-0.0295(4)	0.9287(3)	0.8261(3)	2.6(1)
C51	-0.1236(4)	0.9127(3)	0.7766(2)	2.50(9)
C52	-0.1331(4)	0.9467(3)	0.7066(2)	2.8(1)
C53	-0.2253(4)	0.9257(3)	0.6540(3)	3.6(1)
C54	-0.2327(5)	0.9545(4)	0.5860(3)	4.5(1)
C55	-0.1483(6)	1.0045(4)	0.5664(3)	4.8(1)
C56	-0.0585(5)	1.0271(3)	0.6164(3)	4.3(1)
C57	-0.0489(4)	0.9996(3)	0.6879(3)	3.0(1)
C58	0.0453(4)	1.0214(3)	0.7424(3)	3.1(1)
C59	0.1290(4)	1.0780(3)	0.7300(3)	4.2(1)
C60	0.2178(5)	1.0967(3)	0.7816(4)	4.8(1)
C61	0.2287(4)	1.0584(3)	0.8468(3)	4.6(1)
C62	0.1496(4)	1.0035(3)	0.8614(3)	3.9(1)
C63	0.0556(4)	0.9849(3)	0.8097(3)	2.8(1)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ac(\cos\beta)\beta(1,3)]$.

available as supplementary material and have been deposited with the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany; depositary number CSD-406364.

Crystals suitable for the X-ray diffractometric study were obtained by slow diffusion of heptane into a dilute solution of $[\text{ZrCp}_2(\text{PDA})_2]$ in toluene. The intensity data were collected at 203 K with Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator in the ω -scan mode.

Crystal data. $\text{C}_{48}\text{H}_{36}\text{O}_4\text{Zr}_2$, $M = 859.26 \text{ g mol}^{-1}$, monoclinic, space group $P2_1/n$ (No. 14), $a = 11.647(8)$, $b = 17.07(1)$, $c = 18.80(1) \text{ \AA}$, $\beta = 97.17(6)^\circ$, $V = 3709(7) \text{ \AA}^3$, $Z = 4$, $d_{\text{calc}} = 1.539 \text{ g cm}^{-3}$, $\mu = 5.97 \text{ cm}^{-1}$, $F(000) = 1744$. During data collection and processing, 8293 reflections were measured in the range $3.0^\circ < \theta < 25.0^\circ$; 5060 unique reflections with $I > 1.0\sigma(I)$ were used for further computations. No significant variation in intensity of three standard reflections was observed during the data collection. Atomic coordinates are given in Table 3. Structure solution was performed by direct methods [41]. Full-matrix least-squares refinement [42] was carried out with anisotropic thermal parameters for all non-hydrogen atoms. No absorption correction was applied. Refinement with 487 parameters using a statistical weighting scheme $w = 1/[\sigma^2(F_o)]$ converged at values of $R = 0.050$ and $R_w = 0.052$ with GOF 1.473.

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