Inorganica Chimica Acta 387 (2012) 361-365

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

π -Indenyl substituted zirconium compounds containing terminal bonded phosphanylphosphido ligands [Ind₂Zr(Cl){(Me₃Si)P-PR₂- κ P¹}]. Synthesis, X-ray analysis and NMR studies

Agnieszka Łapczuk-Krygier^a, Katarzyna Baranowska^a, Łukasz Ponikiewski^a, Eberhard Matern^b, Jerzy Pikies^{a,*}

^a Chemical Faculty, Department of Inorganic Chemistry, Gdansk University of Technology, G. Narutowicza St. 11/12, Pl-80-233 Gdansk, Poland ^b Institut für Anorganische Chemie, Universität Karlsruhe (TH), D-76128 Karlsruhe, Germany

ABSTRACT

ARTICLE INFO

Article history: Received 16 September 2011 Received in revised form 7 February 2012 Accepted 15 February 2012 Available online 23 February 2012

Keywords: P ligands Phosphido complexes Zirconium Indenyl complexes

1. Introduction

The chemistry of complexes of group 14 metals bearing cyclopentadienyl ligands and one [1-9] or two [1,2,10-16] organyl phosphido groups is relatively well investigated. The most important synthetic route leading to this class of compounds involves metathesis of the related metallocene dichlorides $[Cp_2MCl_2]$ (M = Zr, Hf; Cp = cyclopentadienyl or substituted cyclopentadienyl) with alkali metal derivatives of primary and secondary phosphanes with bulky organyl groups. To our surprise, however there have been no reports on the reactivity of alkali metal derivatives of phosphanes towards dichloro-bis(indenyl)zirconium(IV).

In the course of our studies upon the reactivity of lithiated diphosphanes R_2P -P(SiMe₃)Li towards group 14 dichlorometallocenes, we have established that these compounds can act as precursors for three types of new diphosphorus ligands: terminal phosphanylphosphinidene R_2P -P ligands [17], side-on bonded phosphanylphosphinidene ligands with a second Cp₂ZrCl group bonded terminally to the phosphinidene phosphorus atom – [μ -(1,2:2- η -tBu₂P = P){Zr(Cl)Cp₂}] [17] and terminal phosphanylphosphiniden ligands R_2P -P(SiMe₃) [18,19].

In this paper we describe the results of our studies on the reactivity of $R_2P-P(SiMe_3)Li$ (R = ^tBu, Et₂N, and ⁱPr₂N) towards

* Corresponding author. Tel.: +48 58 3472874.

E-mail address: jerzy.pikies@pg.gda.pl (J. Pikies).

[Ind₂ZrCl₂]. The described results were presented in a preliminary form at the 18th International Conference on Phosphorus Chemistry [20].

© 2012 Elsevier B.V. All rights reserved.

Dichloro-bis(indenyl)zirconium(IV) reacts with lithium derivatives of diphosphanes R₂P-P(SiMe₃)Li

 $(R = {}^{t}Bu, Et_2N, {}^{i}Pr_2N)$ to form complexes with terminal phosphanylphosphido ligands – $[Ind_2Zr(CI)-$

 $\{(PSiMe_3)P-PR_2-\kappa P^1\}\}$. These compounds are extremely sensitive towards moisture and oxygen. The solid

state structures of these complexes were established by single crystal X-ray diffraction. The nitrogen

bearing groups R (Et_2N or iPr_2N) significantly lengthen the P–P distances in the related complexes and change the geometry around the phosphido phosphorus in such a way that it becomes less planar.

Inorganica

2. Discussion

2.1. Reactivity

The addition of 1 equiv. of $R_2P-P(SiMe_3)Li$ ($R = Et_2N$, iPr_2N and tBu) to [Ind₂ZrCl₂] in toluene or pentane leads to coloured solutions which contain monosubstituted derivatives [Ind₂M(Cl){P(SiMe_3)-PR_2-\kappa P^1}] (compounds **1–3**) (Scheme 1).

Compound **1** is formed as the sole product, whereas **2** and **3** are accompanied by some side products. In spite of the increased steric effect of the η^5 -indenyl ligand the reactivity of [Ind₂ZrCl₂] towards R₂P–P(SiMe₃)Li is comparable to that of [Cp₂ZrCl₂]. For the bis(indenyl)Zr(IV) complexes, lower electron densities at the Zr atoms were estimated compared the related bis(cyclopentadienyl)Zr(IV) derivatives [21]. Thus in the former the nucleophilic substitution at the Zr atom can be facilitated and it compensates the greater steric hindrance of indenyl groups.

All these compounds are very well soluble in hydrocarbons and are very sensitive to moisture and oxygen. The properties of these compounds depend strongly on the sterical properties of the group R.



^{0020-1693/\$ -} see front matter @ 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.ica.2012.02.028



Scheme 1. Reaction of [Ind₂ZrCl₂] with R₂P-P(SiM₃)Li.

Pure **1** is relatively stable in C_6D_6 solution at ambient temperature whereas at 50 °C it decomposes completely yielding the related tetraphosphetane, probably according to the mechanism published previously [18] (Scheme 2). The stability of crude **1** in the reaction solution is much higher. Heating of this solution to 50 °C for 5 h caused only a small increase in the intensity of the tetraphosphetane signals [18] in ³¹P{¹H} spectrum.

Compound 2 does not react at 50 °C according to Scheme 2 due to the steric requirements of the NⁱPr₂ and indenyl groups which prevent the formation of [Ind₂Zr(NⁱPr₂)Cl]. However, **2** is not stable and undergoes significant decomposition after dissolving in toluene-D₈ (see Section 3) under cleavage of the Zr-P bond and the P-P bond in phosphanylphosphido ligand. To our surprise, **3** is the least stable of these three compounds. In the reaction solution we observed only weak signals of $3^{(31)}$ P NMR spectrum) and isolated **3** decomposes rapidly after dissolving in C₆D₆ indicating only ^tBu₂P-P(SiMe₃)H and traces of ^tBu₂PH (³¹P NMR). In conclusion, introducing of Ind-groups in place of Cp-groups strongly enhanced the splitting tendency of the Zr-P bond, and complexes with more voluminous R groups undergo Zr-P bond cleavage more rapidly probably due to an overcrowding effect. The side products especially in the case of **2**, $({}^{i}Pr_{2}N)_{2}P-P(SiMe_{3})H$, $({}^{i}Pr_{2}N)_{2}P-P(SiMe_{3})_{2}$ and (ⁱPr₂N)₂P-P(NⁱPr₂)₂ strongly suggest a radical mechanism of this Zr-P splitting. A similar trend was recently observed in relatively crowded phosphido hafnium complexes: [Cp*CpHf(Me)-(HPDmp] but not [Cp*CpHf(Me)(HPPh] undergo a facile Hf–P bond cleavage and a formation of DHPDmp [22].

2.2. Crystallographic studies of 1-3

X-ray structural studies of **1** (triclinic, $P\overline{1}$ group, Z = 2), **2** (monoclinic, $P2_1/c$ group, Z = 4) and **3** (monoclinic, $P2_1/c$ group, Z = 4) indicate that these complexes display a highly distorted pseudotetrahedral geometry around the Zr atoms. The angles (the centre of Ind1, Zr, the centre of Ind2) are 128.82° for **1**, 126.61° for **2** and 128.12° for **3**. The angle P1–Zr1–Cl1 is 100.05(3)° for **1**, 98.69(9)° for **2** and 94.96(3)° for **3**. The geometries around the metal centres are similar to those of $[Cp_2Zr(Cl){(Me_3Si)P-P^iPr_2-\kappa P^1}]$ (**4**) and $[Cp_2Hf(Cl){(Me_3Si)P-P^iPr_2-\kappa P^1}]$ (**5**) [19] and of $[Cp_2Hf(Cl){(Me_3Si)P-P(NEt_2)_2-\kappa P^1}]$ (**6**) [18].

In **1–3** the indenyl groups are η^5 coordinated. The distances from the centres of the cyclopentadienyl rings of the indenyl groups (average values) to the Zr atoms are 224.1 pm for **1**, 223.8 pm for **2** and 223.4 pm for **3**. In **4** the average distance from the cyclopentadienyl ring centre to the Zr atom is 220.9 pm.

The most important structural features of **1–3** together with related structural data of **4–6** (for comparison) are collected in Table 1.

The data in Table 1 enable us to discuss some factors that influence the structural features of phosphanylphosphido complexes of Zr and Hf. The geometries around P2 are pyramidal in all compounds, the geometries around P1 differ considerably.

Introduction of amido R groups in 1, 2 and 6 compared to 5 lengthens the P1-P2 distance. This is especially evident for 2 $(R = N^{i}Pr_{2})$. Similar elongation was observed in amido substituted diphosphanes [23,24]. The introduction of $R = NEt_2$ in place of ⁱPr leads to an elongation of the M-P1 distance (1 versus 4 and 6 versus 5), thus it diminishes the M-P1 bond order. It is consistent with a more pyramidal geometry around P1 in 1 and 6. The distances M-P and the degree of planarity measured as the sum of angles around phosphido P atoms in 1 and 6 are very similar to some classical Zr phosphido complexes bearing relatively voluminous ligands as PHDmp [3], PHTrip [8] and PHCy [9]. Zr complexes with very voluminous ligands such as P(SiMe₃)Mes* [5] and PHMes* [7] display planarity around the P atom, consistent with the relative short Zr-P distances of about 254 pm. However, compounds **2** ($R = N^{i}Pr_{2}$) and **3** ($R = {}^{t}Bu$) display high degrees of planarity around P1 in spite of long Zr-P1 distances. The relatively voluminous groups NⁱPr₂ in **2** and ^tBu in **3** enlarge the M-P1-P2 angle and thus enlarge the sum of angles around P1 atoms, but long M-P1 distances suggest single M-P1 bonds.

2.3. ³¹P NMR studies of phosphanylphosphido complexes of Zr(IV) and Hf(IV)

The chemical shifts of the phosphido phosphorus P1 and the phosphanyl phosphorus P2 together with ${}^{1}J_{P1-P2}$ for all known phosphanylphosphido complexes of Zr and Hf are collected in Table 2. For the compounds with known X-ray structures we have calculated the dihedral angle τ of the free electron pairs along the P1–P2 bond.

The chemical shifts of the P2 atoms are similar to those observed in related diphosphanes $R_2P-P(SiMe_3)_2$. The chemical shifts of the phosphido P1 atoms in Hf complexes are found at higher field compared to the related Zr complexes. This relationship seems to be general, see [11,27]. The magnitude of ${}^1J_{P1-P2}$ depends on the steric requirements of R groups but not on the distances P1– P2. For compounds with less sterically demanding R groups, the absolute values of ${}^1J_{P-P}$ are low. In the solid state, the lone pairs of the P atoms are in a nearly antiperiplanar conformation. Such conformations may also prevail in solution. In compounds with more sterically demanding R groups the lone pairs adopt nearly gauche conformations which leads to the increased absolute values of ${}^1J_{P-P}$.



Scheme 2. Thermal decomposition of [Ind₂Zr(Cl){P(Me₃Si)P-P(NEt₂)₂}].

Compound		(1)	(2)	(3)	(4) [19]	(5) [18]	(6) [19] ^a	
P1 P1 M M P2	P1 P1 ∑iP1 ∑iP2	P2 M P2 Si Si	222.73(8) 265.51(9) 108.15(4) 112.27(4) 100.71(4) 321.13 311.93	225.9(2) 262.8(1) 142.28(6) 111.34(4) 97.55(3) 351.17 318.5	220.1(1) 265.1(1) 138.82(5) 114.36(5) 93.75(5) 346.93 326.5	218.59(14) 258.35(11) 117.58(5) 119.63(5) 111.17(6) 348.37 313.1	218.5 (1) 256.81 (9) 117.16(4) 119.37(4) 110.80(5) 347.33 313.1	224.7(8)/222.7(9) 264.5(5)/263.2(6) 112.5(3)/115.7(3) 110.9(3)/115.8(3) 99.1(3)/98.5(3) 330.0 318.6/316.1

Table 1		
Structural data for phosphanylphosphido	complexes of zirconium and hafniu	m (distances [pm], angles [deg]).

^a Two molecules in the elementary cell.

³¹ P NMR data for the	phosphanylphosphido	complexes of Zr(IV) and Hf(IV).

Compound		P1 [ppm]	P2 [ppm]	¹ J _{P1-P2} [Hz]	τ [deg]	Lit.
(1)	$[(Et_2N)_2P - P(SiMe_3)Zr(Cl)Ind_2]$	-47.7	125.8	250.9	172.2	a
(6)	[(Et ₂ N) ₂ P–P(SiMe ₃)Hf(Cl)Cp ₂]	-	-	-	164.6, 160.2	[18]
(2)	[(ⁱ Pr2N)2P-P(SiMe3)Zr(Cl)Ind2]	≈59.8 ^b	111.2	541.9	112.7	a
	$[(^{i}Pr_{2}N)_{2}P-P(SiMe_{3})Zr(Cl)Cp_{2}]$	≈59.5 ^b	116.6	539.6		[25] ^c
	$[(^{i}Pr_{2}N)_{2}P-P(SiMe_{3})Hf(Cl)Cp_{2}]$	$\approx 7.0^{b}$	118.7	534.6		[26] ^c
(4)	[ⁱ Pr ₂ P–P(SiMe ₃)Zr(Cl)Cp ₂]	2.2	35.1	428.2	85.0	[19]
(5)	[ⁱ Pr ₂ P–P(SiMe ₃)Hf(Cl)Cp ₂]	-26.0	35.8	22.6	85.0	[19]
(3)	$[^{t}Bu_{2}P-P(SiMe_{3})Zr(Cl)Ind_{2}]$	9.25	67.44	522.1	99.0	a
	$[^{t}Bu_{2}P-P(SiMe_{3})Zr(Cl)Cp_{2}]$	-3.0	68.2	520.3		[19]
	[^t Bu ₂ P–P(SiMe ₃)Hf(Cl)Cp ₂]	-44.51	67.48	511.5		[19]

^a This work.

Table 2

^b Very broad doublets.

^c Not isolated compounds, only ³¹P NMR data.

3. Experimental

3.1. X-ray

Diffraction data were recorded on a KUMA KM4 diffractometer with graphite-monochromated MoK α radiation using a Sapphire-2 CCD detector (Oxford Diffraction Ltd.). The apparatus was equipped with an open flow thermostat (Oxford Cryosystems). The structures were solved with direct methods and refined with the sHELX97 program package [28] with the full-matrix least-squares refinement based on F^2 . The data were corrected for absorption with the CrysAlis RED program [29]. All non-hydrogen atoms were refined anisotropically. All H atoms were positioned geometrically and refined using a riding model C—H = 0.95–0.99 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for CH₃ groups.

3.2. NMR

 31 P and 1 H NMR spectra were recorded on Bruker AMX300, Bruker AV300 and Bruker AV400 MHz spectrometers (external standard 85% H₃PO₄) at ambient temperature. The simulation and iteration of spectra was made using Bruker software [30]. For the numbering of atoms see Figs. 1–3.

3.3. Syntheses

All reactions and manipulations were carried out under the atmosphere of ultra-high purified argon employing flame-dried Schlenk type glassware. Solvents were purified, dried and distilled prior to use from dark blue potassium or sodium diphenyl ketyl solution. Pentane was dried over Na/benzophenone/diglyme and distilled under nitrogen. Literature methods were used to prepare the lithium derivatives of diphosphanes: [(Et₂N)₂P–P(SiMe₃)Li] [31], [ⁱPr₂PP(SiMe₃)Li] and [(ⁱPr₂N)₂P–P(SiMe₃)Li] [32], [^tBu₂PP(Si-



Fig. 1. Molecular structure of **1** showing the atom-numbering scheme (30% probability displacement ellipsoids), important bond lengths (pm) and bond angles (deg). H atoms have been omitted. Zr1–Cl1 241.83(9), Zr1–P1 265.51(9), P1–P2 222.73(8), P1–Si1 227.3(1), P1–Zr1–Cl1 100.05(3), Zr1–P1–P2 108.15(4).

Me₃)Li] [33]. [Ind₂ZrCl₂] was prepared according to the literature [34], but with significant modification resulting in the higher yield.

3.3.1. Synthesis of [Ind₂ZrCl₂]

31.2 mL of a MeLi solution (1.6 M in Et₂O) were added dropwise at -80 °C to a solution of 6 mL (50 mmol) freshly distilled indene in THF (20 mL). To the resulting reaction mixture, a suspension of 5.81 g (25 mmol) ZrCl₄ in cold THF (100 mL) was added. The mixture turned dark red. The solvents were removed in vacuum. The residue was washed with Et₂O and extracted with CH₂Cl₂. The extract was evacuated to dryness, the residue washed with Et₂O and then with pentane, finally dried to give an yellow product. Yield 5.11 g (52%).



Fig. 2. Molecular structure of **2** showing the atom-numbering scheme (30% probability displacement ellipsoids), important bond lengths (pm) and bond angles (deg). H atoms have been omitted. Zr1-Cl1 243.9(1), Zr1-P1 262.8(1), P1-P2 225.9(2), P1-Si1 226.3(3), P1-Zr1-Cl1 98.69(9), Zr1-P1-P2 142.28(6).



Fig. 3. Molecular structure of **3** showing the atom-numbering scheme (30% probability displacement ellipsoids), important bond lengths (pm) and bond angles (deg). H atoms have been omitted. Zr1-Cl1 243.39(8), Zr1-P1 265.1(1), P1-P2 220.1(1), P1-Si1 226.0(1), P1-Zr1-Cl1 94.96(3), Zr1-P1-P2 138.82(5).

¹H NMR (CDCl₃): 6.23 ppm (4H, d, *J* = 3.32 Hz), 6.55 ppm (2H, t, *J* = 3.32 Hz), 7.3 ppm (4H, m), 7.6 ppm (4H, m).

3.3.2. Reaction of $(Et_2N)_2P-P(SiMe_3)Li$ with $[Ind_2ZrCl_2]$. Synthesis of $[Ind_2Zr(Cl){(Me_3Si)P-P(NEt_2)_2-\kappa P^1}]$ (1)

A suspension of $[Ind_2ZrCl_2]$ (0.396 g; 1.01 mmol) in toluene (3 mL) was added to a solution of $[(Et_2N)_2PP(SiMe_3)Li]$ (0.289 g; 1.01 mmol) in toluene (5 mL) at -40 °C. The mixture was vigorously stirred and allowed to warm to room temperature. The mixture turned dark red and the suspension was dissolved. The next day, the reaction solution was evaporated in vacuum. The residue was dissolved in pentane (3 mL), filtrated, and after 2 days at -22 °C red crystals of **1** were deposited (0.170 g, yield 27%). The ³¹P NMR examination of the reaction solution detected **1**, small amounts of $(Et_2N)_2P$ -P(SiMe_3)H, $(Et_2N)_2P$ -P(SiMe_3)₂ and traces of the phosphetane $Et_2NP(\mu_2-PSiMe_3)_2PNEt_2$ [18].

 $^{31}P\{^{1}H\}$ NMR ($C_{6}D_{6}$, ambient temp.): (1) 124.78 ppm (d, P2), –48.83 ppm (d, P1), $^{1}J_{P1-P2}$ = 247.8 Hz. ^{1}H NMR ($C_{6}D_{6}$, ambient temp.): (1) 7.70–7.64 ppm (2.0 H, ms, $C_{9}H_{7}$), 7.15–7.10 ppm (2.0 H, m, $C_{9}H_{7}$), 6.85–6.86 ppm (6 H, ms, $C_{9}H_{7}$), 6.42–6.37 ppm (m, 2H, $C_{9}H_{7}$), 5.43–5.40 ppm (2.0 H, ms, $C_{9}H_{7}$), 3.35 ppm (4 H, quart 7.0 Hz, d 7.0 Hz, d 14.0 Hz, NCH₂CH₃), 3.17 ppm (4 H, quart 7.0 Hz, d 14.0 Hz, d 11.4 Hz NCH₂CH₃), 1.09 ppm (12.8 H, d 7.0 Hz, d 7.0 Hz, NCH₂CH₃), 0.55 ppm (9H, d, 3.3 Hz, (CH₃)₃Si).

Anal. Calc. for $C_{29}H_{43}N_2P_2SiClZr$ (636.38): C, 54.73; H, 6.81; N, 4.40. Found: C, 55.18; H, 6.85; N, 4.14%.

3.3.3. Reaction of $({}^{i}Pr_{2}N)_{2}P-P(SiMe_{3})Li$ with $[Ind_{2}ZrCl_{2}]$. Synthesis of $[Ind_{2}Zr(Cl){(Me_{3}Si)P-P(N^{i}Pr_{2})_{2}-\kappa P^{1}}]$ (2)

A suspension of $[Ind_2ZrCl_2]$ (0.178 g; 0.45 mmol) in toluene (3 mL) was added to a solution of $[({}^{i}Pr_2N)_2PP(SiMe_3)Li\cdot1.1THF]$ (0.367 g; 0.88 mmol) in toluene (5 mL) at -44 °C. The mixture was vigorously stirred and allowed to warm to room temperature. The suspension dissolved, and the colour of the solution changed to dark brown. After 1 day the solvents were removed in vacuum. The residue was dissolved in pentane and filtered. After several days at -22 °C deep red crystal needles of $[({}^{i}Pr_2N)_2P-P-SiMe_3)Zr(-Cl)Ind_2]$ (2) deposited (0.080 g, yield 24%). On dissolving 2 in toluene-d₈ a massive decomposition underwent, 2 and additionally significant amounts of $({}^{i}Pr_2N)_2P-P(SiMe_3)H$, $({}^{i}Pr_2N)_2P-P(SiMe_3)_2$ and $({}^{i}Pr_2N)_2P-P(N^{i}Pr_2)_2$ as well as small amounts of $({}^{i}Pr_2N)_2PH$, $P(SiMe_3)_3$ and $({}^{i}Pr_2N)_2P-P(\mu_2-PN^{i}Pr_2)_2PSiMe_3$ [18] were identified. The ${}^{1}H$ NMR data of 2 were assigned using a ${}^{1}H-{}^{31}P$ HMBC spectrum.

 $^{31}P{^{1}H}$ NMR (toluene-d₈, ambient temp.): (**2**) 111.2 ppm (d, P2), -59.8 ppm (very broad d, P1), $^{1}J_{P1-P2}$ = 541.9 Hz. ^{1}H NMR (toluene-d₈, ambient temp.): (**2**) 3.62 ppm (m, NCH(CH₃)₂), 1.32 ppm (d, 6.5 Hz, NCH(CH₃)₂), 0.68 ppm (d, 4.0 Hz, (CH₃)₃Si).

Anal. Calc. for C₃₃H₅₁N₂P₂ZrClSi (692.49): C, 57.24; H, 7.42; N, 4.05. Found: C, 55.07; H, 8.49; N, 5.19%.

3.3.4. Reaction of ${}^{t}Bu_2P-P(SiMe_3)Li$ with $[Ind_2ZrCl_2]$. Synthesis of $[Ind_2Zr(Cl){(Me_3Si)P-P}{}^{t}Bu_2-\kappa P^{1}]$ (**3**)

A suspension of $[Ind_2ZrCl_2]$ (0.150 g; 0.38 mmol) in pentane (3 mL) was added to a suspension of $[{}^tBu_2PP(SiMe_3)Li-2THF]$ (0.160 g; 0.40 mmol) in pentane (5 mL) at room temperature. The mixture turned immediately dark red. Lithium chloride was separated. The solution was filtered and the volume was reduced to 2/3 under reduced pressure. After 7 days at -22 °C, orange crystals of $[{}^tBu_2P-P(SiMe_3){Zr(Cl)Ind_2}]$ (3) were deposited (0.070 g, yield 29%).

The ³¹P NMR examination of the reaction solution revealed ^tBu₂P–P(SiMe₃)H, ^tBu₂P–P(SiMe₃)₂, small amounts of **3**, ^tBu₂P–P(Si-Me₃)Li and probably a diphosphorus compound (32.3 and –117.7 ppm, ¹J_{P–P} = –392.7 Hz). Dissolving of **3** in C₆D₆ leads to its total decomposition and only ^tBu₂P–P(SiMe₃)H and traces of ^tBu₂PH were found in the resulting solution.

 ${}^{31}P{^{1}H}$ NMR (reaction solution, C₆D₆, ambient temp.): (**3**) 67.2 ppm (d, P2), 9.25 ppm (d, P1), {}^{1}J_{P1-P2} = 522.1 Hz.

Anal. Calc. for $C_{29}H_{41}ClP_2SiZr$ (606.35): C, 57.45; H, 6.82. Found: C, 57.06; H, 6.86%.

Acknowledgements

J.P. and Ł.P. thank the Polish Ministry of Science and Higher Education (Grant Nr. N N204 271535) for financial support. A.Ł.-K. thanks the Polish Ministry of Science and Higher Education (Grant Nr. N N204 145038) for financial support.

Appendix A. Supplementary material

Supplementary material CCDC 808740, CCDC 808739 and CCDC 808808 contains the crystallographic data for the structures of **1**, **2** and **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica. 2012.02.028.

References

- [1] E. Hey-Hawkins, Chem. Rev. 94 (1994) 1661.
- [2] S.R. Wade, G.H. Wallbridge, G.R. Willey, J. Chem. Soc., Dalton Trans. (1983) 2555.
- [3] E. Urnėžius, S.J. Klippenstein, J.D. Protasiewicz, Inorg. Chim. Acta 297 (2000) 181.
- [4] D.M. Roddick, B.D. Santarsiero, J.E. Bercaw, J. Am. Chem. Soc. 107 (1985) 4670.
 [5] A.M. Arif, A.H. Cowley, C.M. Nunn, M. Pakulski, J. Chem. Soc., Chem. Commun. (1987) 994.
- [6] E. Hey, M.F. Lappert, J.L. Atwood, S.G. Bott, Polyhedron 7 (1988) 2083.
- [7] J. Ho, Z. Hou, R. Rosseau, D.W. Stephan, Organometallics 13 (1994) 1918.
- [8] E. Hey-Hawkins, S. Kurz, G. Baum, Z. Naturforsch. 50b (1995) 239.
- [9] U. Segerer, E. Hey-Hawkins, Polyhedron 16 (1997) 2537.
- [10] R.T. Baker, J.F. Whitney, S.S. Wreford, Organometallics 2 (1983) 1049.
- [11] L. Weber, G. Meine, R. Boese, N. Augart, Organometallics 6 (1987) 2484.
- [12] F. Lindenberg, E. Hey-Hawkins, J. Organomet. Chem. 435 (1992) 291.
- [13] Z. Hou, T.L. Breen, D.W. Stephan, Organometallics 12 (1993) 3158.
- [14] E. Hey-Hawkins, S. Kurz, J. Organomet. Chem. 479 (1994) 125.
- [15] R. Bohra, P.B. Hitchcock, M.F. Lappert, W-P. Leung, J. Chem. Soc., Chem. Commun. (1989) 728.
- [16] Z. Hou, D.W. Stephan, J. Am. Chem. Soc. 114 (1992) 10088.
- [17] J. Pikies, E. Baum, E. Matern, J. Chojnacki, R. Grubba, A. Robaszkiewicz, Chem. Commun. (2004) 2478.
- [18] R. Grubba, A. Wiśniewska, K. Baranowska, E. Matern, J. Pikies, Dalton Trans. 40 (2011) 2017.

- [19] R. Grubba, A. Wiśniewska, K. Baranowska, E. Matern, J. Pikies, Polyhedron 30 (2011) 1238.
- [20] 18th International Conference on Phosphorus Chemistry, July 11–15, 2010, Wroclaw, Poland, Book of Abstracts p. 69.
- [21] U. Wieser, D. Babushkin, H.-H. Britzinger, Organometallics 21 (2002) 920.
- [22] R. Waterman, T. Don Tilley, J. Chem. Sci. 2 (2011) 1320.
- [23] H.R. Bender, E. Niecke, M. Nieger, H. Westermann, Z. Anorg, Allg. Chem. 620 (1994) 1194.
- [24] R. Grubba, Ł. Ponikiewski, J. Chojnacki, J. Pikies, Acta Cryst. E65 (2009) o2214.
- [25] R. Grubba, Dissertation, Technical University of Gdańsk, Gdańsk, 2004.
- [26] A. Wiśniewska, Dissertation, Gdańsk University of Technology, Gdańsk, 2010.
- [27] R.T. Baker, T.H. Tulip, Organometallics 5 (1986) 839.
- [28] G.M. Sheldrick, SHEIX-97. Programs for the solution and the refinement of crystal structures from diffraction data.
- [29] CrysAlis RED, Oxford Diffraction Ltd., Version 1.171.33.66 (release 28-04-2010 CrysAlis171 .NET)(compiled April 28 2010, 14:27:37).
- [30] (a) G. Hägele, M. Engelhardt, W. Boenigk, Simulation und automatisierte Analyse von NMR-Spektren, VCH, Weinheim, 1987;
 - (b) Program Daisy, part of Bruker Topspin 2.1, pl. 6.
- [31] I. Kovacs, E. Matern, G. Fritz, Z. Anorg, Allg. Chem. 622 (1996) 935.
- Chem. [32] W. Domańska-Babul, K. Baranowska, R. Grubba, E. Matern, J. Pikies, Polyhedron 26 (2007) 2491.
 - [33] G. Fritz, T. Vaahs, J. Härer, Z. Anorg, Allg. Chem. 552 (1987) 11.
 - [34] D. Balboni, I. Camurati, A. Casico Ingurgio, S. Guidotti, F. Focante, L. Resconi, J. Organomet. Chem. 683 (2003) 2.