

Synthesis of 2-(diphenylphosphino)phenolato- and 2-(diphenylphosphinomethyl)-4-methylphenolato complexes of titanium and zirconium. X-ray characterization of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}(\text{OC}_6\text{H}_4\text{PPh}_2)]$ and $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{OC}_6\text{H}_4\text{PPh}_2)_2]$

Laurent Miquel ^a, Mario Basso-Bert ^a, Robert Choukroun ^{a,*}, Rachid Madhouni ^b, Bettina Eichhorn ^b, Michel Sanchez ^b, Marie-Rose Mazières ^b, Joël Jaud ^c

^a Laboratoire de Chimie de Coordination du CNRS, Unité 8241, 205 route de Narbonne, 31077 Toulouse Cedex, France

^b Laboratoire de Synthèse, Structure et Réactivité de Molécules Phosphorées, Université Paul Sabatier, 118 Route de Narbonne, 31062 Toulouse Cedex, France

^c Centre d'Elaboration de Matériaux et d'Etudes Structurales, CEMES-LOE / CNRS, UPR 8011, 29 rue Jeanne-Marvig, BP 4347, 31055 Toulouse Cedex, France

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Abstract

Complexes $[(\text{C}_5\text{H}_5)_2\text{MCl}_2]$ (M = Ti, Zr) react with the 2-(diphenyl-phosphino)phenol $\text{HO}(\text{C}_6\text{H}_4)\text{PPh}_2$ in the presence of imidazole to give the corresponding complexes $[\text{Cp}_2\text{ZrCl}(\text{OC}_6\text{H}_4\text{PPh}_2)]$, **1** and $[\text{Cp}_2\text{M}(\text{OC}_6\text{H}_4\text{PPh}_2)_2]$ (2: M=Ti; 3: M=Zr). Under the same experimental conditions, the bulkier ligand 2-(diphenylphosphinomethyl)-4-methylphenol $\text{HO}(\text{C}_6\text{H}_3)(\text{CH}_3)\text{CH}_2\text{PPh}_2$ failed to react with $[\text{Cp}_2\text{MCl}_2]$ (Ti or Zr) but with $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$ gives the methyl complex $[\text{Cp}_2\text{Zr}(\text{CH}_3)(\text{O}(\text{C}_6\text{H}_3)(\text{CH}_3)\text{CH}_2\text{PPh}_2)]$, **4** and $[\text{Cp}_2\text{Zr}(\text{O}(\text{C}_6\text{H}_3)(\text{CH}_3)\text{CH}_2\text{PPh}_2)_2]$, **5**. Compounds **1** and **3** crystallize from CH_2Cl_2 solution, and their structures have been determined. The relatively short Zr–O bond distance of 1.979(7) Å, and the Zr–O–C bond angle of 160.2(5)°, in one phenoxy ligand of **3** suggest significant double bonding between Zr and O atoms. Chemical reduction of **1** with Na/Hg gives the expected cyclic *P*-metallated Zr^{III} species $[\text{Cp}_2\text{Zr}(\text{OC}_6\text{H}_4\text{PPh}_2)]$ characterized by EPR ($g = 1.976$; $a(^{31}\text{P}) = 14.6$ G.). Preliminary data indicate that **3** acts as a diphosphine ligand upon reaction with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$.

Keywords: Titanium; Zirconium; X-ray structure; Phenolato complexes; Phosphinophenolato complexes

1. Introduction

The linkage of early transition metals to electron-rich metals such as rhodium, is of great interest because of the potential cooperative reactivity of two widely different metals [1]. Among the various bridging modes via an heteroatom such as P [1b] or S [2] used to create such links, is our development using the diphenylphosphinomethyl groups Ph_2PCH_2 [3], bonded to an early transition metal (Ti or Zr) via metal–carbon bonds and to rhodium via Rh–P bonds. Hydroformylation cataly-

ses were performed, more active and selective than those with simple mononuclear rhodium complexes [3b,4]. Another approach could use a bifunctional *P,O*-ligand [5]. An alkoxy link to an early transition metal and a phosphine link to a late transition metal should both be robust enough to withstand the conditions necessary to affect small molecule reactivity between cooperative metal centres.

In the initial efforts reported here, 2-(diphenylphosphino)phenol $\text{HO}(\text{C}_6\text{H}_4)\text{PPh}_2$ [6] and 2-(diphenylphosphinomethyl)-4-methylphenol $\text{HO}(\text{C}_6\text{H}_3)(\text{CH}_3)\text{CH}_2\text{PPh}_2$ [7] have been used to synthesise bis(cyclopentadienyl) phenolato-titanium and zirconium complexes, and the X-ray structures of $[\text{Cp}_2\text{ZrCl}(\text{OC}_6\text{H}_4\text{PPh}_2)]$ **1** and $\text{Cp}_2\text{Zr}(\text{OC}_6\text{H}_4\text{PPh}_2)_2$ **3** are described. We re-

* Corresponding author.

cently used $\text{HO}(\text{C}_6\text{H}_4)\text{PPh}_2$ in the synthesis of ruthenium complexes [8,9]. To our knowledge no metal complex derived from $\text{HO}(\text{C}_6\text{H}_3)(\text{CH}_3)\text{CH}_2\text{PPh}_2$ has been described.

2. Experimental details

All manipulations were carried out under argon by conventional Schlenk tube techniques or using a dry box (Vacuum Atmosphere Dri-Lab) filled with argon. Liquids were transferred via syringe or cannula. All solvents were dried and distilled under argon and degassed before use. THF was distilled from sodium/benzophenone, and CH_2Cl_2 from calcium dihydride. $[\text{Cp}_2\text{ZrCl}_2]$ and $[\text{Cp}_2\text{TiCl}_2]$ were purchased from Aldrich Chemical Co. and used without further purification. $(\text{Cp}_2\text{ZrHCl})_n$, $(\text{Cp}_2\text{ZrH}_2)_n$ [10], $[\text{Cp}_2\text{Zr}(\text{CH}_3)_2]$ [11], $\text{HO}(\text{C}_6\text{H}_4)\text{PPh}_2$ [6], and $\text{HO}(\text{C}_6\text{H}_3)(\text{CH}_3)\text{CH}_2\text{PPh}_2$ [7] were prepared and isolated as described elsewhere. ^1H , ^{13}C and ^{31}P NMR spectra were recorded on Bruker WH 90 or WM 250 spectrometers. ESR spectra were recorded on a Bruker ER 200 T spectrometer. Elemental analyses were performed by the Service Central de Microanalyse du CNRS.

2.1. ^1H and ^{13}C NMR data of the 2(diphenylphosphino)phenol and 2-(diphenylphosphinomethyl)-4-methylphenol

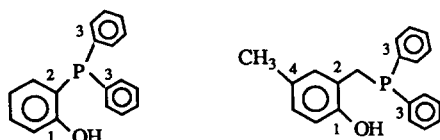
The numbering scheme for assigning ^{13}C aryl NMR resonances (only the quaternary carbon resonances are reported) is as shown.

2.1.1. $(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_4)\text{OH}$

^1H NMR (CDCl_3) δ (ppm) 6.7 (s, broad, 1H, OH); 6.9–7.6 m (m, 14H, aryl). ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3) δ (ppm) 134.5 (d, $^1J_{\text{CP}} = 3.8$ Hz, C3); 134.9 (d, $^1J_{\text{CP}} = 4.7$ Hz, C2); 159.15 (d, $^2J_{\text{CP}} = 17.6$ Hz, C1). ^{31}P $\{^1\text{H}\}$ NMR (CDCl_3) δ (ppm) –27.1.

2.1.2. $(\text{C}_6\text{H}_5)_2\text{PCH}_2(\text{C}_6\text{H}_3)(\text{CH}_3)\text{OH}$

^1H NMR (CDCl_3) δ (ppm) 1.98 (s, 3H, CH_3); 3.36 (s, 2H, CH_2); 4.9–5.7 (s, broad, 1H, OH); 6.5–7.4 (m, 13H, aryl). ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3) δ (ppm) 20.5 (s, CH_3); 30.7 (d, $^1J_{\text{CP}} = 14.5$ Hz, CH_2); 123.8 (d, $^2J_{\text{CP}} = 8.05$ Hz, C2); 129.6 (d, $^4J_{\text{CP}} = 0.5$ Hz, C4); 138.9 (d,



Scheme 1.

$^1J_{\text{CP}} = 14.5$ Hz, C3); 152.4 (d, $^3J_{\text{CP}} = 3.6$ Hz, C1). ^{31}P $\{^1\text{H}\}$ NMR (CDCl_3) δ (ppm) –16.3.

2.2. Preparation of compound $[\text{Cp}_2\text{ZrCl}\{\text{O}(\text{C}_6\text{H}_4)\text{PPh}_2\}]$, 1

A solution of 0.48 g (1.7 mmol) of $\text{HO}(\text{C}_6\text{H}_4)\text{PPh}_2$ in 10 ml of CH_2Cl_2 was added dropwise to a solution of 0.50 g (1.71 mmol) of $[\text{Cp}_2\text{ZrCl}_2]$ in 20 ml of CH_2Cl_2 mixed with a solution of 0.12 g (1.76 mmol) of imidazole in 20 ml of CH_2Cl_2 . The resulting mixture was stirred for 2 h at room temperature, and the course of the reaction was monitored by ^{31}P NMR spectroscopy. The hydrochloride salt was separated by filtration and the solvent removed in vacuo to give 1 as a white solid. Yield 0.82 g (90%). Crystalline 1 may be obtained from CH_2Cl_2 at 0°C . Anal. Calc. for $\text{C}_{28}\text{H}_{24}\text{ClOPZr}$: C, 62.98; H, 4.48. Found C, 63.3; H, 4.82%. ^1H NMR (CDCl_3) δ (ppm) 6.2 (s, 10 H, Cp); 6.6–7.4 (m, 14H, aryl). ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3) δ (ppm) 114.9 (s, Cp); 124.3 (d, $^1J_{\text{CP}} = 7.3$ Hz, C3); 136.8 (d, $^1J_{\text{CP}} = 10.4$ Hz, C2); 167.6 (d, $^2J_{\text{CP}} = 17.9$ Hz, Cl). ^{31}P $\{^1\text{H}\}$ NMR (CDCl_3) δ (ppm) –16.7.

2.3. Chemical reduction of 1 with Na/Hg

1 (100 mg, 0.135 mmol) in 0.5 ml of THF was treated with 1.1 equivalent of Na/Hg amalgam. The dark brown solution was stirred for 12 h, and monitored by the ESR technique.

2.4. Preparation of $[\text{Cp}_2\text{Ti}\{\text{O}(\text{C}_6\text{H}_4)\text{PPh}_2\}_2]$, 2

The procedure described above was used to synthesize compound 2 starting from $[\text{Cp}_2\text{TiCl}_2]$ (0.45 g; 1.82 mmol), $\text{HO}(\text{C}_6\text{H}_4)\text{PPh}_2$ (1.0 g; 3.64 mmol) and imidazole (0.25 g; 3.6 mmol). White crystalline 2 was obtained from a mixture of CH_2Cl_2 and cyclohexane (1/1). Yield 0.8 g (60%). Anal. Calc. for $\text{C}_{46}\text{H}_{38}\text{O}_2\text{P}_2\text{Ti}$: C, 75.4; H, 5.2. Found: C, 74.8; H, 5.7%. ^1H NMR (CDCl_3) δ (ppm) 5.8 (s, 10H, Cp); 6.5–7.6 (m, 28H, aryl). ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3) δ (ppm) 116.3 (s, Cp); 124.3 (d, $^1J_{\text{CP}} = 5.0$ Hz, C3); 137.5 (d, $^1J_{\text{CP}} = 11$ Hz, C2); 171.8 (d, $^2J_{\text{CP}} = 17.9$ Hz, Cl). ^{31}P $\{^1\text{H}\}$ NMR (CDCl_3) δ (ppm) –16.

2.5. Preparation of $[\text{Cp}_2\text{Zr}\{\text{O}(\text{C}_6\text{H}_4)\text{PPh}_2\}_2] \cdot \text{CH}_2\text{Cl}_2$, 3

The procedure described above was used to synthesize compound 3 starting from $[\text{Cp}_2\text{ZrCl}_2]$ (0.47 g, 1.62 mmol), imidazole (0.22 g, 3.24 mmol) and $\text{HO}(\text{C}_6\text{H}_4)\text{PPh}_2$ (0.90 g, 3.24 mmol). After work up, slow diffusion of hexane into the CH_2Cl_2 solution gave crystals suitable for an X-ray structure determination. Yield 0.65 g (48%). Anal. Calc. for $\text{C}_{47}\text{H}_{40}\text{Cl}_2\text{O}_2\text{P}_2\text{Zr}$:

C, 65.59; H, 4.64. Found C, 66.5; H, 4.61%. ^1H NMR (CDCl_3) δ (ppm) 6.2 (s, 10 H, Cp); 6.6–7.4 (m, 28H, aryl.). ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3) δ (ppm) 113.6 (s, Cp); 124.8 (d, $^1J_{\text{CP}} = 6.7$ Hz, C3); 137.4 (d, $^1J_{\text{CP}} = 11.4$ Hz, C2); 167.8 (d, $^2J_{\text{CP}} = 17.9$ Hz, C1). ^{31}P $\{^1\text{H}\}$ NMR (CDCl_3) δ (ppm) –16.9.

2.6. Preparation of $[\text{Cp}_2\text{Zr}(\text{CH}_3)\{O(\text{C}_6\text{H}_3)(\text{CH}_3)-\text{CH}_2\text{PPh}_2\}]$, 4

To a stirred solution of $[\text{Cp}_2\text{Zr}(\text{CH}_3)_2]$ (0, 40 g 1.59 mmol) in 10 ml CH_2Cl_2 at 0°C was added dropwise a solution of $\text{HO}(\text{C}_6\text{H}_3)(\text{CH}_3)\text{CH}_2\text{PPh}_2$ (0.48 g, 1.59 mmol) in 10 ml of CH_2Cl_2 . The mixture was warmed to room temperature and stirred for 15 h. The solution was evaporated to dryness and the product crystallized from CH_2Cl_2 /hexane at low temperature. Yield 0.29 g (34%). Anal. Calc. for $\text{C}_{31}\text{H}_{31}\text{OPZr}$: C, 68.73; H, 5.77. Found: C, 68.90; H, 5.79%. ^1H NMR (CD_2Cl_2) δ (ppm) 0.3 (s, 3H, CH_3Zr); 2.1 (s, 3H, CH_3); 3.2 (s, 2H, CH_2); 6.1 (s, 10 H, Cp); 7.5–6.3 (m, 13H, aryl). ^{13}C $\{^1\text{H}\}$ NMR (CD_2Cl_2) δ (ppm) 20.5 (s, CH_3Zr); 22.6 (s, CH_3); 29.6 (d, $^1J_{\text{CP}} = 14.8$ Hz, CH_2P); 111.6 (s, Cp); 124.70 (d, $^2J_{\text{CP}} = 5.5$ Hz, C2); 139.8 (d, $^1J_{\text{CP}} = 13.6$ Hz, C3); 161.0 (d, $^3J_{\text{CP}} = 4.3$ Hz, C1). ^{31}P $\{^1\text{H}\}$ NMR (CDCl_3) δ (ppm) –13.4.

2.7. Preparation of $[\text{Cp}_2\text{Zr}\{O(\text{C}_6\text{H}_3)(\text{CH}_3)\text{CH}_2\text{PPh}_2\}_2]$, 5

The procedure described above was used to synthesize compound 5 starting from $[\text{Cp}_2\text{Zr}(\text{CH}_3)_2]$ (0.19 g, 0.75 mmol) and $\text{HO}(\text{C}_6\text{H}_3)(\text{CH}_3)\text{CH}_2\text{PPh}_2$ (0.46 g, 1.51 mmol). Yield 0.25 g (40%). Anal. calc. for $\text{C}_{50}\text{H}_{46}\text{O}_2\text{P}_2\text{Zr}$: C, 72.22; H, 5.57. Found, C, 71.75; H, 5.7%. ^1H NMR (CD_2Cl_2) δ (ppm) 2.1 (s, 3H, CH_3); 3.3 (s, 2H, CH_2); 6.4 (s, 10H, Cp); 7.5–6.5 (m, 13H, aryl). ^{13}C $\{^1\text{H}\}$ NMR (CD_2Cl_2) δ (ppm) 20.6 (s, CH_3); 30.2 (d, $^1J_{\text{CP}} = 15$ Hz, CH_2P); 113.8 (s, Cp); 125.15 (d, $^2J_{\text{CP}} = 7.2$ Hz, C2); 139.7 (d, $^1J_{\text{CP}} = 16.6$ Hz, C3); 161.6 (d, $^3J_{\text{CP}} = 4.5$ Hz, C1). ^{31}P $\{^1\text{H}\}$ NMR (CDCl_3) δ (ppm) –15.1.

2.8. Reaction of 3 with $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]$

Complex 3 (0.223 g, 0.287 mmol) in THF (5 ml) was added slowly to a THF solution of $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]$ (0.056 g, 0, 143 mmol), at room temperature. The resulting solution was evacuated from time to time during the addition to remove CO evolved. After addition, the solution was stirred for 2 h and a yellow precipitate was filtered off, washed with 5 ml THF and dried in vacuo. Anal. Calc. for $\text{C}_{47}\text{H}_{38}\text{ClO}_3\text{P}_2\text{RhZr}$: C, 59.87; H, 4.04. Found, C, 59.60; H, 4.60%. ^1H NMR (CD_2Cl_2) δ (ppm) 6.31 (s, 10H, Cp); 7.5–6.3 (m, 14 H,

Table 1

Crystallographic data and details of data collection and structure solution and refinement for compounds 1 and 3

Formula	$\text{ZrClPOC}_{28}\text{H}_{24}$	$\text{ZrP}_2\text{O}_2\text{C}_{46}\text{H}_{38}$, CH_2Cl_2
<i>f</i> w	534.1	960.9
System	monoclinic	triclinic
Space group	$P 2_1/a$	$P\bar{1}$
<i>a</i> , Å	13.270(9)	8.893(8)
<i>b</i> , Å	14.061(4)	11.055(8)
<i>c</i> , Å	14.024(8)	21.165(5)
α		83.5(1)
β	108.4(1)	86.5(1)
γ		88.4(1)
<i>V</i> , Å ³	2483	2063
<i>Z</i>	4	2
<i>d</i> _{calc} , g cm ^{−3}	1.429	1.386
$\mu(\text{Mo-K}\alpha)$, cm ^{−1}	6.24	5.05
<i>F</i> (000)(e)	1088	884
θ range, deg	$1 < \theta < 25$	$1 < \theta < 30$
<i>T</i> (K)	295	295
<i>h</i> range	−15–15	−12–12
<i>k</i> range	0–16	−15–15
<i>l</i> range	0–16	0–29
Scan type	$\omega/2\theta$	$\omega/2\theta$
Scan width, deg	$0.55 + 0.35 \tan \theta$	$0.7 + 0.35 \tan \theta$
Scan speed, deg min ^{−1}	variable	variable
Diffractometer	Enraf Nonius CAD 4	Enraf Nonius CAD 4
No. of unique reflections	8943	8875
No. of reflections with $I > 2\sigma(I)$	1648	3828
No. of refined parameters	290	488
<i>R</i> ^a	0.0391	0.0479
<i>R</i> _w ^b	0.0457	0.0544

$$^a R = \sum \|F_o| - k|F_c|\| / \sum |F_o|$$

$$^b R_w = [\sum_w (|F_o| - |F_c|)^2 / \sum_w F_o^2]^{1/2}$$

aryl). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3) δ (ppm) 191.9 ppm (dt, CO, $^1J_{\text{RhC}} = 70.4$ Hz; $^2J_{\text{CPA}} = ^2J_{\text{CPB}} = 15$ Hz); 174.2 (dd, C₂, C₃, $^1J_{\text{CP}} = 7.0$ Hz, $^2J_{\text{RhC}} = 30.2$ Hz); 161.6 (d, C₁, $^1J_{\text{CP}} = 9.7$ Hz); 114.4 (s, Cp). ^{31}P $\{^1\text{H}\}$ NMR (CDCl_3) δ (ppm) 46.95 ($^1J_{\text{RhP}} = 131.1$ Hz, $^2J_{\text{PP}} = 304.3$ Hz); 25.45 ($^1J_{\text{RhP}} = 136.0$ Hz, $^2J_{\text{PP}} = 304.3$ Hz); 4.62 ($^1J_{\text{RhP}} = 134.1$ Hz, $^2J_{\text{PP}} = 312.7$ Hz); the second minor set is overlapped by the peaks observed at high field at δ 25.45.

2.9. X-ray crystal structure determination of $[\text{Cp}_2\text{ZrCl}\{O(\text{C}_6\text{H}_4)\text{PPh}_2\}]$ (1) and $[\text{Cp}_2\text{Zr}\{O(\text{C}_6\text{H}_4)\text{PPh}_2\}_2]$ (3). Collection and reduction of X-ray data

Data were collected on an Enraf Nonius CAD 4 four-circle diffractometer with graphite monochromated Mo K α radiation at room temperature. Unit cell parameters and basic information about data collection and structure refinement are given in Table 1. Accurate lattice parameters and orientation matrix were obtained from least-squares refinement of the setting angles of 25 well-centred reflections found by

an automated search routine. During data collection, no deorientation or decay was detected. The intensity data were corrected for Lorentz and polarization effects. The structure was solved using Patterson methods of SHELX 86 [12]. Final positional and equivalent or isotropic temperature factors are listed in Tables 2 and 3. A complete list of bond lengths and angles, and tables of anisotropic temperature factors and hydrogen atom coordinates, have been deposited at the Cambridge Crystallographic Data Centre.

3. Results and discussion

All complexes can be obtained in relatively good yields, and in crystalline form from CH_2Cl_2 . We were unable to prepare the chlorotitanium complex $[\text{Cp}_2\text{TiCl}\{\text{O}(\text{C}_6\text{H}_4)\text{PPh}_2\}]$ by this method and only a mixture of $[\text{Cp}_2\text{TiCl}_2]$ and **2** was obtained. Complex **3** crystallizes with one molecule of solvent whereas **1** is always contaminated with some CH_2Cl_2 . A long drying period is required to eliminate the solvent. Others routes can be envisaged that may lead to the desired Zr compounds: $(\text{Cp}_2\text{ZrHCl})_n$ or $(\text{Cp}_2\text{ZrH}_2)_n$ in the presence of 2-(diphenylphosphino)phenol also lead to **1** and **3**. Reaction of 2-(diphenylphosphinomethyl)-4-methyl phenol, $\text{HO}(\text{C}_6\text{H}_3)(\text{CH}_3)\text{CH}_2\text{PPh}_2$, with $[\text{Cp}_2\text{MCl}_2]$ under the same experimental conditions of solvent (CH_2Cl_2) and with imidazole as HCl trap does not give the expected complexes cleanly, and other unidentified species are observed by ^1H NMR spectroscopy. Another route from $[\text{Cp}_2\text{Zr}(\text{CH}_3)_2]$ and $\text{HO}(\text{C}_6\text{H}_3)(\text{CH}_3)\text{CH}_2\text{PPh}_2$ via methane evolution successfully gave the corresponding zirconium complexes $[\text{Cp}_2\text{Zr}(\text{CH}_3)\{\text{O}(\text{C}_6\text{H}_3)(\text{CH}_3)\text{CH}_2\text{PPh}_2\}]$ **4** and $[\text{Cp}_2\text{Zr}\{\text{O}(\text{C}_6\text{H}_3)(\text{CH}_3)\text{CH}_2\text{PPh}_2\}_2]$ **5**.

Complexes **1–5** were characterized by elemental analysis, ^1H , ^{13}C and ^{31}P NMR spectroscopy, and by two X-ray crystallographic studies of **1** and **3**. The ^1H and ^{13}C $\{^1\text{H}\}$ NMR spectra show the expected resonances for the Cp ligands, which are magnetically equivalent. The ^{13}C $\{^1\text{H}\}$ NMR resonances of the quaternary carbon attached to the oxygen atom exhibits the expected resonance at a lower value than in the poreligand. The ^{31}P $\{^1\text{H}\}$ NMR spectra display a single peak for all compounds ($\delta^{31}\text{P} = -16$ ppm), in the range of the unreacted (diphenylphosphino)phenol and 2-diphenylphosphino-4-methylphenol (-27.1 ppm and

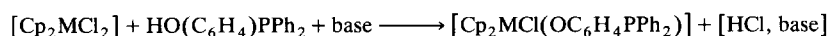
Table 2

Fractional atomic coordinates for $[\text{Cp}_2\text{ZrCl}(\text{OC}_6\text{H}_4\text{PPh}_2)]$

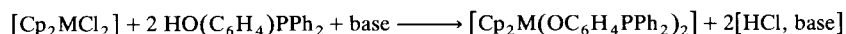
Atom	x	y	z	U_{iso}
Zr(1)	0.08999(7)	0.22875(7)	0.43950(7)	0.0267
Cl(1)	0.0113(2)	0.1760(2)	0.5680(2)	0.0478
P(1)	-0.0153(2)	0.2476(2)	0.1170(2)	0.0384
O(1)	-0.0371(5)	0.2149(4)	0.3181(4)	0.0342
C(1)	-0.0955(8)	0.1509(7)	0.2511(7)	0.0334
C(2)	-0.1012(7)	0.1603(7)	0.1500(7)	0.0304
C(3)	-0.1656(9)	0.0948(8)	0.0818(7)	0.0422
C(4)	-0.2208(9)	0.0252(8)	0.1121(9)	0.0475
C(5)	-0.2116(9)	0.0167(7)	0.2117(9)	0.0468
C(6)	-0.1496(8)	0.0799(7)	0.2814(7)	0.0337
C(7)	-0.0734(9)	0.3625(7)	0.1288(7)	0.0294
C(8)	-0.1697(9)	0.3758(8)	0.1479(8)	0.0435
C(9)	-0.203(1)	0.466(1)	0.1630(9)	0.0629
C(10)	-0.142(1)	0.5433(8)	0.158(1)	0.0603
C(11)	-0.050(1)	0.533(1)	0.137(1)	0.0682
C(12)	-0.017(1)	0.4427(8)	0.1232(9)	0.0515
C(13)	-0.0535(8)	0.2335(9)	-0.0199(6)	0.0400
C(14)	-0.1460(8)	0.2688(8)	-0.0868(7)	0.0462
C(15)	-0.1689(9)	0.2539(8)	-0.1891(8)	0.0591
C(16)	-0.098(1)	0.207(1)	-0.2244(9)	0.0692
C(17)	-0.009(1)	0.172(1)	-0.160(1)	0.0857
C(18)	0.0177(9)	0.185(1)	-0.0561(9)	0.0647
C(19)	0.2062(9)	0.3721(8)	0.477(1)	0.0403
C(20)	0.158(1)	0.3712(8)	0.5511(8)	0.0450
C(21)	0.049(1)	0.3891(8)	0.501(1)	0.0541
C(22)	0.0349(9)	0.3997(8)	0.399(1)	0.0494
C(23)	0.129(1)	0.3869(8)	0.3838(8)	0.0468
C(24)	0.240(1)	0.1659(9)	0.388(1)	0.0528
C(25)	0.155(1)	0.104(1)	0.3465(9)	0.0519
C(26)	0.136(1)	0.0586(8)	0.424(1)	0.0540
C(27)	0.207(1)	0.089(1)	0.514(1)	0.0610
C(28)	0.269(1)	0.1549(9)	0.490(1)	0.0574

-16.3 ppm respectively), ruling out any direct Zr–P interaction in solution [13].

The chemical reduction of **1** with sodium amalgam Na/Hg in THF for 12 h gives, an intense Zr^{III} ESR signal although the reduction requires a long time by comparison with other Zr^{III} species generated by chemical reduction [14]. The remarkably stable ESR signal consists of a doublet centred at $g = 1.976$ consistent with splitting by one Zr^{III} nucleus and one P nucleus ($a(^{31}\text{P}) = 14.6$ G, $I = 1/2$, 100%; $a(^{91}\text{Zr}) = 11$ G, $I = 5/2$, 11.23%) as a monophosphidozirconium(III) species [3a,14b,15]. Although the ESR data are not sufficient to confirm a direct Zr^{III} –P interaction, we postulate a structure as a *P*-cyclometallated $[\text{Cp}_2\text{ZrO}(\text{C}_6\text{H}_4)\text{PPh}_2]$ species [3a,14b].



1: M = Zr



2: M = Ti

3: M = Zr

Scheme 2.

Table 3
Fractional atomic coordinates for $[\text{Cp}_2\text{Zr}(\text{OC}_6\text{H}_4\text{PPh}_2)_2]$

Atom	x	y	z	U_{iso}
Zr(1)	0.29811(8)	0.36935(7)	0.22650(4)	0.0366
P(1)	0.3661(2)	0.2867(2)	0.02909(9)	0.0385
P(2)	0.3594(2)	0.0119(2)	0.34052(9)	0.0442
O(1)	0.3348(5)	0.2395(4)	0.1681(2)	0.0415
O(2)	0.2659(6)	0.2643(4)	0.3081(2)	0.0489
Cl(1)	−0.1289(3)	0.7554(3)	0.3325(1)	0.0944
Cl(2)	−0.1935(4)	0.5149(3)	0.3939(1)	0.1031
C(1)	0.0244(9)	0.3625(9)	0.1956(5)	0.0599
C(2)	0.0189(9)	0.4177(9)	0.2519(4)	0.0611
C(3)	0.094(1)	0.5275(8)	0.2397(5)	0.0629
C(4)	0.141(1)	0.5412(9)	0.1747(5)	0.0687
C(5)	0.098(1)	0.439(1)	0.1493(4)	0.0599
C(6)	0.566(1)	0.3737(9)	0.2623(7)	0.0702
C(7)	0.576(1)	0.398(1)	0.1973(6)	0.0647
C(8)	0.505(1)	0.508(1)	0.1815(6)	0.0751
C(9)	0.454(1)	0.552(1)	0.236(1)	0.0826
C(10)	0.487(1)	0.470(1)	0.2856(5)	0.0720
C(11)	0.2694(7)	0.1516(6)	0.1409(3)	0.0352
C(12)	0.2831(7)	0.1526(6)	0.0744(3)	0.0347
C(13)	0.2189(8)	0.0574(6)	0.0475(3)	0.0420
C(14)	0.1440(8)	−0.0357(7)	0.0846(4)	0.0478
C(15)	0.1320(9)	−0.0341(7)	0.1506(4)	0.0491
C(16)	0.1926(9)	0.0599(7)	0.1785(4)	0.0472
C(17)	0.3535(8)	0.2497(6)	−0.0522(3)	0.0386
C(18)	0.4598(8)	0.1799(7)	−0.0835(4)	0.0455
C(19)	0.444(1)	0.1548(7)	−0.1447(4)	0.0521
C(20)	0.316(1)	0.1966(8)	−0.1757(4)	0.0592
C(21)	0.210(1)	0.2654(9)	−0.1458(4)	0.0620
C(22)	0.2302(8)	0.2942(7)	−0.0851(4)	0.0510
C(23)	0.5682(7)	0.2649(6)	0.0401(3)	0.0386
C(24)	0.6309(8)	0.1629(7)	0.0732(4)	0.0492
C(25)	0.787(1)	0.1521(8)	0.0809(4)	0.0549
C(26)	0.8787(9)	0.2441(9)	0.0556(5)	0.0615
C(27)	0.818(1)	0.3455(9)	0.0232(5)	0.0630
C(28)	0.6637(9)	0.3575(7)	0.0151(4)	0.0511
C(29)	0.2289(8)	0.2306(7)	0.3692(3)	0.0418
C(30)	0.2639(8)	0.1095(6)	0.3949(3)	0.0409
C(31)	0.218(1)	0.0744(8)	0.04581(4)	0.0590
C(32)	0.140(1)	0.153(1)	0.4950(4)	0.0671
C(33)	0.114(1)	0.2711(9)	0.4702(4)	0.0653
C(34)	0.1568(9)	0.3096(7)	0.4084(4)	0.0538
C(35)	0.5570(8)	0.0604(6)	0.3386(4)	0.0463
C(36)	0.645(1)	0.0474(8)	0.2831(5)	0.0663
C(37)	0.794(1)	0.076(1)	0.2789(6)	0.0828
C(38)	0.858(1)	0.117(1)	0.3271(8)	0.0782
C(39)	0.773(1)	0.1372(9)	0.3823(5)	0.0742
C(40)	0.619(1)	0.1086(8)	0.3871(4)	0.0616
C(41)	0.3675(9)	−0.1357(7)	0.3891(4)	0.0474
C(42)	0.478(1)	−0.1739(8)	0.4309(4)	0.0623
C(43)	0.475(1)	−0.2887(9)	0.4641(5)	0.0775
C(44)	0.360(1)	−0.3668(8)	0.4565(6)	0.0722
C(45)	0.250(1)	−0.330(1)	0.4161(6)	0.0892
C(46)	0.255(1)	−0.2157(8)	0.3821(5)	0.0717
C(47)	−0.244(1)	0.631(1)	0.3381(5)	0.0816

Preliminary results show that **3** can form bimetallic complexes $[\text{Zr}, \text{Rh}]$ via a bridging P atom. Upon adding the dinuclear rhodium complex $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]$ to **3** in THF, under a partial vacuum to aid CO evolution, the heterometallic $\{\text{Cp}_2\text{Zr}(\text{OC}_6\text{H}_4\text{PPh}_2)_2(\text{Rh}(\text{CO})\text{Cl})\}_n$, **6**

Table 4
Selected bonds lengths (Å) and angles (°) of compound **1** with estimated standard deviations in parentheses

Zr–Cp(A) ^a	2.209(4)	Zr–Cp(B) ^a	2.216(9)
Zr–Cl	2.465(3)	Zr–O	1.993(6)
C(1)–O	1.35(1)	C(2)–P	1.83(1)
C(7)–P	1.82(1)	C(13)–P	1.836(9)
Cp(A)–Zr–Cp(B) ^a	130.5(3)	O–Zr–Cp(A) ^a	105.8(8)
O(1)–Zr–Cp(B) ^a	105.7(1)	Cl–Zr–Cp(A) ^a	107.3(9)
Cl–Zr–Cp(B) ^a	106.0(1)	O–Zr–Cl	99.0(2)
Zr–O(1)–C(1)	144.3(3)	C(2)–P(1)–C(7)	104.9(5)
C(2)–P(1)–C(13)	101.0(3)	C(7)–P(1)–C(13)	101.9(5)

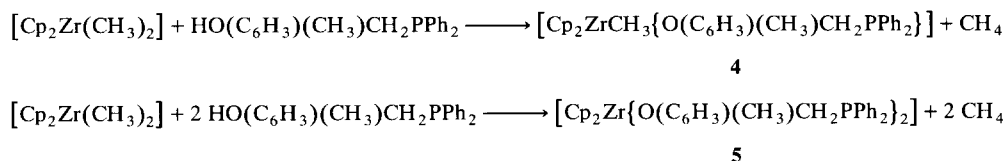
^a Cp(A) and Cp(B) are the centres of the cyclopentadienyl [C(13)–C(23)] and [C(24)–C(28)] rings, respectively.

($n = 1$ or 2) is obtained, but its insolubility in C_6H_6 prevents cryoscopic measurements. The ^1H NMR spectrum shows the expected peak of the Cp signal at lower field than for **3**. A characteristic doublet of triplets is observed in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at 191.9 ppm attributed to the CO resonance ($^1J_{\text{RhC}} = 70.4$ Hz; $^2J_{\text{CpA}} = ^2J_{\text{CpB}} = 15$ Hz). The IR spectrum shows a characteristic CO frequency at 1960 cm^{-1} in CH_2Cl_2 solution. The room temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a principal ABX pattern (δP_A , 46.95; δP_B , 25.45 ppm) with $^2J_{\text{PP}} = 304.3$ Hz, a coupling characteristic of *trans* for the phosphorus atoms around rhodium (a minor ABX pattern is observed also at lower field δP_A , 46.2 ppm, $^2J_{\text{PP}} = 312.7$ Hz; the other part of this ABX system overlaps the peaks observed at δ 25.45). Although diphosphine rhodium complexes are well documented, there are very few cases where the rhodium metal is *trans* chelated by a diphosphine, though precedents were already observed in $[\text{Cp}_2\text{Zr}(\text{CH}_2\text{PPh}_2)_2\text{RhH}(\text{PPh}_3)]$ [4e], $[\text{Cp}_2\text{Zr}(\text{CH}_2\text{PPh}_2)_2\text{Rh}(\text{CO})\text{Cl}]$ [16] and $[\text{Cp}_2\text{ZrCl}(\text{CH}_2\text{PPh}_2)_2\text{Rh}(\text{CO})\text{Cl}]$ [17]. We cannot, however, yet distinguish between a monomeric and a dimeric form. Further studies will be undertaken to prepare other bimetallic systems $[\text{Zr}, \text{Rh}]$.

Table 5
Selected bond lengths (Å) and angles (°) of compound **3** with estimated standard deviations in parentheses

Zr–Cp(A) ^a	2.246(8)	Zr–Cp(B) ^a	2.37(5)
Zr–O(1)	2.004(1)	Zr–O(2)	1.979(7)
C(11)–O(1)	1.348(8)	C(29)–O(2)	1.327(8)
C(12)–P(1)	1.821(7)	C(30)–P(2)	1.821(7)
Cp(A)–Zr–Cp(B) ^a	127.7(5)	O(1)–Zr–Cp(A) ^a	105.8(8)
O(1)–Zr–Cp(B) ^a	107.3(9)	O(2)–Zr–Cp(A) ^a	107.5(7)
O(2)–Zr–Cp(B) ^a	105.6(1)	O(1)–Zr–O(2)	99.0(2)
Zr–O(1)–C(11)	144.3(3)	Zr–O(2)–C(2)	160.2(5)
C(12)–P(1)–C(17)	101.0(3)	C(12)–P(1)–C(23)	103.6(3)
C(17)–P(1)–C(23)	101.8(3)	C(30)–P(2)–C(35)	102.4(6)
C(30)–P(2)–C(41)	102.7(3)	C(35)–P(2)–C(41)	101.7(3)

^a Cp(A), Cp(B) are the centres of the cyclopentadienyl [C(1)–C(5)] and [C(6)–C(10)] rings, respectively.

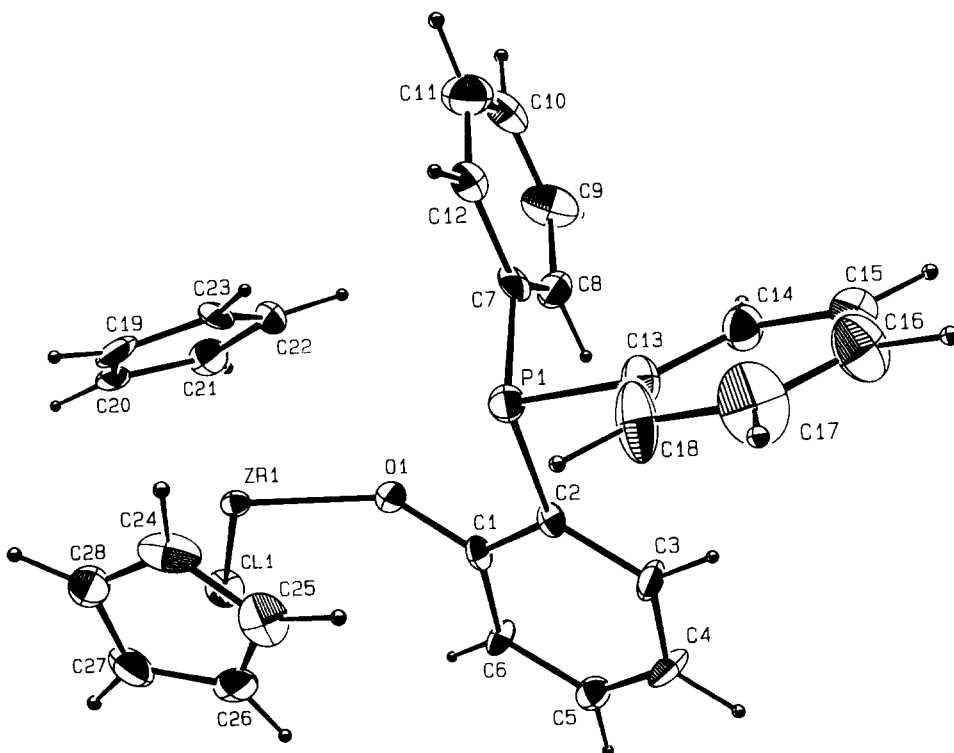


Scheme 3.

4. Structure descriptions

The complexes **1** and **3** were crystallized from dichloromethane solution as colourless crystals, and the structures were determined by X-ray diffraction. Compound **3** crystallizes as the solvate $[\text{Cp}_2\text{Zr}(\text{OC}_6\text{H}_4\text{PPh}_2)_2] \cdot \text{CH}_2\text{Cl}_2$. ORTEP representations of complexes **1** and **3** are given in Figs. 1 and 2 respectively. Selected bond distances and angles for **1** and **3** are given in Tables 4 and 5, respectively. The coordination geometry of the Zr is pseudotetrahedral for both molecules, and there are some structural analogies. The Cp(A)–Zr–Cp(B) angle for **1** ($130.5(3)^\circ$) and **3** ($127.7(5)^\circ$) as well as the Zr–C and/or Zr–Cp and Zr–Cl bond lengths appear to be normal compared with those of the zirconocene complexes [18]. The angles of O(1)–Zr–Cl in **2** and O(1)–Zr–O(2) in **3** are similar ($99.0(2)^\circ$). The molecular fragment [Zr–O(1)–C–C–P(1)], corresponding to the $\text{O}(\text{C}_6\text{H}_4)\text{PPh}_2$ group, shows nearly identical structural characteristics in both molecules; in

particular, Zr–O(1)–C(1) and Zr–O(1)–C(11) angles are practically equivalent in **1** and **3** ($143.4(6)^\circ$ and $144.3(3)^\circ$) respectively). However, in compound **3**, which contains a second $-\text{O}(\text{C}_6\text{H}_4)\text{PPh}_2$ ligand, the Zr–O(2)–C(29) angle ($160.2(5)^\circ$) is larger than those discussed above. The relatively short Zr–O(2) distance ($1.979(7) \text{ \AA}$) associated with the large angle in this fragment is indicative of a π bonding between the Zr and O atoms. Similar early transition metal oxygen π bonding has been implied in several other systems [19] and in particular for $[(\text{MeOCH}_2\text{CH}_2\text{OMe})\text{ZrCl}_2(\text{OSiPh}_3)_2]$ [20] ($d(\text{Zr}-\text{O}) 1.91(1) \text{ \AA}$; Zr–O–Si angle $171(1)^\circ$). No evidence for any direct Zr–P interaction in the solid state was found in the structural data. The intramolecular Zr–P distances (**1**: $4.30 \text{ \AA}$; **3**: $4.379 \text{ \AA}$ and $4.429 \text{ \AA}$ for Zr–P(1) and Zr–P(2) respectively) are significantly longer than in related compounds where such interactions exist [21]. A *trans* orientation of both organic fragments relative to the O(1)ZrO(2) plane appears in **3** with P(1) and P(2) phosphorus atoms

Fig. 1. ORTEP drawing of a molecule of complex **1**. Thermal ellipsoids are drawn at 30% probability.

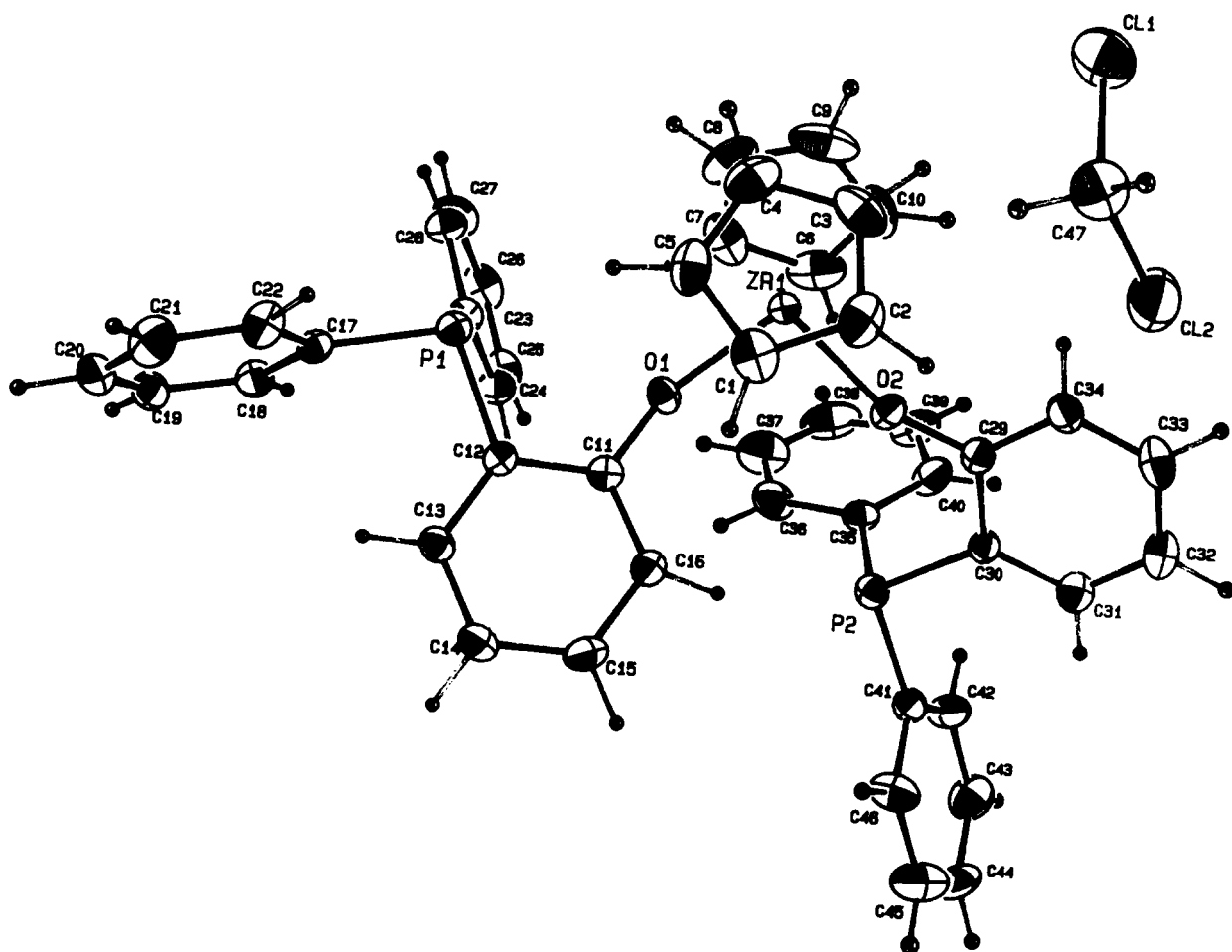


Fig. 2. ORTEP drawing of a molecule of complex 3. Thermal ellipsoids are drawn at 30% probability.

above and below the plane by $-0.344 \text{ \AA}$ and $0.903 \text{ \AA}$, respectively, the three phenyl groups being in a helical arrangement.

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References

- [1] (a) D.A. Roberts and G.L. Geoffroy, in G. Wilkinson, F.G.A. Stone and E.W. Abel (eds.), *Comprehensive Organometallic Chemistry*, Vol. 6, Pergamon, Oxford, 1982, Ch. 40; (b) D.W. Stephan, *Coord. Chem. Rev.*, **95** (1989) 41; (c) R.T. Baker, W.C. Fultz, T.B. Morder and I.D. Williams, *Organometallics*, **9** (1990) 2357 and references therein; (d) R.M. Bullock and C.P. Casey, *Acc. Chem. Res.*, **20** (1987) 167; (e) G.K. Anderson and M. Lin, *Organometallics*, **7** (1988) 2285; (f) G.S. Ferguson and P.T. Wolczanski, *Organometallics*, **4** (1985) 1601.
- [2] (a) L. Gelmini and D.W. Stephan, *Organometallics*, **7** (1988) 849; T.T. Nadashi and D.W. Stephan, *Organometallics*, **11** (1992) 116 and references therein.
- [3] (a) R. Choukroun, F. Dahan, D. Gervais and C. Rifai, *Organometallics*, **9** (1990) 1982 and references therein. (b) A.M. Trzeciak, J.J. Ziolkowski and R. Choukroun, *J. Organomet. Chem.*, **420** (1991) 353. (c) A.M. Larssonneur, R. Choukroun, J.C. Daran, C. Cuenca, J.C. Flores and P. Royo, *J. Organomet. Chem.*, **444** (1993) 83.
- [4] (a) F. Senocq, C. Randrianalimanana, A. Thorez, P. Kalck, R. Choukroun and D. Gervais, *J. Chem. Soc., Chem. Commun.* (1984) 1376; (b) F. Senocq, C. Randrianalimanana, A. Thorez, P. Kalck, R. Choukroun and D. Gervais, *J. Mol. Catal.*, **35** (1986) 213; (c) Choukroun, A. Iraqi and D. Gervais, *J. Organomet. Chem.*, **311** (1986) C60; (d) R. Choukroun, D. Gervais, P. Kalck and F. Senocq, *J. Organomet. Chem.*, **335** (1987) C9; (e) R. Choukroun, A. Iraqi, D. Gervais, J.C. Daran and Y. Jeannin, *Organometallics*, **6** (1987) 1197; (f) R. Choukroun, A. Iraqi, C. Rifai and D. Gervais, *J. Organomet. Chem.*, **353** (1988) 45; (g) R. Choukroun, F. Dahan, D. Gervais and C. Rifai, *Organometallics*, **9** (1990) 1983.
- [5] (a) A. Bader and E. Lindner, *Coordination Chem. Rev.*, **108** (1991) 27–110; (b) G.S. Ferguson and P.T. Wolczanski, *Organometallics*, (1985), 1601.
- [6] H.D. Empsall, *J. Chem. Soc., Dalton Trans.*, (1976) 1500.
- [7] K. Kellner, S. Rothe, E.M. Steyer and A. Tzschach, *Phosphorus and Sulfur*, **8** (1984) 269.

- [8] (a) C.E. Jones, B.L. Shaw and B.L. Turtle, *J. Chem. Soc., Dalton Trans.*, (1974) 992; (b) H.D. Empsall, B.L. Shaw and B.L. Turtle, *J. Chem. Soc., Dalton Trans.*, (1976) 1500.
- [9] M. Canestrari, B. Chaudret, F. Dahan, Y.S. Huang, R. Poilblanc, T.C. Kim and M. Sanchez, *J. Chem. Soc., Dalton Trans.*, (1990) 1179.
- [10] P.C. Wailes and H. Weigold, *J. Organomet. Chem.*, **24** (1970) 405.
- [11] H. Weigold, A.P. Bell and R.I. Willing, *J. Organomet. Chem.*, **73** (1974) C23.
- [12] G.M. Sheldrick, in G.M. Sheldrick, C. Kruger and R. Goddard (eds.), *Crystallographic Computing*, Vol. 3, Oxford University Press, 1985, pp. 175–179.
- [13] (a) N.E. Schore and J. Hope, *J. Am. Chem. Soc.*, **102** (1980) 4251. (b) N.E. Schore, S.J. Young, M.M. Olmstead and P. Hofmann, *Organometallics*, **2** (1983) 1769.
- [14] (a) A.M. Larssonneur, R. Choukroun and J. Jaud, *Organometallics*, **12** (1993) 321. (b) E. Etienne, R. Choukroun and D. Gervais, *J. Chem. Soc., Dalton Trans.*, (1984) 915. (c) R. Choukroun, D. Gervais and C. Rifai, *J. Organomet. Chem.*, **368** (1989) C11.
- [15] J.G. Kenworthy, J. Myatt and P.F. Todd, *J. Chem. Soc., Chem. Commun.*, (1969) 263.
- [16] R. Choukroun and D. Gervais, *J. Organomet. Chem.*, **266** (1984) C37.
- [17] R. Choukroun and D. Gervais, *J. Chem. Soc., Chem. Commun.*, (1982) 1301.
- [18] D.J. Cardin, M.F. Lappert and C.L. Raston, *Chemistry of Organozirconium and Hafnium compounds*, Section A, Ellis Horwood Limited, 1986, p. 70.
- [19] W.R. Tikkanen and J.L. Petersen, *Organometallics*, **3** (1984) 1651.
- [20] E.A. Babaian, D.C. Hrnecir, S.G. Bott and J.L. Atwood, *Inorg. Chem.*, **25** (1986) 4818, and references therein.
- [21] N. Dufour, J.P. Majoral, A.M. Caminade, R. Choukroun and Y. Dromzée, *Organometallics*, **10** (1991) 45.