



ELSEVIER

Journal of Organometallic Chemistry 515 (1996) 19–25

Journal
of Organometallic
Chemistry

Dinuclear phosphido- and arsenido-bridged early/late transition metal complexes. Efficient catalysts for ethylene polymerization

Frank Lindenberg^a, Tal Shribman^b, Joachim Sieler^a, Evamarie Hey-Hawkins^{a,*},
Moris S. Eisen^{b,*}

^a *Institut für Anorganische Chemie der Universität Leipzig, Talstrasse 35, D-04103 Leipzig, Germany*

^b *Department of Chemistry, Technion-Israel Institute of Technology, Haifa 32000, Israel*

Received 17 July 1995

Abstract

The reaction of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}\{\mu\text{-P}(\text{SiMe}_3)_2\}_2$ with $\text{Ni}(\text{CO})_4$ yields the heterodinuclear phosphido-bridged complex $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}\{\mu\text{-P}(\text{SiMe}_3)_2\}_2\text{Ni}(\text{CO})_2$ (**1**). **1** was characterised spectroscopically and by X-ray structure determination. The central four-membered ZrP_2Ni ring is slightly puckered (dihedral angle between planes $\text{ZrP}_2/\text{NiP}_2 = 1.8^\circ$). The Zr–P bond lengths are equivalent (Zr–P1 2.655(1), Zr–P2 2.652(1) Å), as are the Ni–P bond lengths (Ni–P1 2.264(1), Ni–P2 2.266(1) Å). The long Zr...Ni distance of 3.038(1) Å indicates the absence of a metal–metal bond. The heterodinuclear phosphido- and arsenido-bridged complexes $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}\{\mu\text{-E}(\text{SiMe}_3)_2\}_2\text{M}(\text{CO})_n$ [E = P; $\text{M}(\text{CO})_n = \text{Ni}(\text{CO})_2$ (**1**) or $\text{Mo}(\text{CO})_4$ (**2**); and E = As, $\text{M}(\text{CO})_n = \text{Cr}(\text{CO})_4$ (**3**)] react rapidly with methylaluminoxane, yielding catalytically active complexes which rival the known cationic systems for the polymerization of ethylene.

Keywords: Early/late heterodinuclear phosphido- and arsenido-bridged complexes; Zirconocene; Ethylene polymerization; Crystal structure

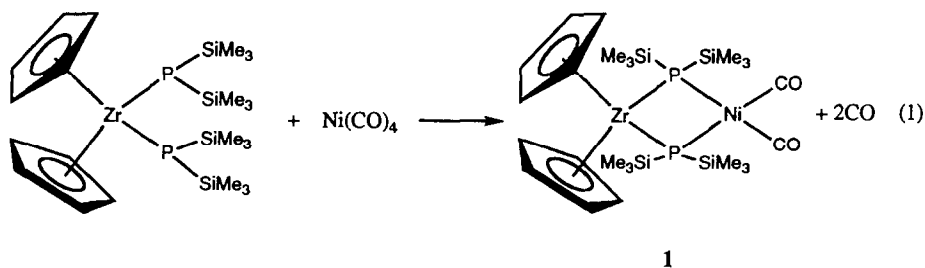
1. Introduction

Many of the recent advances in early/late bridged transition metals can be attributed to the beneficial characteristics of the early transition metal supporting ligation in the catalytic properties of the late transition metal towards reactions with organic substrates [1,2]. This cooperative reactivity stems from the possibility of the early, electron poor transition metal and the late, electron rich transition metal creating an ideal environment for heterolytic bond cleavage of polar substrates. Although many early/late transition metal heterobimetallic complexes have been prepared, few of them have shown a truly cooperative synergetic reactivity with organic substrates [3]. The observed reactivity has been shown to occur at a single metal centre, presumably because the large distance between the metal centres does not allow any synergetic effect. This reactivity

is found normally at the late transition metal centre due to coordinative saturation of the early transition metal centre. Nevertheless, some cases have been published where there was an influence of the early transition metal on the reactivity of the late transition metal centre [4]. Only in a few reactions has participation of both metals in a reaction with an organic substrate been observed [5].

Preparation of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\mu\text{-PRR}')_2\text{Mo}(\text{CO})_4$ (R = R' = Me; R = Ph, R' = H; R = Ph, R' = SiMe₃) was reported as early as 1977 [6] but it was only in 1985 that studies of heterobimetallic phosphido-bridged zirconocene or hafnocene complexes were resumed [1]. Two synthetic routes to the preparation of heterobimetallic complexes have been described: (i) reaction of a metallocene bisphosphido complex with an appropriate transition metal compound and (ii) reaction of zirconocene dichloride with a dilithio(bisphosphido) transition metal complex. We have shown earlier that the PSiMe₃- or AsSiMe₃-functionalised heterodinuclear zirconocene complexes $(\eta^5\text{-C}_5\text{H}_4\text{R})_2\text{Zr}\{\mu\text{-E}(\text{SiMe}_3)_2\}_2\text{M}(\text{CO})_n$ [R = H, E = P; $\text{M}(\text{CO})_n = \text{Mo}(\text{CO})_4$

* Corresponding authors.



(2); R = H, E = As, $M(\text{CO})_n = \text{Cr}(\text{CO})_4$ (3); R = Me, E = P, $M(\text{CO})_n = \text{Cr}(\text{CO})_4$ (4)] can be obtained by the synthetic route (i) [7].

We report here the synthesis of a heterodinuclear zirconocene–nickel complex ($\eta^5\text{-C}_5\text{H}_5$)₂Zr{ $\mu\text{-E}(\text{SiMe}_3)_2$ }₂M(CO)_n [E = P; M(CO)_n = Ni(CO)₂ (1) (Eq. (1))] and the comparative reactivity properties of some early/late bridging phosphido and arsenido complexes ($\eta^5\text{-C}_5\text{H}_5$)₂Zr{ $\mu\text{-E}(\text{SiMe}_3)_2$ }₂M(CO)_n ($n = 2$, E = P, M = Ni (1), $n = 4$, E = P, M = Mo (2) and $n = 4$, E = As, M = Cr (3)) as catalytic precursors for the polymerization of ethylene [8–10].

2. Synthesis, spectroscopic properties and molecular structure of 1

While ($\eta^5\text{-C}_5\text{H}_4\text{Me}$)₂Zr{P(SiMe₃)₂}₂ failed to react with Ni(PEt₃)₄, Ni(CO)₂(PPh₃)₂ or NiCl₂(PPh₃)₂ in the presence of Mg to give Zr/Ni dinuclear complexes [7], ($\eta^5\text{-C}_5\text{H}_5$)₂Zr{P(SiMe₃)₂}₂ reacts rapidly with Ni(CO)₄ (1 : 1) yielding ($\eta^5\text{-C}_5\text{H}_5$)₂Zr{ $\mu\text{-P}(\text{SiMe}_3)_2$ }₂Ni(CO)₂ (1) as yellow–orange platelets in good yield. The dialkyl- or diarylphosphido-bridged complexes ($\eta^5\text{-C}_5\text{H}_5$)₂Zr($\mu\text{-PPh}_2$)₂Ni(CO)₂ [11,12] and ($\eta^5\text{-C}_5\text{H}_5$)₂Hf($\mu\text{-PEt}_2$)₂Ni(CO)₂ [13] are comparable and were also prepared according to the synthetic route (i). Whereas the 2 : 1 reaction of ($\eta^5\text{-C}_5\text{H}_5$)₂Zr(PEt₂)₂ with Ni(COD)₂ (COD = 1,5-cyclooctadiene) gave the trinuclear spiro compound {($\eta^5\text{-C}_5\text{H}_5$)₂Zr($\mu\text{-PEt}_2$)₂}₂Ni, no corresponding product was obtained in the reaction of ($\eta^5\text{-C}_5\text{H}_5$)₂Zr(PCy₂)₂ or ($\eta^5\text{-C}_5\text{H}_5$)₂Zr(PPh₂)₂ with Pt(COD)₂ (2 : 1) [12]. Similarly, the 2 : 1 reaction of ($\eta^5\text{-C}_5\text{H}_5$)₂Zr{P(SiMe₃)₂}₂ with Ni(CO)₄ yields only 1. Obviously, bulky bridging ligands, such as PCy₂, PPh₂ or P(SiMe₃)₂, thwart the formation of a trinuclear complex.

Like other heterobimetallic phosphido-bridged zirconocene complexes which formally have a mirror plane [1b], 1 exhibits only one signal for the cyclopentadienyl protons in the ¹H NMR spectrum (5.43 ppm), which is shifted to high field by 0.6 ppm compared with the starting material ($\eta^5\text{-C}_5\text{H}_5$)₂Zr{P(SiMe₃)₂}₂ (6.03 ppm) [14]. This effect, which was also observed in other phosphido-bridged heterodinuclear complexes [15], can

be attributed to an increase of electron density at the Zr atom, which is consistent with a dative Ni(d¹⁰) ⇒ Zr(d⁰) interaction. However, no interaction is observed in the solid state, with a rather long Zr···Ni distance of 3.038(1) Å. Additional signals for toluene, which is included in the crystals (one molecule per 1), are observed. In the ³¹P NMR spectrum of 1, a singlet is observed at –42.1 ppm, which is shifted to low field compared with the starting material [($\eta^5\text{-C}_5\text{H}_5$)₂Zr{P(SiMe₃)₂}₂ –71.1 ppm [14]]. This trend is also observed in comparable known complexes [1b].

The symmetry of compound 1 is close to C_{2v}. Thus, two absorptions are observed for the carbonyl groups of the M(CO)₂P₂ fragment, at 1980 and 1938 cm^{–1}. These are in the same range as those of ($\eta^5\text{-C}_5\text{H}_5$)₂Zr{ $\mu\text{-PPh}_2$ }₂Ni(CO)₂ (2000, 1941, 1936 cm^{–1}) [11,12], ($\eta^5\text{-C}_5\text{H}_5$)₂Hf{ $\mu\text{-PEt}_2$ }₂Ni(CO)₂ (1984, 1920 cm^{–1}) [13] and ($\eta^5\text{-C}_5\text{Me}_5$)₂Th{ $\mu\text{-PPh}_2$ }₂Ni(CO)₂ (1988, 1944 cm^{–1}) [16]. No molecular ion peak is observed in the mass spectrum of 1. The fragment of highest mass (m/z 634) can be attributed to [M–2CO]⁺. The base peak corresponds to toluene. Additional signals arise from P(SiMe₃)₃ and fragmentation products thereof.

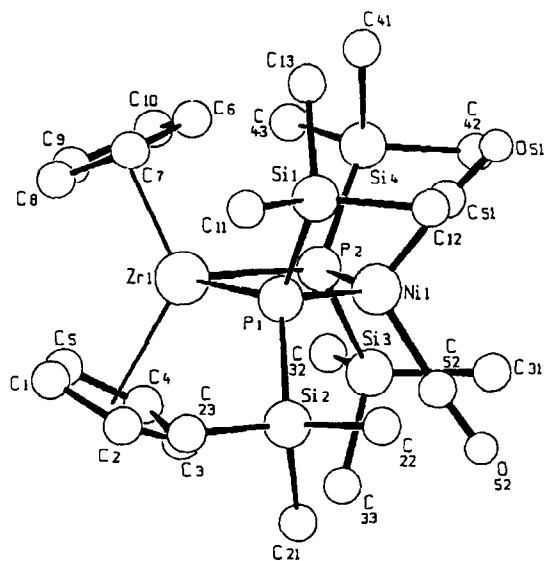


Fig. 1. Molecular structure of ($\eta^5\text{-C}_5\text{H}_5$)₂Zr{ $\mu\text{-P}(\text{SiMe}_3)_2$ }₂Ni(CO)₂ (1) showing the numbering scheme employed. Hydrogen atoms are omitted for clarity.

Table 1

Selected bond lengths (Å) and bond angles (°) of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}\{\mu\text{-P}(\text{SiMe}_3)_2\}_2\text{Ni}(\text{CO})_2 \cdot \text{toluene} (\mathbf{1})$

Zr...Ni	3.038(1)
Zr(1)–P(1)	2.655(1)
Zr(1)–P(2)	2.652(1)
Ni(1)–C(51)	1.784(3)
Ni(1)–C(52)	1.786(3)
Ni(1)–P(1)	2.264(1)
Ni(1)–P(2)	2.266(1)
P(2)–Si(3)	2.267(1)
P(2)–Si(4)	2.267(1)
P(1)–Si(2)	2.260(1)
P(1)–Si(1)	2.272(1)
Si(1)–C(12)	1.867(4)
Si(1)–C(13)	1.871(5)
Si(1)–C(11)	1.878(4)
Si(2)–C(22)	1.867(4)
Si(2)–C(21)	1.870(4)
Si(2)–C(23)	1.877(4)
Si(3)–C(32)	1.869(4)
Si(3)–C(33)	1.871(4)
Si(3)–C(31)	1.878(4)
Si(4)–C(42)	1.860(5)
Si(4)–C(41)	1.874(4)
Si(4)–C(43)	1.899(4)
C(51)–O(51)	1.142(4)
C(52)–O(52)	1.139(4)
C(Cp)–C(Cp) *	1.389(6)–1.418(5)
Zr(1)–C(Cp)	2.496(3)–2.529(3)
P(2)–Zr(1)–P(1)	92.59(3)
C(51)–Ni(1)–C(52)	110.0(2)
C(51)–Ni(1)–P(1)	107.9(1)
C(52)–Ni(1)–P(1)	108.0(1)
C(51)–Ni(1)–P(2)	107.1(1)
C(52)–Ni(1)–P(2)	108.1(1)
P(1)–Ni(1)–P(2)	115.73(3)
O(51)–C(51)–Ni(1)	175.7(3)
O(52)–C(52)–Ni(1)	175.9(3)
Ni(1)–P(2)–Si(3)	109.54(4)
Ni(1)–P(2)–Si(4)	114.20(4)
Si(3)–P(2)–Si(4)	101.72(4)
Ni(1)–P(2)–Zr(1)	75.85(3)
Si(3)–P(2)–Zr(1)	128.01(4)
Si(4)–P(2)–Zr(1)	123.70(4)
Si(2)–P(1)–Ni(1)	114.97(4)
Si(2)–P(1)–Si(1)	101.10(4)
Ni(1)–P(1)–Si(1)	108.88(4)
Si(2)–P(1)–Zr(1)	124.20(4)
Ni(1)–P(1)–Zr(1)	75.81(3)
Si(1)–P(1)–Zr(1)	128.19(4)
C(12)–Si(1)–C(13)	104.3(3)
C(12)–Si(1)–C(11)	107.6(2)
C(13)–Si(1)–C(11)	106.9(3)
C(12)–Si(1)–P(1)	111.6(2)
C(13)–Si(1)–P(1)	114.7(2)
C(11)–Si(1)–P(1)	111.2(2)
C(22)–Si(2)–C(21)	104.9(2)
C(22)–Si(2)–C(23)	107.6(3)
C(21)–Si(2)–C(23)	108.5(3)
C(22)–Si(2)–P(1)	112.7(2)
C(21)–Si(2)–P(1)	114.0(2)
C(23)–Si(2)–P(1)	109.0(2)
C(32)–Si(3)–C(33)	107.9(2)
C(32)–Si(3)–C(31)	108.7(2)

* Cp = $\eta^5\text{-C}_5\text{H}_5$.

An X-ray structural investigation was carried out on orange-red crystals of **1** [17]. The compound crystallises in the triclinic space group $P\bar{1}$ (No. 2) with two molecules in the unit cell. Additionally, one non-bonding disordered molecule of toluene is present per formula unit of **1**. Two $\text{P}(\text{SiMe}_3)_2$ ligands bridge a Zr and an Ni atom, both of which are coordinated in a distorted tetrahedral fashion (C51–Ni1–C52 110.0(2)°) (Fig. 1, Table 1). **1** exhibits large P–Zr–P (P1–Zr1–P2 92.59(3)°) and P–Ni–P (P1–Ni1–P2 115.73(3)°) bond angles and small Zr–P–Ni bond angles (Zr1–P1–Ni1 75.81(3)°, Zr1–P2–Ni1 75.85(3)°). The central ZrP_2Ni four-membered ring is slightly puckered (dihedral angle $\text{ZrP}_2/\text{NiP}_2$ 1.8°), while in comparable dinuclear complexes both puckered (dihedral angle up to 28°) and planar ZrP_2M four-membered rings are observed [1b]. Presumably, the distortion of the four-membered ring is due to packing effects and metal–metal interaction [13,15,18].

The Zr–P bond lengths (Zr1–P1 2.655(1), Zr1–P2 2.652(1) Å) and the Ni–P bond lengths (Ni1–P1 2.265(1), Ni1–P2 2.266(1) Å) are in the same range as those of comparable complexes. In $(\eta^5\text{-C}_5\text{H}_4\text{Me})_2\text{Zr}\{\text{P}(\text{SiMe}_3)_2\}_2$ (Zr–P 2.634(2), 2.600(2) Å; P1–Zr–P2 96.95(7)°) [19], the Zr–P bond lengths are slightly smaller than in **1**; however, the P1–Zr1–P2 bond angle of 92.59(3)° in **1** is much smaller due to the phosphido groups being bridging.

The Zr...Ni distance of 3.038(1) Å in **1** is larger than the sum of the covalent radii [20]: thus, even though the spectroscopic data indicate a metal–metal interaction, this can be excluded. However, extended Hückel molecular orbital calculations performed on the model complexes $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\mu\text{-PH}_2)_2\text{M}'\text{L}_n$ ($\text{M}'\text{L}_n = \text{Pt}(\text{PH}_3)_2$, $\text{Pt}(\text{Me}_2\text{PClI}_2)_2$, $\text{Rh}(\eta\text{-indenyl})$), $\text{Ni}(\mu\text{-PH}_2)_2\text{Zr}(\eta^5\text{-C}_5\text{H}_5)_2$, and $\text{Mo}(\text{CO})_4$ indicate the presence of $\text{M}' \Rightarrow \text{Zr}$ donor–acceptor metal–metal bonds that become weaker in the series $\text{Pt} > \text{Rh} > \text{Ni} > \text{Mo}$ [18d].

3. Catalytic polymerization of ethylene promoted by heterobimetallic complexes (1–3)

Complexes **1–3** are stable compounds with no catalytic reactivity toward olefins in the presence of dihy-

Table 1 (continued)

C(33)–Si(3)–C(31)	103.6(2)
C(32)–Si(3)–P(2)	110.4(2)
C(33)–Si(3)–P(2)	114.5(1)
C(31)–Si(3)–P(2)	111.4(2)
C(42)–Si(4)–C(41)	105.7(3)
C(42)–Si(4)–C(43)	107.8(3)
C(41)–Si(4)–C(43)	108.0(2)
C(42)–Si(4)–P(2)	112.9(2)
C(41)–Si(4)–P(2)	113.2(1)
C(43)–Si(4)–P(2)	109.0(2)
C(Cp)–C(Cp)–C(Cp)	107.3(3)–108.5(4)

Table 2
Activity data for the polymerization of ethylene by bimetallic early zirconocene–late transition metal complexes

Entry	Catalyst	[Catal.] ^a	Temp.	[Cocatal.] ^b	Cat./MAO	Activity ^c
1	2	6.38	25	6.38	1:1000	4.70×10^6
2	2	6.38	65	6.38	1:1000	4.79×10^6
3	2	6.38	0	8.62	1:1350	2.05×10^5
4	2	6.38	25	8.62	1:1350	1.89×10^6
5	2	6.38	60	8.62	1:1350	1.23×10^6
6	2	6.38	0	17.24	1:2700	4.98×10^5
7	2	6.38	25	17.24	1:2700	6.98×10^5
8	2	6.38	60	17.24	1:2700	6.77×10^5
9	3	6.03	25	8.62	1:1350	4.68×10^5
10	3	6.03	60	8.62	1:1350	5.44×10^5
11	1	7.24	25	8.62	1:1350	7.46×10^5

^a [Catalyst] (μmol).

^b [Cocatalyst] (mmol), MAO was prepared by removing the solvent from a 20 wt.% solution (Schering) at 25°C and 10^{-6} Torr.

^c Grams total polymer per (mole Zr atm ethylene h).

drogen and/or carbon monoxide, presumably due to the electronic and coordinative saturation of both early and late transition metals. However, these complexes can be activated by the use of the strong Lewis acids, such as methylaluminoxane (MAO). These precursor complexes in the presence of MAO were found to be active catalysts for the polymerization of ethylene, rivalling the cationic metallocene systems. To our best knowledge, 1–3 are the first examples of an early/late hetero-bimetallic bridging phosphido/arsenido complex used as a catalytic precursor in polymerization reactions in which the electron-rich late transition metal influences the oxophilic electron-poor early transition metal.

The catalytic polymerization of ethylene was studied using the catalytic precursors 1–3. Active species were generated by the reaction of the corresponding complexes with MAO. Ethylene polymerizations were carried out under vigorously anaerobic/anhydrous vacuum line conditions, and reactions were quenched after measured time intervals with methanol/HCl solutions prior to polymer collection, washing with pentane and acetone, and drying. Polymer microstructure of the high density polyethylene obtained was characterised by ^{13}C NMR using standard analysis [21].

Several interesting trends are evident in the ethylene polymerization data (Table 2). The activity of the catalysts is strongly dependent on the temperature (entries 3–5). Thus, raising the temperature from 0 to 25°C increases the catalytic activity by a factor of around 9, although a further temperature increase to 60°C causes a small decrease in the catalytic activity. Large effects have also been observed for the Al:Zr ratio (compare entries 1, 4 and 7). Increasing the Al:Zr ratio results in a small decrease in the catalytic activity. Hence, the smaller the ratio of MAO/catalyst used, the higher the catalytic activity (limit 1:1000). This behaviour is opposite to that normally exhibited by metallocene early transition metal systems, but is similar to that obtained

in the polymerization of ethylene by cationic zirconium benzamidinato systems [22]. This result can be rationalised by the effect of the cocatalyst concentration on the catalysis of various possible elimination routes, alkyl transfer pathways, and other deactivation processes [23].

Interestingly, by increasing the donor interaction of the late transition metal towards the oxophilic centre, a lower catalytic reactivity towards olefins was obtained. Furthermore, the electronic effect of these electron-rich late transition metal moieties is clearly shown by comparing their CO stretching bands in the IR spectrum (Table 3). The molybdenum moiety of complex 2 is more electronegative (red shift) than that of 3, indicating a lower donor interaction towards the oxophilic centre, inducing a more reactive complex. The electronic effect of the component in the Ni complex (1) falls between those of complexes 2 and 3. These results are in agreement with the theoretically expected reactivity order $\text{Mo} > \text{Cr} \approx \text{Ni}$.

We suggest that the above reactivity results are a consequence of the strength of the interaction between

Table 3
CO stretching bands (cm^{-1}) for the bridged catalyst before and after addition of the aluminoxane cocatalyst

Catalyst	Before MAO addition	After MAO addition
1	1954.3	1943.2
	1990.1	1989.7
2	1942.8	1874.5
	1995.1	1909.7
	2000.9	2000.4
	2011.4	
3	1852.3	
	1865.9	1988.5 (broad)
	1882.0	
	1976.2	

the oxophilic centre and the late transition organometallic moiety [2a,23c,24]. The reactions of these and other binuclear complexes with other α -olefins, and the characterisation of the active species, are currently being investigated.

4. Experimental

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual manifold Schlenk line, or interfaced to a high vacuum (10^{-5} Torr) line, or in a nitrogen-filled 'Vacuum Atmospheres' glove box with a medium capacity recirculator (1–2 ppm O_2). Argon, ethylene and nitrogen were purified by passage through an MnO oxygen-removal column and a Davison 4 Å molecular sieve column. Ether solvents (THF- d_8) were distilled under argon from sodium benzophenone ketyl. Hydrocarbon solvents (toluene- d_8 , benzene- d_6) were distilled under nitrogen from Na/K alloy. All solvents for vacuum line manipulations were stored in vacuo over Na/K alloy in resealable bulbs [25]. NMR spectra were recorded on Bruker DRX 400, Bruker AM 200 and Bruker AM 400 spectrometers. Chemical shifts for 1H NMR and ^{13}C NMR are referenced to internal solvent resonances and are reported relative to tetramethylsilane. ^{31}P NMR is reported relative to external 85% H_3PO_4 . The NMR experiments were conducted in teflon valve-sealed tubes (J-Young) after vacuum transfer of the liquids in a high-vacuum line. The IR spectrum was recorded as a KBr mull on a Zeiss Specord M80 in the range 300–4000 cm^{-1} or on a Nicolet 400 FTIR spectrometer with Na/K dried Nujol in an air-tight container. MS: Varian MAT 711 (EI, 70 eV, variable source temperature). The melting point was determined in a sealed capillary under argon and is uncorrected.

The synthesis of $(\eta^5-C_5H_5)_2Zr\{\mu-P(SiMe_3)_2\}_2Ni(CO)_2$ (**1**) was carried out under purified dry argon. $(\eta^5-C_5H_5)_2Zr\{P(SiMe_3)_2\}_2$ [14], $(\eta^5-C_5H_5)_2Zr\{\mu-P(SiMe_3)_2\}_2Mo(CO)_4$, and $(\eta^5-C_5H_5)_2Zr\{\mu-As(SiMe_3)_2\}_2Cr(CO)_4$ [7] were prepared by literature procedures. $Ni(CO)_4$ is commercially available (Strem Chemicals).

4.1. Synthesis of $(\eta^5-C_5H_5)_2Zr\{\mu-P(SiMe_3)_2\}_2Ni(CO)_2$ (**1**)

Using a pipette, $Ni(CO)_4$ (0.35 ml, 0.46 g, 2.71 mmol) was added to a solution of $(\eta^5-C_5H_5)_2Zr\{P(SiMe_3)_2\}_2$ (1.57 g, 2.73 mmol) in 25 ml toluene. Evolution of CO was observed and the colour of the solution changed from deep red to orange during 30 min. The solution was stirred over night, and then concentrated to half its volume. Cooling to $-20^\circ C$ gave

yellow–orange platelets of **1**. According to the 1H NMR spectrum, **1** crystallises with one molecule of toluene. Yield 1.02 g (48.1%), m.p. $232^\circ C$, decomposition with evolution of gas (red melt).

1H NMR (C_6D_6 , 400 MHz, δ (ppm)): 7.00–7.14 m (5 H, toluene), 5.43 s (10 H, Cp), 2.09 s (3 H, toluene), 0.50 d (36 H, $SiMe_3$, $^3J(^1H-^{31}P)$ 3.8 Hz).

^{31}P NMR (C_6D_6 , 161 MHz, δ (ppm)): -42.1 s.

IR spectrum (KBr): 1980 vs (CO), 1938 vs (CO), 1610 m, br, 1490 w, 1432 m [Cp , $P(SiMe_3)_2$] ($Cp = \eta^5-C_5H_5$), 1400 w [Cp , $P(SiMe_3)_2$], 1310 w, 1248 vs [$P(SiMe_3)_2$], 1050 s, br, 1030 s, 1010 s [Cp , $P(SiMe_3)_2$], 990 m, 928 m, 880 m, sh [$P(SiMe_3)_2$], 830 vs [$P(SiMe_3)_2$], 805 vs [$P(SiMe_3)_2$], 760 s, 740 m, sh, 690 m, 680 m (SiC_3), 630 s (SiC_3), 440 m, sh, 398 w, 372 w, 355 w, 335 w, br.

When the reaction of $(\eta^5-C_5H_5)_2Zr\{P(SiMe_3)_2\}_2$ (2.69 g, 4.67 mmol, in 50 ml toluene) with $Ni(CO)_4$ (0.31 ml, 0.40 g, 2.34 mmol) is carried out in the molar ratio 2:1, only **1** is obtained (m.p. $235-237^\circ C$ dec., characterised by IR and NMR spectroscopy).

4.2. Olefin polymerization experiments

These experiments were conducted in a 100 ml flamed round-bottomed reaction flask attached to a high-vacuum line. In a typical experiment 6 mg (7.7×10^{-3} mmol) of the catalyst and 200 mg of MAO ($M_w = 1200$) were charged into a 100 ml flask containing a magnetic stir bar. The reaction vessel was connected to a high vacuum line, pumped-down and back-filled three times, the flask re-evacuated, and a measured quantity of toluene (30 ml) was vacuum transferred into the reaction flask from Na/K. Next, gaseous ethylene was admitted to the vessel, after temperature equilibration, through the gas purification column. The gas pressure was continuously maintained at 1.0 atm with a mercury manometer. Rapid stirring of the solution was initiated and, after a measured time interval, the polymerization was quenched by injecting a mixture of methanol/HCl. The polymeric product was collected by filtration, washed with acetone and pentane and dried under vacuum.

4.3. Data collection and structural refinement of $(\eta^5-C_5H_5)_2Zr\{\mu-P(SiMe_3)_2\}_2Ni(CO)_2 \cdot toluene$ (**1**)

Data (Mo $K\alpha = 0.71069$ Å) were collected with a STOE STADI IV diffractometer. 25 reflections (2θ range $3-25^\circ$) were used for determination of the unit cell parameters. Absorption correction: psi scans. The structure was solved by direct methods (SHELXS-86) [26] and subsequent difference Fourier syntheses and refined by full-matrix least-squares on F^2 (SHELXL-93) [27]. Restrictions: Ni, O, P, Si, Zr and C atoms anisotropic H atoms located by difference maps and refined isotropi-

Table 4

Crystal data and structure refinement for $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}\{\mu\text{-P}(\text{SiMe}_3)_2\}_2\text{-Ni}(\text{CO})_2 \cdot \text{toluene}$ (1)

Formula	$\text{C}_{31}\text{H}_{54}\text{NiO}_2\text{P}_2\text{Si}_4\text{Zr}$
Molecular weight	782.97
Temperature (K)	180
Crystal system	triclinic
Space group	$P\bar{1}$ (No. 2)
Cell constants	
a (Å)	12.161(3)
b (Å)	12.693(2)
c (Å)	14.063(3)
α (°)	112.91(2)
β (°)	96.80(2)
γ (°)	96.27(2)
V (Å ³)	1956.6(7)
Z	2
d_{calc} (g cm ⁻³)	1.329
Scan technique	ω/θ -scan
2θ range (°)	3–52
h (min, max)	–14, 14
k (min, max)	–15, 14
l (min, max)	0, 17
Total reflections	8650
Independent reflections	7677 [$R_{\text{int}} = 0.0544$]
$F(000)$	820
Parameters	525
Absorption coefficient (μ cm ⁻¹)	9.77
Largest difference peak/hole (e/Å ³)	0.716/ \pm 0.321
Final R indices	$R_1 = 0.033$
[for 5629 reflections with $I > 2\sigma(I)$]	$wR_2 = 0.081$
R indices (all data)	$R_1 = 0.059$
	$wR_2 = 0.091$
Goodness-of-fit (F^2)	1.025

cally. A summary of data collection parameters is given in Table 4 [17].

Acknowledgements

The German team gratefully acknowledges support of this work by the Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie and thank the company Chemetall for a generous donation of lithium alkyls. For the Israeli team, the research was supported by the Fund for the Promotion of Research at the Technion, and by the Promotion of Sponsor Research: The Technion V.P.R. Fund. We are indebted to D. Müller, University of Karlsruhe, for the mass spectrum.

References and notes

- [1] For a review of early/late heterobimetallic complexes, see: (a) D.W. Stephan, *Coord. Chem. Rev.*, **95** (1989) 41; (b) E. Hey-Hawkins, *Chem. Rev.*, **94** (1994) 1661; (c) R.M. Bullock and C.P. Casey, *Acc. Chem. Res.*, **20** (1987) 167 and references cited therein.
- [2] (a) D.G. Dick, Z. Hou and D.W. Stephan, *Organometallics*, **11** (1992) 2378. (b) F.R. Lemke, D.J. Szalda and R.M. Bullock, *Organometallics*, **11** (1992) 876. (c) B.D. Steffey, J.C. Vites and A.R. Cutler, *Organometallics*, **10** (1991) 3432. (d) K.V. Katti and R.G. Cavell, *Organometallics*, **10** (1991) 539. (e) T.E. Glassman, A.H. Liu and R.R. Schrock, *Inorg. Chem.*, **30** (1991) 4723 and references cited therein.
- [3] (a) A.M. Baranger, F.J. Hollander and R.G. Bergman, *J. Am. Chem. Soc.*, **115** (1993) 7890. (b) M.J. Hostetler, M.D. Butts and R.G. Bergman, *J. Am. Chem. Soc.*, **115** (1993) 2743. (c) R. Choukroun, F. Dahan, D. Gervais and C. Rifai, *Organometallics*, **9** (1990) 1982.
- [4] (a) A.M. Baranger and R.G. Bergman, *J. Am. Chem. Soc.*, **116** (1994) 3822. (b) L. Gelmini and D.W. Stephan, *Organometallics*, **7** (1988) 849. (c) R. Choukroun, D. Gervais, J. Jaud, P. Kalck and F. Senocq, *Organometallics*, **5** (1986) 67.
- [5] (a) G.S. Ferguson, P.T. Wolczanski, M.L. Párkányi and M.C. Zonneville, *Organometallics*, **7** (1988) 1967. (b) C.P. Casey, *J. Organomet. Chem.*, **400** (1990) 205. (c) F. Ozawa, J.W. Park, P.B. Mackenzie, W.P. Schaefer, L.M. Henling and R.H. Grubbs, *J. Am. Chem. Soc.*, **111** (1989) 1319.
- [6] O. Stelzer and E. Unger, *Chem. Ber.*, **110** (1977) 3430; G. Johannsen and O. Stelzer, *Chem. Ber.*, **110** (1977) 3438.
- [7] F. Lindenberg, T. Gelbrich and E. Hey-Hawkins, *Z. Anorg. Allg. Chem.*, **621** (1995) 771.
- [8] For recent reviews of olefin polymerization catalysts, see: (a) R.P. Quirk (ed.), *Transition Metal Catalyzed Polymerizations*, Cambridge University Press, Cambridge, 1988; (b) W. Kaminsky and H. Sinn (eds.), *Transition Metals and Organometallics for Catalysts for Olefin Polymerization*, Springer, New York, 1988; (c) J.A. Ewen, in T. Keii and K. Soga (eds.), *Catalytic Polymerization of Olefins*, Elsevier, New York, 1986, p. 271; (d) R.F. Jordan, P.K. Bradley, R.E. LaPointe, and D.F. Taylor, *New J. Chem.*, **14** (1990) 499; (e) R.F. Jordan, *Adv. Organomet. Chem.*, **32** (1991) 325.
- [9] For some recent references, see: (a) X. Yang, C.L. Stern and T.J. Marks, *J. Am. Chem. Soc.*, **116** (1994) 10015; (b) G. Erker, M. Aulbach, C. Kruger and S. Werner, *J. Organomet. Chem.*, **450** (1993) 1; (c) M. Farina, G. Disilvestro and P. Sozzani, *Macromolecules*, **26** (1993) 946; (d) W. Kaminsky, A. Bark and R. Steiger, *J. Mol. Cat.*, **74** (1992) 109; (e) J.C.W. Chien, G.H. Llinas, M.D. Rausch, Y.G. Lin, H.H. Winter, J.L. Atwood and S.G. Bott, *J. Polym. Sci., A* **30** (1992) 2601; (f) J. Okuda, *Angew. Chem., Int. Ed. Engl.*, **31** (1992) 47; (g) L. Resconi, L. Abis and G. Franciscano, *Macromolecules*, **25** (1992) 6814; (h) K. Mashima, S. Fujikawa and A. Nakamura, *J. Am. Chem. Soc.*, **115** (1993) 10990; (i) G. Erker, *Pure Appl. Chem.*, **64** (1992) 393; (j) W. Spaleck, M. Antberg, J. Rohrmann, A. Winter, B. Bachmann, P. Kiprof, J. Behm and W.A. Herrmann, *Angew. Chem., Int. Ed. Engl.*, **31** (1992) 1347 and references cited therein.
- [10] See, for example: (a) S. Collins, W.J. Gauthier, D.A. Holden, B.A. Kuntz, N.J. Taylor and D.G. Ward, *Organometallics*, **10** (1991) 2061; (b) W. Roll, H.H. Brintzinger, B. Rieger and R. Zolk, *Angew. Chem., Int. Ed. Engl.*, **29** (1990) 279; (c) I.M. Lee, W.J. Gauthier, J.M. Ball, B. Iyengar and S. Collins, *Organometallics*, **11** (1992) 2115; (d) S.L. Borkowsky, N.C. Baenziger and R.F. Jordan, *Organometallics*, **12** (1993) 486; (e) Y.W. Alelynnas, Z. Guo, R.E. LaPointe and R.F. Jordan, *Organometallics*, **12** (1993) 544; (f) M. Bochmann and S.J. Lancaster, *Organometallics*, **12** (1993) 633; (g) M. Bochmann and A.J. Jaggar, *J. Organomet. Chem.*, **434** (1992) C1.
- [11] L. Gelmini and D.W. Stephan, *Inorg. Chim. Acta*, **111** (1986) L17.
- [12] L. Gelmini and D.W. Stephan, *Inorg. Chem.*, **25** (1986) 1222.
- [13] R.T. Baker, T.H. Tulip and S.S. Wreford, *Inorg. Chem.*, **24** (1985) 1379.

- [14] E. Hey-Hawkins, M.F. Lappert, J.L. Atwood and S.G. Bott, *J. Chem. Soc., Dalton Trans.*, (1991) 939.
- [15] L. Gelmini, L.C. Matassa and D.W. Stephan, *Inorg. Chem.*, **24** (1985) 2585.
- [16] J.M. Ritchey, A.J. Zozulin, D.A. Wroblewski, R.R. Ryan, H.J. Wassermann, D.C. Moody and R.T. Paine, *J. Am. Chem. Soc.*, **107** (1985) 501.
- [17] Additional information concerning the crystal structure determination can be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, citing the deposition number CSD 404104, the authors and the journal.
- [18] (a) R.T. Baker and T.H. Tulip, *Organometallics*, **5** (1986) 839. (b) M.G.B. Drew, S.R. Wade, M.G.H. Wallbridge and G.R. Willey, *J. Chem. Soc., Dalton Trans.*, (1986) 713. (c) P.Y. Zheng and D.W. Stephan, *Can. J. Chem.*, **67** (1989) 1584. (d) R.T. Baker, W.C. Fultz, T.B. Marder and I.D. Williams, *Organometallics*, **9** (1990) 2357. (e) T.S. Targos, R.P. Rosen, R.R. Whittle and G.L. Geoffroy, *Inorg. Chem.*, **24** (1985) 1375. (f) R.A. Jones, A.L. Stuart, J.L. Atwood and W.E. Hunter, *Organometallics*, **2** (1983) 874.
- [19] F. Lindenberg and E. Hey-Hawkins, *J. Organomet. Chem.*, **435** (1992) 291.
- [20] (a) *Tables of Interatomic Distances and Configuration in Molecules and Ions*, The Chemical Society, London, Special Publications No. 11, 1958 and No. 18, 1965. (b) J.E. Huheey, *Inorganic Chemistry*, Harper & Row, New York, 3rd edn., 1983, pp. 258–259.
- [21] J.L. Koenig, *Spectroscopy of Polymers*, American Chemical Society, Washington, DC, 1992, p. 137.
- [22] D. Herscovics-Korine and M.S. Eisen, *J. Organomet. Chem.*, in press.
- [23] For a summary of possible elimination reaction pathways, see: (a) H. Sinn and W. Kaminsky, *Adv. Organomet. Chem.*, **18** (1980) 99; (b) M. Bochmann, T. Cuenca and D.T. Hardy, *J. Organomet. Chem.*, **484** (1994) C10; (c) M. Giardello, M.S. Eisen, C. Stern and T.J. Marks, *J. Am. Chem. Soc.*, in press.
- [24] M.A. Giardello, M.S. Eisen, C.L. Stern and T.J. Marks, *J. Am. Chem. Soc.*, **115** (1993) 3326 and references cited therein.
- [25] D.D. Perrin, W.L.F. Armarego and D.R. Perrin, *Purification of Laboratory Chemicals*, Pergamon Press, New York, 1980.
- [26] G. Sheldrick, *SHELXS-86, Program for Crystal Structure Solution*, Göttingen, 1986.
- [27] G. Sheldrick, *SHELXL-93, Program for Crystal Structure Determination*, Göttingen, 1993.