

An Efficient Keim-Type Catalyst Based on an Electron-Poor *P,O*-Chelate; Tuning the Selectivity of Ethylene Oligomerisation towards Short α -Olefins

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The tertiary phosphane $\text{Ph}_2\text{P-pzONa}$, in which the phosphorus atom is substituted by an electron-withdrawing pyrazolonato unit, reacts with *trans*- $[\text{NiPhCl}(\text{PPh}_3)_2]$ to afford quantitatively *trans*- P,P' - $[\text{NiPh}(\text{Ph}_2\text{P-pzO})(\text{PPh}_3)]$ (**4**), the first Keim-type catalyst derived from an amide. In the absence of any cocatalyst, complex **4** converts ethylene in high selectivity and activity into α -olefins. The product distribution is drastically shifted towards lower oligomers when compared to the outcome of the reaction carried out with the conven-

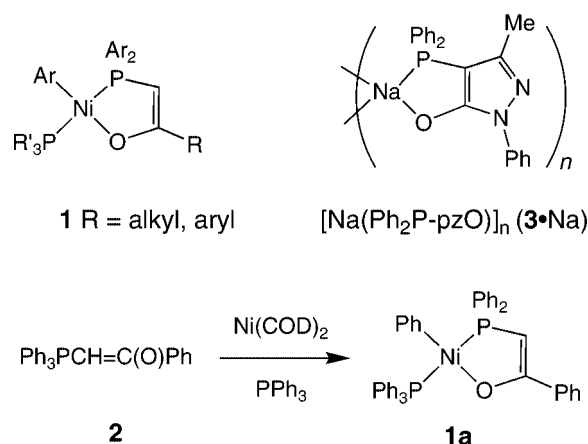
tional SHOP catalyst. Thus, when operating at 1 bar, over 99 wt.-% of the oligomers formed are C_4 – C_{16} oligomers. In ethylene-free solvents, **4** was shown to slowly undergo reductive elimination to produce the stabilised phosphorus ylide $\text{Ph}_3\text{P-pzO}$ (**5**). Both compounds (**4** and **5**) were characterised by single-crystal X-ray diffraction analyses.

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Introduction

Square-planar nickel(II) complexes of the general formula *trans*- P,P' - $[\text{NiAr}\{\text{Ar}_2\text{PCH}=\text{C}(\text{O})\text{R}'\}(\text{PR}_3)]$ (**1**; R, R' = aryl, alkyl) have been extensively studied over the last 25 years, mainly because of their ability to oligomerise ethylene into α -olefins under mild conditions.^[1–7] The discovery of this catalyst type stretches back to the early seventies, when researchers at SHELL discovered that mixing Ni^0 complexes with phosphorus ylides, e.g. $\text{Ph}_3\text{PCH}=\text{C}(\text{O})\text{Ph}$ (**2**), produced highly active oligomerisation catalysts.^[8] Later, Keim et al. showed that reaction of **2** with $\text{Ni}(\text{cod})_2$ in the presence of PPh_3 resulted in an oxidative addition reaction with cleavage of a P–Ph(ylide) bond and subsequent formation of the phosphanyl-enolato complex $[\text{NiPh}\{\text{Ph}_2\text{PCH}=\text{C}(\text{O})\text{Ph}\}(\text{PPh}_3)]$ (**1a**), known as Keim's oligomerisation catalyst.^[9] Since Keim's pioneering studies, a number of related *P,O*-nickel complexes (*P,O* = 3-electron chelate) have been prepared and studied, but surprisingly little is known about variants in which the *P,O*-chelate behaves as an electron-poor donor, although the complex $[\text{NiH}\{\text{Ph}_2\text{PCH}_2\text{C}(\text{CF}_3)_2\text{O}\}\text{PCy}_3]$ was reported to be inactive. Note that several recent publications have focussed on

nickel complexes with electron-rich *P,O*-chelates,^[10,11] while a few nickel complexes in which the *P,O* ligand behaves as a neutral 4-electron donor have also been studied.^[12]



We now describe the convenient, direct synthesis of the new Keim-type catalyst **4** starting from a P^{III} derivative, namely the sodium pyrazolonato-phosphane $\text{Ph}_2\text{P-pzONa}$ ($\mathbf{3}\cdot\text{Na}$).^[13] Our investigations show how the presence of the strong electron-withdrawing pyrazolonato ring,^[14] known to be stronger than CF_3 , drastically drives the product distribution towards shorter olefins. The present study further demonstrates that “Keim catalysts” may undergo reductive elimination with formation of a phosphorus ylide. The reported complex **4** is the first example of a Keim-type catalyst derived from an amide.

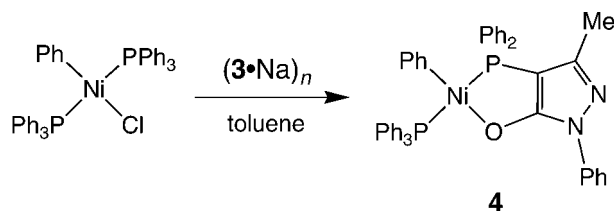
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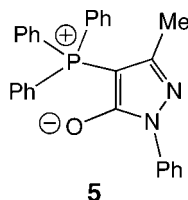
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Supporting information for this article is available on the WWW under <http://www.eurjic.org> or from the author.

Results and Discussion

Reaction of $[\text{NiPhCl}(\text{PPh}_3)_2]$ with one equiv. of $\text{Ph}_2\text{P-pzONa}$ in toluene afforded complex **4** in ca. 90% yield. It is noteworthy that this reaction constitutes a rare case in which a **1a**-analogue was obtained from a phosphanylenolate rather than a phosphorus ylide. The ^{31}P NMR spectrum of **4** displays an AB quartet ($\delta_{\text{A}}/\delta_{\text{B}} = 20.2/-8.6$ ppm) with a $J(\text{PP}')$ coupling constant of 280 Hz, typical for *trans*-arranged phosphorus atoms. The phosphorus signal of the P-enolato moiety ($\delta = -8.6$ ppm) is strongly shifted to high field with respect to that of other diphenylphosphanylenolates reported in the literature, thus reflecting the high electron-withdrawing nature of the pyrazolonato ring. The solid-state structure of **4** was elucidated by an X-ray diffraction study (Figure 1), which reveals a significant deviation from the usual square-planar coordination geometry observed in other $[\text{NiPh}(\text{PO})\text{PPh}_3]$ complexes. Thus, while the C(23) and oxygen atoms lie on one side of the mean-squares coordination plane, the two P atoms are turned towards the other side [distances to the plane: C(23) $-0.154(1)$; O $-0.160(1)$; P1 $+0.184(1)$; P2 $+0.185(1)$ Å]. Consistent with the electronic features of the pyrazolonato ring, the Ni–O and the Ni–P(1) bonds [$1.955(1)$ Å and $2.210(1)$ Å, respectively] are somewhat longer than their counterparts in **1a** (1.914 Å; 2.168 Å). The shortness of the P(1)–C(2) bond [$1.770(2)$ Å] is in keeping with electron delocalisation within the PO chelate.



Interestingly, we noted that on standing, colourless crystals slowly formed from toluene solutions containing **4**. An X-ray analysis of the product reveals the formation of the phosphorus ylide **5** (Figure 2). Surprisingly, a similar reductive elimination reaction had not been reported for **1a**. A careful reinvestigation of the latter complex showed that, in fact, **1a** undergoes the same slow transformation in toluene, resulting in the formation of $\text{Ph}_3\text{PCH}=\text{C}(\text{O})\text{Ph}$. Possibly, this transformation is triggered by the presence of trace amounts of air, since we found that bubbling air through a C_6D_6 solution of **4** rapidly produced **5**.



Typically for a Keim-type catalyst, complex **4** displays high activity in the low pressure oligomerisation of ethylene without requiring any activating agent to trigger the reaction. Turnover frequencies (TOF) as high as

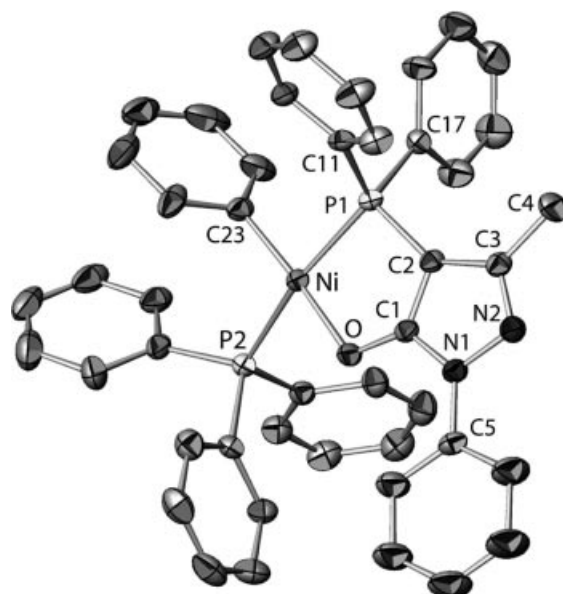


Figure 1. Molecular structure of complex **4**. Important distances [Å] and angles [°]: NiC(23) 1.885(2); NiO 1.955(1); NiP(1) 2.210(1); NiP(2) 2.224(1); P(1)C(2) 1.770(2); P(1)C(17) 1.820(2); P(1)C(11) 1.823(2); OC(1) 1.296(2); C(2)C(1) 1.393(2); C(2)C(3) 1.419(3); N(1)C(1) 1.370(2); N(1)N(2) 1.400(2) P(1)NiP(2) 167.26(2); C(23) NiO 173.83(7).

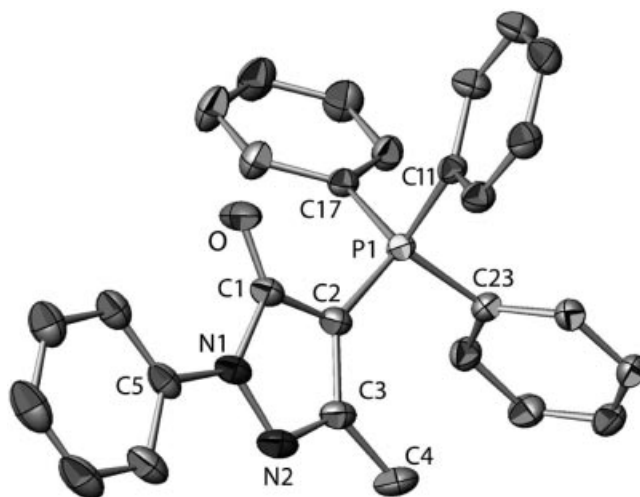


Figure 2. Molecular structure of the phosphorus ylide **5**. Important distances [Å]: P(1)C(2) 1.736(2); P(1)C(23) 1.797(3); P(1)C(17) 1.806(2); P(1)C(11) 1.808(2); OC(1) 1.249(3); C(2)C(1) 1.430(3); C(2)C(3) 1.429(3); N(1)C(1) 1.400(3); N(1)N(2) 1.395(3).

$6600 \text{ mol}_{\text{ethylene}} \cdot \text{mol}_{\text{Ni}}^{-1} \cdot \text{h}^{-1}$ were observed when operating in toluene at 70°C under a constant ethylene pressure of 5 bar and a nickel concentration of $0.25 \mu\text{mol/mL}$ (cf. TOF = 7500 for **1a**) [2 h experiments]. At this pressure, the selectivity in the α -olefins surpassed 95% (Table 1).

The most striking feature of **4** involves the product distribution which considerably shifts towards lower oligomers in comparison with the outcome of Keim's catalyst. Thus, under the conditions outlined above, ca. 72 wt.-% of the oligomers produced after 60 min were C_4 – C_{16} olefins; this fraction represents only 15 wt.-% of the total amount of

Table 1. Ethylene oligomerisation with **1a** and **4**. General conditions: toluene 30 mL, 70 °C, calibrated on heptane.

Ni complex (7.5 μmol) ^[a]	P(C ₂ H ₄) [bar]	Time [h]	BF ₃ [μmol]	TOF [mol _{ethylene} ·mol _{Ni} ⁻¹ ·h ⁻¹]	C ₄ –C ₁₆ distribution [wt.-%]
1a	1	2		3400	60.2
1a	5	2		7500	15.3
1a	5	1		15500	15.3
1a ^[a]	20	1		19900	9.6
1a ^[a]	20	1	7.5	9400	9.6
4	1	2		1800	98.9
4	5	2		6600	45.2
4	5	1		9700	72.5
4 ^[a]	20	1		6600	25.1
4 ^[a]	20	1	7.5	3800	97.0

[a] Batch experiments, toluene 20 mL, 70 °C.

oligomers produced with **1a** in the same period of time. When applying a constant ethylene pressure of 1 bar, this ratio rose to 99 wt.-% (versus 60% for **1a**). The performances of **4** and **1a** were also compared with those in batch experiments carried out at higher pressures. Thus, when applying an initial pressure of 20 bar ([Ni] = 0.25 μmol/mL), the amount of C₄–C₁₆ olefins produced with **4** after 1 h was 25 wt.-% of the total amount of oligomers, versus only 9.6% for **1a**. It must be mentioned here that a SHOP catalyst in which the oxygen atom was involved in hydrogen bonding has been reported to also favour β elimination, hence the formation of shorter oligomers, but not to such an extent.^[2] Interestingly, the observed effect can be drastically enhanced by using BF₃ as an additive. For example, in experiments where stoichiometric amounts of BF₃ were used (batch autoclave, P_{initial} = 20 bar, [4] = 0.25 μmol/mL), the fraction of C₄–C₁₆ olefins obtained after 1 h represented 97% of all oligomers formed. It appears plausible that the BF₃ unit binds to the pyrazole ring, probably through a nitrogen atom,^[15] hence increasing the electron deficiency of the nickel atom. Overall, the effect observed by adding BF₃ is reminiscent of the properties of [Ni{Ph₂PC₆H₄C(O)O}(Me-2-allyl)],^[16] which upon addition of B(C₆F₅)₃ shifts ethylene oligomerisation towards the formation of low-weight olefins (butene and hexene).^[17]

Finally, we noted that mixing complex **4** with Ni(cod)₂ in excess afforded, as expected,^[11,18,19] a catalyst which polymerises ethylene. Its activity compares with that of **1a**, but analysis of the polymer reveals that the polyethylene chains are considerably shorter (*M_w* = 650 g mol⁻¹) than those obtained with **1a** (*M_w* = 4500 g mol⁻¹) under similar conditions. These findings confirm the remarkable electronic properties of the phosphanyl-pyrazolonato ligand. Further investigations are in progress which aim at the use of electron poor *P,O* chelators that allow the controlled production of industrially relevant α-olefins in the absence of any cocatalyst.

Experimental Section

General: All manipulations were performed in Schlenk-type flasks under dry nitrogen. Solvents were dried by conventional methods and distilled immediately prior to use. CDCl₃ was passed down a

5 cm-thick alumina column and stored under nitrogen over molecular sieves (4 Å). IR spectra were measured with a Perkin–Elmer 1605 spectrometer. Routine ¹H and ³¹P{¹H} spectra were recorded with FT Bruker instruments (AC-300 or Bruker AM-400). ¹³C{¹H} were recorded with an FT Bruker AC-200 spectrometer. ¹H NMR spectra are referenced to residual protiated solvents (δ = 7.26 ppm for CDCl₃ and 5.32 ppm for CD₂Cl₂); ¹³C chemical shifts are reported relative to deuterated solvents (δ = 77.0 ppm for CDCl₃ and 53.8 ppm for CD₂Cl₂); ³¹P NMR spectroscopic data are given relative to external H₃PO₄. The catalytic solutions were analysed with a Varian 3900 gas chromatograph equipped with a WCOT fused silica column (25 m, 0.32 mm inside diameter, 0.25 mm film thickness). High temperature size exclusion chromatography (HT SEC) measurements were performed at 150 °C with a “PL220” apparatus (Column set HT-MixedB-TCB-01) in 1,2,4-trichlorobenzene (with 0.2% Irganox). Calibration was made with linear PS samples. Ph₂P-pzONa^[13] and [NiPhCl(PPh₃)₂]^[20,21] are reported according to procedures reported in the literature.

[NiPh{Ph₂P-pzO}(PPh₃)] (4): To a stirred suspension of Ph₂P-pzONa (0.766 g, 2.14 mmol) in toluene (30 mL) was added a solution of [NiPhCl(PPh₃)₂] (1.491 g, 2.14 mmol) in toluene (40 mL). After stirring for 4 h, the mixture was filtered through Celite in order to remove NaCl. The solution was concentrated to ca. 10 mL. On standing, dark yellow crystals formed overnight. After removal of the supernatant solution, the crystals were washed successively with cold toluene (5 mL) and pentane (10 mL), and then dried in vacuo. Yield: 1.088 g, 60%. Addition of pentane to the mother liquor afforded further amounts of **4** as a yellow powder which increases the yield to 90 %. C₄₆H₃₈N₂NiOP₂·C₇H₈ (*M_r* = 755.46 + 92.14 = 847.60); calcd. C 75.1, H 5.47, N 3.31; found C 74.6, H 5.39, N 3.34. IR (KBr): 1592.6 (m), 1515.5 (s), 1495.0 (s), 1425.8 s cm⁻¹. ¹H NMR (300 MHz, C₆D₆): δ = 8.25–6.44 (35 H, arom. H), 2.02 (s, 3 H, CH₃) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 140.76–118.06 (arom. C), 89.83 (d, *J*(P,C) = 63 Hz, PCH), 14.77 (s, CH₃) ppm. ³¹P{¹H} NMR (121 MHz, CDCl₃): δ = 20.2 and –8.6 (AB spin system, *J*(PP') = 280 Hz).

Ph₃P-pzO (5): [NiPh{Ph₂P-pzO}(PPh₃)] (**4**; 0.100 g, 0.13 mmol) was dissolved in toluene (5 mL). Upon standing in air, crystals of Ph₃P-pzO appeared after 48 h. The supernatant was removed by suction, and the crystals were dried under high vacuum. Yield: 0.056 g, 70%. C₂₈H₂₃N₂OP (*M_r* = 434.48); calcd. C 77.41, H 5.34, N 6.45; found C 77.49, H 5.38, N, 6.41. ³¹P{¹H} NMR (121 MHz, CDCl₃): δ = 10.6 ppm (lit.: 12.6^[22])

X-ray Crystal Structure Determination of 4-toluene: Single crystals of **4** suitable for X-ray diffraction analysis were obtained from a

Table 2. Crystallographic data for **4**·toluene and **5**·benzene.

Formula	C ₄₆ H ₃₈ N ₂ NiOP ₂ ·C ₇ H ₈ (4 ·toluene)	C ₂₈ H ₂₃ N ₂ OP·C ₆ H ₆ (5 ·benzene)
Formula weight	847.57	512.56
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>C2/c</i>
<i>a</i> [Å]	10.939(1)	29.361(5)
<i>b</i> [Å]	13.283(1)	9.314(1)
<i>c</i> [Å]	16.156(1)	22.758(5)
α [°]	72.29(5)	90
β [°]	75.29(5)	119.06(5)
γ [°]	87.71(5)	90
<i>V</i> [Å ³]	2161.2(3)	5440(3)
<i>Z</i>	2	8
<i>D</i> _{calcd.} [g·cm ⁻³]	1.302	1.252
μ (Mo- <i>K</i> α) [mm ⁻¹]	0.565	0.131
<i>F</i> (000)	888	2160
Crystal Size [mm]	0.08 × 0.10 × 0.13	0.06 × 0.07 × 0.09
Temperature [K]	173(2)	173(2)
Radiation [Å]	Mo- <i>K</i> α 0.71069	Mo- <i>K</i> α 0.71069
θ min/max [°]	1.4/30.0	1.6/30.0
Data set	–15/15; –17/18; –22/21	–41/36; 0/13; 0/32
Total, Unique data,	34952, 12654	7963, 7962
<i>R</i> (int)	0.035	0.036
Observed data [<i>I</i> > 2.0 σ (<i>I</i>)]	9904	5436
Number of reflections,	12654	7962
Number of parameters	532	333
<i>R</i> ₁ , <i>wR</i> ₂ , <i>S</i>	0.0442, 0.1468, 0.993	0.0781, 0.2297, 1.156
Min. and max. residual density [e·Å ⁻³]	–0.664, 0.453	–0.864, 1.829

concentrated toluene solution of the complex. Data were collected on a Nonius KappaCCD diffractometer (graphite Mo-*K* α radiation, $\lambda = 0.71073$ Å). The structure was solved by direct methods with the SHELXS-97 program and refined by full-matrix least-squares techniques (SHELXL-97) on *F*².^[23] Hydrogen atoms were located by using the geometric method. The crystal data and structural refinement details are listed in Table 2. The compound was found to crystallise with one molecule of toluene (CCDC 242626).

X-ray Crystal Structure Determination of **5·benzene:** Single crystals of **5** suitable for X-ray diffraction analysis were obtained from a toluene solution of the complex on standing in air. Data collection and structure solution were as for compound **4**. The compound crystallised with one molecule of benzene. The benzene molecules occupy special positions (–1). CCDC-242627 and CCDC-242626 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Catalytic runs

Ethylene oligomerisation: The low pressure catalytic runs (≤ 5 bar) were carried out in a Büchi miniclave (200 mL) equipped with a Teflon-coated magnetic stirrer. For higher pressures, a stainless steel autoclave was used (100 mL). Both reactors were dried under vacuum at 100 °C for 1 h before use. In a typical procedure, a Schlenk flask was charged with the complex (7.5 μ mol) and toluene (10 mL). The resulting solution was injected into the autoclave together with additional toluene (20 mL). The autoclave was then pressurised with ethylene and heated at 70 °C. After completion of the reaction, the autoclave was cooled with an ice bath and depressurized over 1 h. The solution was analysed by GC. Heptane (200 μ L) was used as internal reference. For details see Tables S1–S3.

Ethylene Polymerisation: Polymerisations were carried out in a mini-Büchi glass reactor (200 mL), equipped with a Teflon-coated

magnetic stirrer and heating (temperature-controlled oil bath), at constant ethylene pressure. The autoclave was heated at 100 °C under vacuum for 1 h before use and purged with ethylene. The reaction temperature refers to the bath temperature.

In a typical run, the reactor was charged at ambient temperature under an ethylene atmosphere, with a solution of catalyst (7.5 μ mol) in toluene (15 mL), followed by a solution of Ni(cod)₂ (75 μ mol) in toluene (15 mL). The autoclave temperature was raised to 70 °C, and pressurised to 5 bar. The reaction was quenched by venting the autoclave, and the reaction mixture was subsequently poured into a stirring solution of methanol (300 mL) and concentrated HCl (10 mL) to precipitate the polymer. The white powder was isolated by filtration, washed with methanol, and dried in vacuo at 50 °C. By using Keim's catalyst (**1a**), 1.80 g of a polymer was obtained and was characterised by $M_w = 4500$ g mol⁻¹ and $M_w/M_n = 1.87$ (Catalyst activity: 240 g·mmol_{cat}⁻¹·h⁻¹). The polymer (1.51 g) obtained with **4** has the following characteristics: $M_w = 650$ g mol⁻¹ and $M_w/M_n = 1.31$ (Activity: 201 g·mmol_{cat}⁻¹·h⁻¹).

Supporting Information Available: See also footnote on the first page of this article. Ethylene oligomerisation with the Keim-type complex **1a** (constant pressure) (Table S1). Ethylene oligomerisation with Keim-type complex **4** (constant pressure) (Table S2). Comparison of ethylene oligomerisation with **1a** and **4** in batch experiments (Table S3).

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