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Linear, high molecular weight polyethylene from a discrete, mononuclear phosphinoarenesulfonate complex of nickel(11)[†]

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A well-defined, homogeneous catalyst, $[(Ph)(2-(2',6'-(OMe)_2-C_6H_3)-C_6H_4)P(2-SO_3-C_6H_4)]Ni(Ph)PPh_3$, in which a single, bulky *ortho*-biphenyl substituent on the chelating phosphine blocks one axial position, is very active for formation of linear polyethylene ($M_n = 403\,000$ g mol⁻¹, $M_w/M_n = 1.87$).

Discrete palladium(II) complexes bearing an ortho-phosphinoare nesulfonate ligand ([PO] = $[Ar_2P(2-SO_3-C_6H_4)])$ display the remarkable ability to produce linear polyethylene as well as linear copolymers of ethylene with polar vinyl monomers.^{1–10} However, the polymers are generally formed only in modest yields and with low molecular weights (typically, $M_n < 10^4$).^{11–13} Nickel-based analogues of these catalysts are attractive targets because of their lower metal cost and, often, significantly higher activities.¹⁴⁻¹⁶ For example, Rieger and co-workers describe discrete nickel(II) complexes [PO]Ni(Ph)(PPh₃) that catalyze the homopolymerization of ethylene, although they obtained only low molecular weight materials $(M_n \leq 1000 \text{ g mol}^{-1})$.¹⁷ Much higher polymerization activities are observed in the presence of a PPh₃ scavenger such as Ni(COD)₂ or $B(C_6F_5)_3$. Replacing PPh₃ by a weaker σ -donor ligand such as DMSO or an amine also improves the catalytic activity, leading to turnover frequencies as high as 10^6 h⁻¹ without the need for a scavenger.¹⁸⁻²⁰ However, there is no improvement in the molecular weight of the polyethylene. Base-free [PO]Ni(II) complexes with η^3 -benzyl or η^3 -allyl ligands were reported to produce polyethylene with very slightly increased molecular weights $(1300 < M_n < 2,100 \text{ g mol}^{-1})$, at the expense of lower activities.21,22

In a significant advance towards the production of high molecular weight polyethylene using this family of catalysts,

Mecking *et al.* found that a heptane-insoluble complex, [PO]NiMe(pyridine), produces strictly linear, high molecular weight polyethylene ($M_n = 184\,000 \text{ g mol}^{-1}$) in that reaction medium.¹⁸ The finding was tentatively attributed to the aggregated nature of the active sites of the heterogeneous catalyst, making it difficult to develop a rational strategy for new ligand design. Recently, Shen and Jordan reported polyethylene with very high molecular weight ($M_w = 915\,000 \text{ g mol}^{-1}$) as well as polydispersity ($M_w/M_n = 29$) from a self-assembled, tetranuclear {[PO]Pd(II)}₄ cluster.²³ The authors considered the possibility of cooperative effects between the Pd(II) centers, but attributed the formation of high molecular weight polymer primarily to blocking of one of the axial faces of each Pd(II) site due to their aggregation.

In the well-known α -diimine family of Pd(II) and Ni(II) polymerization catalysts, steric bulk in the pseudo-axial positions causes the molecular weight of the resulting polyethylene to increase.¹⁵ By applying this strategy, the production of relatively high molecular weight polyethylene ($M_n = 189000 \text{ g mol}^{-1}$) was recently achieved using a mononuclear [PO]Pd(II) complex bearing two bulky, *ortho*-biphenyl substituents on the chelating



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Fig. 1 Molecular structure of **2a** (50% probability). Hydrogen atoms and co-crystallized benzene molecules have been omitted for clarity.

phosphine.⁵ Here we report that a simple modification of this approach suffices to allow the production of linear, high molecular weight polyethylene from a discrete, monomeric [PO]Ni(II) complex.

Our initial attempts to prepare a PPh₃-stabilized phenyl-Ni(II) complex using the [PO] ligand **1a**, bearing two (2',6'dimethoxy[1,1'-biphenyl]-2-yl) substituents, failed, presumably because of the competing steric demands of the two phosphines. However, the base-free allyl complex **2a**[‡] was obtained in moderate yield after deprotonation of the ligand by Na₂CO₃ and transmetallation with 0.5 equiv. [NiBr(allyl)]₂,²⁴ Scheme 1. **2a** was characterized by ¹H, ¹³C and ³¹P NMR, elemental analysis and electrospray ionization mass spectrometry (ESI-MS, see ESI[†]). Its structure was confirmed by single-crystal X-ray diffraction, Fig. 1. One of the two *ortho*aryl groups sits above an axial coordination site, and may show a very weak interaction between Ni and C_{ipso} (Ni–C(16), 3.10 Å).²⁵

Ethylene polymerization by **2a** at 90 °C in toluene gave polyethylene with moderate molecular weight $(M_n = 66\,000 \text{ g mol}^{-1})$, Table 1 (entry 1). The low productivity of this catalyst presumably arises from the low reactivity of the η^3 -allyl ligand. In addition, steric crowding of the Ni(II) center may limit access to an incoming monomer, precluding optimization using related [PO]Ni(R)L systems (R, alkyl, aryl; L, labile ligand).

We sought to address the issue of steric bulk with the design of the novel *o*-phosphinoarenesulfonate ligand **1b**, in which

 Table 1
 Ethylene polymerization results^a

Entry	Cat	$T/^{\circ}\mathrm{C}$	Yield/g	10^{-3} TOF ^f	$10^{-3} M_n^{g}$	PDI	$T_{\rm m}^{\ h}/^{\circ}{\rm C}$
1 ^b	2a	90	0.14	0.26	66	2.10	133.6
2^b	2a	25	0				
3^b	2b	90	0				
4^b	3b	25	5.31	18.4	403	1.87	136.1
5^c	3b	90	24.2	251	10	2.25	118.1
6^b	3b ^d	25	10.1	36.1	440	1.89	136.9
7^c	3b ^e	25	8.64	95.6	6	6.74	127.1

^{*a*} 300 mL reactor, 20 µmol Ni (entries 1–3) or 10 µmol Ni (entries 4–7), 80 mL toluene, 400 psi ethylene added on demand. ^{*b*} Polymerization time 1 h. ^{*c*} Polymerization time 20 min. ^{*d*} With 1 equiv. Ni(COD)₂. ^{*e*} With 1 equiv. $B(C_6F_5)_3$. ^{*f*} Turnover frequency = mol C₂H₄ polymerized (mol Ni)⁻¹ h⁻¹. ^{*g*} In g mol⁻¹, determined by GPC. ^{*h*} Measured by DSC.



Fig. 2 Molecular structure of 2b (50% probability). Hydrogen atoms and co-crystallized benzene molecules have been omitted for clarity. The central carbon of the $-CH_2-CH=-CH_2$ group is disordered (2 positions).

one biphenyl group has been replaced by a less stericallydemanding phenyl substituent. Since only one ortho-aryl group interacts with Ni(II) in 2a, we predicted that this ligand modification would allow the complex to retain its axial aryl-Ni(II) interaction.²⁶ This presumably disfavors the formation of bis-olefin hydride species that lead to chain transfer, while affording more design versatility for the Ni(II) complex. The Zwitterionic ligand 1b was prepared according to the one-pot procedure in Scheme 1, and was characterized by multinuclear NMR, elemental analysis and ESI-MS (see ESI[†]). 1b was subsequently deprotonated with Na₂CO₃ and combined with either [Ni(Br)allyl]₂ or trans-[Ni(PPh₃)₂(Ph)Cl] to generate 2b and 3b, respectively. In the ³¹P{¹H} NMR spectrum, the large ${}^{2}J_{PP}$ value (280 Hz) for 3b is consistent with a trans-arrangement of the phosphines. These complexes were also characterized by ¹H and ¹³C NMR and ESI-MS (see ESI[†]). The molecular structure of 2b appears by its geometry to display the expected apical Ni-Ar interaction, Fig. 2, although the distance between Ni and Cipso (Ni-C(16), 3.15 Å) is slightly longer than in 2a.

Ethylene polymerizations with **2b** and **3b** were conducted in toluene, in which both complexes are readily soluble.²⁷ The results are summarized in Table 1. While **2b** was unreactive at room temperature and afforded only a trace of polymer at 90 °C, **3b** produced high molecular weight polyethylene $(M_n = 403\,000 \text{ g mol}^{-1})$ with good activity $(1.8 \times 10^4 \text{ TO h}^{-1})$ at 25 °C. The high melting point of the polymer (136.1 °C) is consistent with highly linear polyethylene.

When the reactor containing **3b** was pressurized with ethylene at an initial temperature of 60 °C, a large exotherm $(\Delta T = +55 \text{ °C})$ was observed. When the reaction was conducted at 90 °C, the temperature was stable ($\pm 3 \text{ °C}$), but resulted in the formation of a large amount of low molecular weight polyethylene (10000 g mol⁻¹, entry 5). While partly due to the decreased solubility of ethylene at elevated temperatures, this experiment implies a dramatic increase in the rate of chain transfer with polymerization temperature, which may be due in part to thermal disruption of the aryl–Ni interaction. Similar decreases in molecular weight with increased temperature have been reported for both $(\alpha$ -diimine)nickel(II) complexes²⁸ and Ni(II) catalysts with chelating P,O ligands.²⁹

The polymerization activity of **3b** in the absence of a PPh₃ scavenger is remarkable, compared to other [PO]NiPh(PPh₃) systems^{17,21} or SHOP-type Ni(π) catalysts,³⁰ which show much lower activities without a scavenger (<4000 TO h⁻¹). It appears that the bulky ligand **1b** promotes dissociation of the Lewis base.

Nevertheless, addition of one equiv. Ni(COD)₂ to **3b** increased the productivity of the catalyst by a factor of two, without affecting either M_n or the polydispersity index (PDI) significantly. The latter remains unchanged at *ca.* 2 (compare entries 4 and 6), and the high T_m value is consistent with highly linear PE. The effect of the strong Lewis acid B(C₆F₅)₃ on the activity of **3b** was even more pronounced, but resulted in low molecular weight polyethylene with a high polydispersity index (entry 7), suggesting the presence of multiple catalytically active sites. A small-scale experiment in a NMR tube with **3b** and a stoichiometric amount of B(C₆F₅)₃ revealed the formation of a complex mixture of species, although the adduct Ph₃P–B(C₆F₅)₃ was not detected.³¹

In sum, we report a single-component nickel(II) catalyst that produces linear, high molecular weight polyethylene. Blocking only one of the transition metal faces is sufficient to inhibit associative displacement of the growing polymer chain by an incoming monomer. Also, by analogy to recent work with dialkyl(biaryl)phosphine ligands in Pd-catalyzed coupling catalysts where metal–arene interactions are observed,^{32,33} it is possible that a weak interaction between Ni and the aryl C_{ipso} (*e.g.*, C16 in Fig. 2) contributes to the formation of high molecular weight polyethylene. Most important, this work points to new opportunities regarding [PO] ligand design. We are currently exploring the reactivity of these complexes in the copolymerization of ethylene with polar monomers.

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Notes and references

‡ Crystal data for complex **2a** + 2C₆H₆. C₄₉H₄₇NiO₇PS, M = 869.6, triclinic, space group $P\bar{1}$, a = 11.165(7), b = 11.531(7), c = 17.445(11)Å, $\alpha = 72.330$ (9)°, $\beta = 90.065$ (10)°, $\gamma = 83.002$ (10)°, V = 2122(2)Å³, T = 150 K, Z = 2, $F_{(000)} = 912$, reflections measured: 15 376, unique reflections: 7172 [$R_{(int)} = 0.0414$]. The final wR2 was 0.1936. Complex **2b** + C₆H₆. C₃₅H₃₃NiO₅PS, M = 655.35, monoclinic, space group P2(1)/c, a = 12.848(4), b = 11.461(4), c = 22.104(7)Å, $\beta = 106.795(5)^\circ$, V = 3116.1(17)Å³, T = 150 K, Z = 4, $F_{(000)} = 1368$, reflections measured: 24 608, unique reflections: 6423 [$R_{(int)} = 0.0827$]. The final wR2 was 0.1313. CCDC 806742 and 806743.

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