

The surprisingly beneficial effect of soft donors on the performance of early transition metal olefin polymerisation catalysts†

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Group 4 metal complexes containing phenoxy-amide ligands bearing soft pendant donors are shown to give more highly active ethylene polymerisation catalysts than counterparts containing hard donors or systems without a pendant donor.

In recent years, there have been tremendous advances in the design of non-metallocene catalysts for olefin polymerisation.^{1,2} While ligands containing relatively hard nitrogen and oxygen donors have featured in catalyst systems across the transition series, reports of highly active catalysts incorporating soft tertiary phosphine donors have, for understandable reasons, been largely restricted to the mid-to-late transition metals. Notable examples include nickel-based catalysts supported by bidentate $[P,O]^2$ and $[P,P]^3$ ligands. The hard-soft mis-match of the early transition metal-phosphine combination, although occasionally broached,⁴ has not to date held any general promise of affording highly active catalyst systems. Here, we report the first examples of Group 4 metal catalysts whose activities are dramatically enhanced upon inclusion of soft neutral donor groups, tertiary phosphines in particular.

Monoanionic phenoxy-imines are amongst the most versatile ligands to have emerged in olefin polymerisation catalysis over the past 5 years or so.⁵⁻⁷ A key attraction of these ligands is their ready availability and amenability to modification *via* straightforward Schiff-base condensation procedures. We became attracted to building on this platform to prepare a family of dianionic chelate ligands derivable by simple reduction of iminophenol precursors.

The starting point for our studies were bidentate ligand systems. As an example, the 2,6-dimethylphenyl aminophenol was synthesised in good yield by $LiAlH_4$ reduction of the iminophenol precursor (Scheme 1). Its treatment with $Ti(CH_2Ph)_4$ or $Zr(CH_2Ph)_4$ in toluene gave the mononuclear dibenzyl complexes **1** and **2**, respectively.

Crystals of **2** were grown from a saturated pentane solution at $-30\text{ }^\circ\text{C}$.[†] Considering the benzyl units as monodentate, the geometry at zirconium is distorted tetrahedral (Fig. 1) with angles in the range $88.76(10)$ – $123.33(13)^\circ$, the most acute angle being associated with the bite of the chelating $[N,O]$ ligand. The Zr–C–Ar angles at each benzyl CH_2 moiety are distinctly contracted from ideal, being $87.0(2)^\circ$ at C(24) and $91.0(2)^\circ$ at C(31), with associated Zr–C(Ar) separations of $2.643(3)$ and $2.730(4)$ Å to C(30) and

C(37) respectively, values typical of η^2 interactions in related systems⁸⁻¹⁰ and distinctly different to those for η^1 -bound benzyl units.^{8,11} The short Zr–N(7) bond length of $2.025(3)$ Å clearly reflects the formal anionic nature of this donor atom which adopts a markedly distorted trigonal planar geometry; though N(7) lies only 0.09 Å out of the plane of its substituents, the angles at this centre range between $106.6(2)$ and $137.5(2)^\circ$, a consequence of the formation of the six-membered chelate ring. This ring has a twisted conformation with $\{Zr, O(1), C(1), N(7)\}$ coplanar to within 0.01 Å, C(6) and C(7) lying 0.49 and 0.99 Å out of this plane (on the same side) respectively. Preliminary ethylene polymerization tests revealed that **1** and **2** were not particularly active catalysts, affording activities of 22 and 32 gPE $\text{mmol}^{-1} \text{h}^{-1}$ (gPE = grams of polyethylene), respectively, in 1 atmosphere ethylene pressure tests.

We therefore decided to extend the study to tridentate derivatives containing hard and soft pendant donors, *viz.* where R = *o*-C₆H₄(OPh), quinoly1, *o*-C₆H₄(SPh), and *o*-C₆H₄(PPh₂). Treatment of these aminophenols with $Ti(CH_2Ph)_4$ gave the mononuclear products **3–6** in good yields. We were unable to obtain crystals of **3–6** suitable for X-ray analysis, but a closely related dimethylamide derivative **3b**, synthesised by treatment of $Ti(NMe_2)_4$ with the aminophenol, has been structurally characterised.[†] The geometry at titanium is distorted trigonal bipyramidal (Fig. 2) with the metal centre lying *ca.* 0.24 Å “below” the equatorial N₃ plane in the direction of the phenoxide oxygen O(1) [Ti–O(1) $1.885(2)$ Å]; the phenylether oxygen O(14) is comparatively loosely bound [Ti–O(14) $2.244(2)$ Å] and the axial O(1)–Ti–O(14) angle is $161.27(8)^\circ$.

The Ti–NMe₂ bond lengths of $1.892(3)$ and $1.886(3)$ Å to N(29)

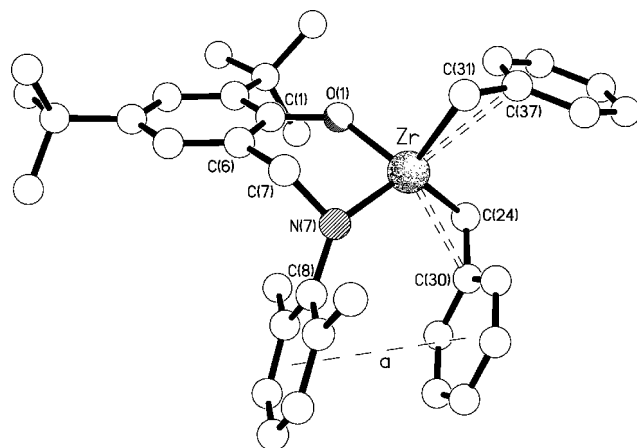
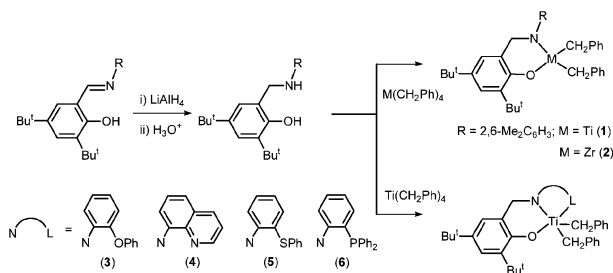


Fig. 1 The molecular structure of **2**. Selected bond lengths (Å) and angles ($^\circ$): Zr–O(1) $1.961(2)$, Zr–N(7) $2.025(3)$, Zr–C(24) $2.277(4)$, Zr–C(30) $2.643(3)$, Zr–C(31) $2.282(4)$, Zr–C(37) $2.730(4)$, C(24)–C(30) $1.465(5)$, C(31)–C(37) $1.460(5)$, O(1)–Zr–N(7) $88.76(10)$, O(1)–Zr–C(24) $108.75(12)$, O(1)–Zr–C(31) $102.53(12)$, N(7)–Zr–C(24) $123.33(13)$, N(7)–Zr–C(31) $108.42(13)$, C(24)–Zr–C(31) $118.64(13)$, C(30)–C(24)–Zr $87.0(2)$, C(37)–C(31)–Zr $91.0(2)$. The intramolecular π – π interaction **a** has centroid–centroid and mean interplane separations of *ca.* 3.67 and 3.37 Å respectively; the rings are inclined by *ca.* 3° .



Scheme 1

[†] Electronic supplementary information (ESI) available: crystal structures of **2** and **3b**. See <http://www.rsc.org/suppdata/cc/b4/b409870f/>

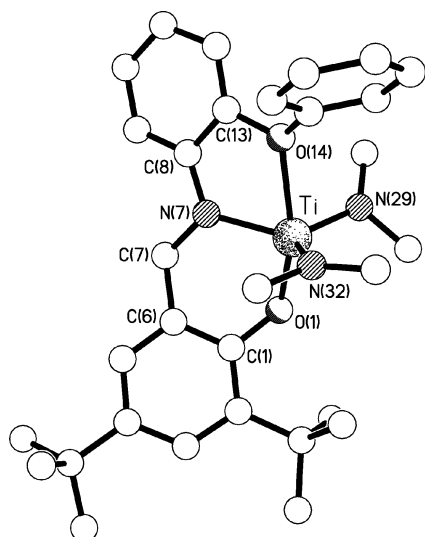


Fig. 2 The molecular structure of **3b**. Selected bond lengths (Å) and angles (°): Ti–O(1) 1.885(2), Ti–N(7) 1.986(2), Ti–O(14) 2.244(2), Ti–N(29) 1.892(2), Ti–N(32) 1.886(3), O(1)–Ti–N(7) 88.86(8), O(1)–Ti–O(14) 161.27(8), O(1)–Ti–N(29) 99.52(9), O(1)–Ti–N(32) 103.36(10), N(7)–Ti–O(14) 73.52(8), N(7)–Ti–N(29) 123.29(10), N(7)–Ti–N(32) 117.41(11), N(29)–Ti–O(14) 85.43(9), N(32)–Ti–O(14) 90.66(10), N(29)–Ti–N(32) 114.77(12).

and N(32) respectively are noticeably shorter than that to the amide nitrogen N(7) [1.986(2) Å], though in each case the nitrogen centre adopts an essentially trigonal planar geometry with N(7), N(29) and N(32) lying *ca.* 0.11, 0.08 and 0.01 Å out of the planes of their respective substituents. The 5-membered [N,O] chelate ring adopts an envelope conformation with the metal lying *ca.* 0.40 Å out of the C₂NO plane (which is coplanar to better than 0.01 Å). The 6-membered [N,O] chelate ring has a boat conformation with O(1) and C(7) lying *ca.* 0.56 and 0.37 Å respectively out of the {Ti, C(1), C(6), N(7)} plane (which is coplanar to within 0.09 Å).

The ³¹P NMR spectrum of **6** gave a singlet signal at 16.70 ppm (*cf.* –19.94 ppm for the pendant phosphine in the free amino-phenol), consistent with a coordinated tertiary phosphine unit. This signal remained unchanged in VT NMR spectra recorded to 90 °C. It is therefore reasonable to conclude that **6** is thermally robust with a closely related structure to **3b**, *i.e.* with a tridentate [O,N,P] ligand. The results of ethylene polymerization tests on compounds **3–6** (Table 1), activated by methylaluminoxane (MAO), revealed marked activity enhancements for catalysts containing the soft donor substituents. The phenyl ether adduct **3** and the quinolyl adduct **4** afforded activities <100 gPE mmol⁻¹ h⁻¹, values comparable to those obtained for the bidentate derivative **1**. By contrast, the phenylthioether derivative **5** afforded a much

Table 1 Polymerisation results for complexes **3–6**^a

Pre-catalyst (amount/ μmol)	Yield PE/g	Activity/g mmol ⁻¹ h ⁻¹ bar ⁻¹	<i>M</i> _n	<i>M</i> _w	<i>M</i> _w / <i>M</i> _n
3 (10.0)	0.44	88	83 700	306 500	3.7
4 (10.0)	0.48	96	17 400	617 500	35.5
5 (2.0)	3.53	3530	163 250	594 700	3.6
6 (0.2)	1.95	19 500	466 700	1 803 000	3.8

^a Conditions: 400 ml Fisher–Porter glass reactor, mechanical stirring, 25 °C, 2000 equiv. MAO, heptane solvent (200 ml), 1 bar ethylene pressure, 30 min.

more active catalyst system under the same conditions, giving an activity of 3530 gPE mmol⁻¹ h⁻¹. This was surpassed by the diphenylphosphine complex **6** which gave an activity of 19 500 gPE mmol⁻¹ h⁻¹. A comparison of the effect of temperature on catalyst performance for **4** *versus* **6** revealed that the activity for the hard donor ligand falls off rapidly above room temperature. By contrast, the activity for catalyst **6**/MAO increases with temperature, to an optimum *ca.* 70 °C. A possible explanation for this is binding of the hard aluminium centres within MAO to the hard O and N centres of the ether and quinolyl pendant groups leading to their dissociation from the metal centre. This would be anticipated to be less favourable for the soft thioether and phosphine donors, and would be further lowered for the phosphine derivative as a result of the additional steric protection afforded by its two phenyl substituents. Examination of the ³¹P NMR spectrum of a sample of **6** treated with excess MAO revealed a new tertiary phosphine resonance at 19.64 ppm, consistent with a bound phosphine in the active species. Although there is no evidence for a hemilabile effect from the available data, further studies of the active species will be required for a full assessment of this possibility.

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Notes and references

‡ Crystal data for **2**: C₃₇H₄₅NOZr, *M* = 610.96, monoclinic, *P*2₁/*n* (no. 14), *a* = 13.2413(15), *b* = 14.9424(15), *c* = 16.766(2) Å, β = 101.462(8)° *V* = 3251.2(6) Å³, *Z* = 4, *D*_c = 1.248 g cm⁻³, μ(Cu–Kα) = 2.969 mm⁻¹, *T* = 193 K, pale yellow blocks; 4818 independent measured reflections, *F*² refinement, *R*₁ = 0.039, *wR*₂ = 0.090, 3938 independent observed absorption-corrected reflections [*F*_o] > 4σ(*F*_o), 2θ_{max} = 120°], 362 parameters. CCDC 236411. Crystal data for **3b**: C₃₁H₄₃N₃O₂Ti·0.5C₅H₁₂, *M* = 573.66, monoclinic, *C*2/*c* (no. 15), *a* = 28.1195(8), *b* = 12.6087(7), *c* = 18.9179(13) Å, β = 94.379(4)° *V* = 6687.8(6) Å³, *Z* = 8, *D*_c = 1.139 g cm⁻³, μ(Cu–Kα) = 2.401 mm⁻¹, *T* = 183 K, yellow/orange prisms; 4970 independent measured reflections, *F*² refinement, *R*₁ = 0.047, *wR*₂ = 0.108, 3921 independent observed absorption-corrected reflections [*F*_o] > 4σ(*F*_o), 2θ_{max} = 120°], 368 parameters. CCDC 236412. See <http://www.rsc.org/suppdata/cc/b4/b409870f/> for crystallographic data in .cif or other electronic format.

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