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Ethylene polymerisation by a copper catalyst bearing α-diimine ligands

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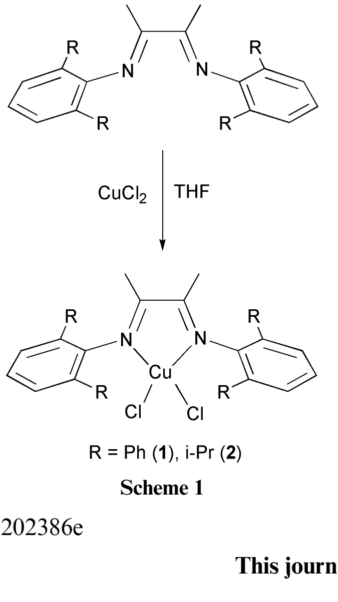
A copper α-diimine complex containing 2,6-diphenylphenylimino substituents is found to give good activities for ethylene polymerisation upon activation with methylaluminoxane (MAO), a result of the special stabilising effect of the *ortho*-phenyl groups.

In recent years there has been much interest in the development of new molecular catalyst families for the controlled polymerisation and co-polymerisation of olefinic monomers. Over the past 5 years in particular, a wide variety of new catalyst systems have been described.[1,2] Some of the most significant advances have occurred for late transition metal systems[3,4] where the greater tolerance of heteroatom functionalities leads to reduced poison sensitivity and offers the prospect of incorporating polar monomers into these otherwise solely hydrocarbon materials. Among the very late transition metals, copper presents an attractive candidate as a polymerisation-active centre, especially for the co-polymerisation of olefins with functional monomers. To date there have been no reports in the academic literature of copper catalysts for the polymerisation of olefins such as ethylene, propylene or 1-hexene, though a recent disclosure in the patent literature has described an active copper system bearing benzimidazole ligands.[5]

Here we report an active copper catalyst for the polymerisation of ethylene based on α-diimine ligands and the finding that *ortho*-phenyl substituents play a special role in the stabilisation of the active site.

The yellow–brown copper complexes **1**† and **2** were synthesised in good yields by treatment of $CuCl_2$ with the corresponding α-diimine in tetrahydrofuran at room temperature (Scheme 1).



R = Ph (**1**), i-Pr (**2**)

Scheme 1

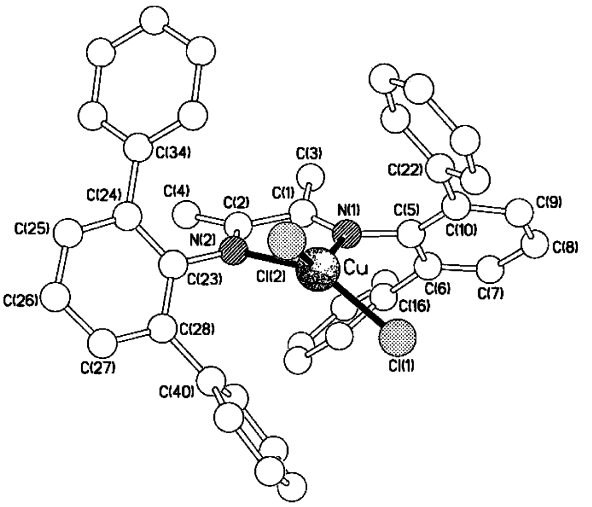


Fig. 1 The molecular structure of **1**. Selected bond lengths (Å) and angles (°): Cu–Cl(1) 2.1922(9), Cu–Cl(2) 2.1997(2), Cu–N(1) 2.038(2), Cu–N(2) 2.024(2), N(1)–C(1) 1.282(4), N(2)–C(2) 1.284(4); Cl(1)–Cu–Cl(2) 103.99(4), N(1)–Cu–N(2) 79.60(9), Cl(1)–Cu–N(1) 98.34(7), Cl(1)–Cu–N(2) 148.38(7), Cl(2)–Cu–N(1) 142.84(7), Cl(2)–Cu–N(2) 95.45(7).

Crystals of **1** suitable for an X-ray structure determination were grown from a dichloromethane solution of the complex layered with pentane; a view of the molecular structure is shown in Fig. 1. The structure analysis‡ shows the molecule to have approximate non-crystallographic C_2 symmetry about an axis passing through the copper atom and the centre of the C(1)–C(2) bond. The geometry at copper is intermediate between tetrahedral and square planar, the $CuCl_2$ unit being rotated about the molecular C_2 axis by *ca.* 46° out of the CuN_2 plane. Distortions of this type for four-coordinate copper(II) species are commonplace.[6] The independent Cu–N and Cu–Cl distances exhibit marginal differences, but are otherwise unexceptional. The five-membered chelate ring is slightly twisted (coplanar to within only 0.05 Å) such that C(3) and C(4) lie 0.26 and 0.18 Å respectively 'above' and 'below' its plane. Both C=N bonds have retained their multiple bond character. The torsional twists about the bonds linking the chelate and the aryl ring and between the aryl ring and its phenyl substituents are all very similar and range between 50 and 58°. It is interesting to note that the C(22) and C(40) phenyl rings are each rotated so as to effectively sandwich the $CuCl_2$ unit; the Cu ··· C(22) and Cu ··· C(40) distances are 3.32 and 3.23 Å respectively and these two vectors subtend an angle of 174° at copper. Surprisingly there is no intermolecular π–π stacking, though there are several aromatic edge-to-face interactions,

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Table 1 Ethylene polymerisation with complexes **1** and **2**[a]

No.	Catalyst/μmol	MAO/eq.	*P*/bar	PE yield/g	*A*/g mmol^{-1} h^{-1}
1	**1** (5.8)	500	30	1.8	300
2	**1** (20.0)	500	4.5	0.4	22.5[b]
3	**2** (20.0)	500	5.0	Trace	—

[a] Reaction conditions: toluene, 70 °C, 1 hour. [b] Polymerisation carried out at room temperature.

the shortest C–H ··· π contact having an H ··· π distance of 2.66 Å and C–H ··· π angle of 146°.

Ethylene polymerisation studies have been carried out in a Fisher–Porter glass reactor or in a stainless steel Parr reactor covering the pressure range 4–35 bar. Thus in a typical polymerisation experiment 100 ml of a 20 μM solution of complex **1** was treated with 500 eq. MAO and the resultant solution was exposed to an ethylene pressure of *ca.* 4 bar at 70 °C for 1 hour. The resultant polyethylene was filtered, washed with acidified methanol and dried under reduced pressure. The results were reproduced several times and are collected in Table 1. It can be seen that catalyst **1**/MAO shows a significant catalytic activity compared to its counterpart **2**/MAO which gave only trace quantities of product. Since the two complexes both possess bulky *ortho* substituents which afford a similar degree of steric protection of the active centre, the difference in their activity is likely due to a special effect of the *ortho*-phenyl substituents. A possibility is the stabilisation of the active centre through weak interactions with the *ortho*-phenyl substituents. Such effects have been proposed for nickel systems bearing 2,6-diphenylphenyl or other 2,6-diphenyl substituted aromatic groups attached to the imine nitrogens of α-diimine type ligands.[7]

The polymer obtained by both complexes **1** and **2** is very high molecular weight and could not be analysed either by GPC or by NMR spectroscopy.§

The investigations on the homo- and co-polymerisation of ethylene with polar monomers with these and other copper based catalysts are under way and will be reported in due course.

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Notes and references

† Synthesis of **1**. A mixture of 0.20 g (0.37 mmol) 1,4-bis(2,6-diphenylphenyl)-1,4-diazabutadiene and 0.05 g (0.37 mmol) anhydrous $CuCl_2$ in 20 ml THF was stirred at room temperature for 48 hours. The formed gold coloured precipitate was filtered, washed with 3 × 5 ml THF and dried *in vacuo*. Yield 0.16 g (64.1%). Analysis: Elemental analysis, Found C 71.25, H 4.89, N 3.98%. $C_{40}H_{32}N_2Cl_2Cu$ requires C 71.16, H 4.78, N 4.15%. ^1H NMR (250 MHz, CD_2Cl_2), δ/ppm: 1.48 (s, 4H), 1.82 (m, 1H), 3.68 (m, 1H), 5.32 (s, 6H), 7.56 (br. s, 6H), 9.06 (br. s, 14H). +FAB MS, *m*/*z*: 638 $(M - Cl)^+$, 603 $(M - 2Cl)^+$. FT IR (KBr)/cm^{-1}: 3053 (m), 3028 (m), 1591 (m), 1578 (m), 1495 (s), 1459 (s), 1439 (s), 1414 (v.s), 1376 (v.s), 1228 (s), 1143 (s), 1073 (s), 1030 (m), 845 (m), 811 (v.s), 763 (v.s), 697 (v.s).

‡ Crystal data for **1**: $C_{40}H_{32}N_2Cl_2Cu$, M = 675.1, monoclinic, space group $P2_1/c$ (no. 14), a = 11.3714(3), b = 14.5373(7), c = 20.1934(9) Å, β = 92.238(6)°, Z = 4, D_c = 1.344 g cm^{-3}, μ(Cu-Kα) = 2.63 cm^{-1}, $F(000)$ = 1396, T = 293 K; green prismatic needles, 0.67 × 0.20 × 0.17 mm, Siemens P4/PC diffractometer, ω-scans, 4961 independent reflections. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically using full matrix least-squares based on F^2 to give R_1 = 0.042, wR_2 = 0.098 for 3907 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \le 120°$] and 359 parameters. CCDC reference number 181355. See http://www.rsc.org/suppdata/dt/b2/b202386e/ for crystallographic data in CIF or other electronic format.

§ The solubility of the polymer sample in 1,2,4-trichlorobenzene was lower than 0.2 mg ml^{-1} at 160 °C, over 6 hours, indicating a molecular weight in excess of 5×10^6 g mol^{-1}.

1 G. J. P. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem., Int. Ed.*, 1999, **38**, 429.

2 S. D. Ittel, L. K. Johnson and M. Brookhart, *Chem. Rev.*, 2000, **100**, 1169.

3 For Ni and Pd, see: (*a*) L. K. Johnson, C. M. Killian and M. Brookhart, *J. Am. Chem. Soc.*, 1995, **117**, 6414; (*b*) L. K. Johnson, S. Mecking and M. Brookhart, *J. Am. Chem. Soc.*, 1996, **118**, 267; (*c*) A. Tomov, J. P. Broyer and R. Spitz, *Macromol. Symp.*, 2000, **150**, 53; (*d*) A. Held, F. M. Bauers and S. Mecking, *Chem. Commun.*, 2000, 301; (*e*) T. R. Younkin, E. F. Conner, J. I. Henderson, S. K. Friedrich, R. H. Grubbs and D. A. Bansleben, *Science*, 2000, **287**, 460; (*f*) V. C. Gibson, A. Tomov, A. J. P. White and D. J. Williams, *Chem. Commun.*, 2001, 719; (*g*) V. C. Gibson and A. Tomov, *Chem. Commun.*, 2001, 1964; (*h*) F. A. Hicks and M. Brookhart, *Organometallics*, 2001, **20**, 3217; (*i*) N. A. Cooley, S. M. Green, D. F. Wass, K. Heslop, A. G. Orpen and P. G. Pringle, *Organometallics*, 2001, **20**, 4769.

4 For Fe and Co, see: (*a*) G. J. P. Britovsek, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. J. McTavish, G. A. Solan, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1998, 849; (*b*) B. L. Small, M. Brookhart and A. M. A. Bennett, *J. Am. Chem. Soc.*, 1998, **120**, 4049; (*c*) G. J. P. Britovsek, M. Bruce, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. Mastroianni, S. J. McTavish, C. Redshaw, G. A. Solan, S. Stromberg, A. J. P. White and D. J. Williams, *J. Am. Chem. Soc.*, 1999, **121**, 8728; (*d*) G. J. P. Britovsek, V. C. Gibson, S. Mastroianni, D. C. H. Oakes, C. Redshaw, G. A. Solan, A. J. P. White and D. J. Williams, *Eur. J. Inorg. Chem.*, 2001, 431.

5 R. Stibrany, D. Shultz, S. Kacker and A. Patil, (Exxon Research and Engineering), WO 99/30822, 1999.

6 F. A. Cotton, G. Wilkinson, C. A. Murillo and M. Bochmann, *Advanced Inorganic Chemistry*, John Wiley & Sons, 1999, p. 865.

7 P. Mackenzie, L. S. Moody, C. M. Killian, J. A. Ponasik, G. G. Lavoie, J. C. Pearson, T. W. Smith, L. A. Tucker, M. M. Moore, A. Farthing, G. King, M. Meadows, C. Sass and E. Savitski, *Polym. Mater. Sci. Eng.*, 2001, **84**, 326.