ORGANOMETALLICS

Volume 23, Number 26, December 20, 2004

Communications

Diphosphine Complexes of Nickel(II) Are Efficient Catalysts for the Polymerization and Oligomerization of Ethylene: Steric Activation and Ligand Backbone Effects

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Received August 3, 2004

Summary: Nickel(II) complexes of ligands of the type $Ar_2PCH_2PAr_2$ and 1,2-$Ar_2PC_6H_4PAr_2$ (Ar = ortho-substituted phenyl) are active catalysts for polymerization and oligomerization of ethylene.

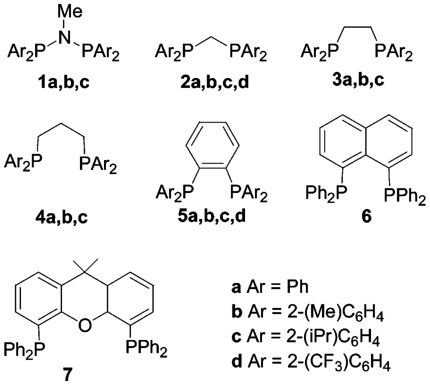

Figure 1. Ligand families.

The growing number of late-transition-metal olefin polymerization catalysts is almost exclusively based on "hard" nitrogen or oxygen donor ligands,[1] and despite the central role of diphosphine ligands in many other areas of homogeneous catalysis, "softer" phosphine donors generally yield very poor catalysts for this application.[2] We recently reported that the four-membered nickel(II) chelates derived from the aminodiphosphines **1a**−**c** (Figure 1) are very efficient catalysts for polymerization of ethylene, giving high-molecular-weight linear polymer.[3] Here we show that ligands **1a**−**c** are not unique, that other diphosphines give active polyethylene catalysts when suitably activated, and that catalytic activity and polymer structure are acutely sensitive to the nature of the ligand backbone and the substituents on the phosphorus.

Nickel complexes of the bis(diarylphosphino)methane ligands **2a**−**d** were activated and screened for polyethylene catalysis under the same conditions that

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[1] (a) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414. (b) Gates, D. P.; Svejda, S. A.; Oñate, E.; Killian, C. M.; Johnson, L. K.; White, P. S.; Brookhart, M. *Macromolecules* **2000**, *33*, 2320. (c) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283. (d) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 429. (e) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169.

10.1021/om0494014 CCC: $27.50 © 2004 American Chemical Society
Publication on Web 11/16/2004

Table 1. Ethylene Polymerization Results

entry	ligand[a]	yield[b]/g	activity/g mmol^{-1} h^{-1}	M_n[f]	M_w	M_w/M_n	total branches[c]
1	**2a**	4.0	200	C_4–C_{16} [d]			29
2	**2b**	5.4	260	C_4–C_{20}[d]			39
3	**2c**	10.0	500	500[c]			29
4	**2d**	12.0	600	540[c]			62
5[e]	**2b**	4.3	215	C_4–C_{20}[d]			34
6	**5a**	0.3	15	1 100	1 800	1.6	20
7	**5b**	5.0	250		11 000	g	6
8	**5c**	0.2	10	10 000	31 000	3.1	5
9	**5d**	0.2	10	67 000	170 000	2.5	1

[a] Activation method: ligand + [Ni(COD)$_2$] + H(OEt$_2$)$_2$BArF (where BArF = B(3,5-$C_6H_3(CF_3)_2)_4$) in toluene unless otherwise indicated. Conditions: 0.02 mmol catalyst, 40 cm^3 of toluene, 1 bar of ethylene, ambient temperature, 1 h run time (see Supporting Information). [b] Detemined by mass gain of Schlenk tube, corrected against blank run. [c] Methyl branches predominate in all cases, although longer branch types are also observed. More details, including typical branching distributions, are given in the Supporting Information. [d] Determined by GC-MS. A large number of isomers are present for each (even) carbon number. [e] Activation method: [Ni(acac)$_2$] (acac = acetylacetonate) + ligand, subsequently activated with 300 equiv of MAO in toluene. [f] Determined by GPC (gel permeation chromatography) unless otherwise stated. [g] Bimodal distribution with small high-molecular-weight peak; molecular weight given is M peak.

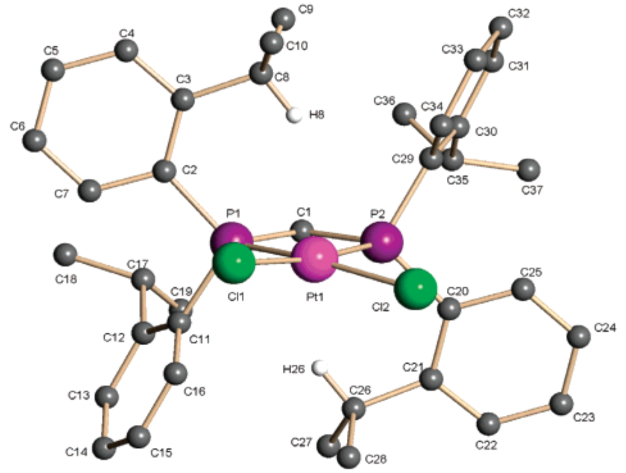

Figure 2. Molecular structure and numbering scheme for [PtCl$_2$(**2c**)]. All but isopropyl tertiary hydrogen atoms have been omitted for clarity. Important molecular dimensions include the following bond lengths (Å), bond angles (deg), and torsion angles (deg): Pt(1)–P(1) = 2.2301(9), Pt(1)–P(2) = 2.2202(9), Pt(1)–Cl(1) = 2.3627(9), Pt(1)–Cl(2) = 2.3465(9); P(1)–Pt(1)–P(2) = 75.96(3), Cl(1)–Pt(1)–Cl(2) = 91.99(3); Pt(1)–P(1)–C(2)–C(3) = 61.4, Pt(1)–P(2)–C(20)–C(21) = 54.7. Deviations from PtP2 plane (Å): Cl(1), 0.235; Cl(2), −0.306.

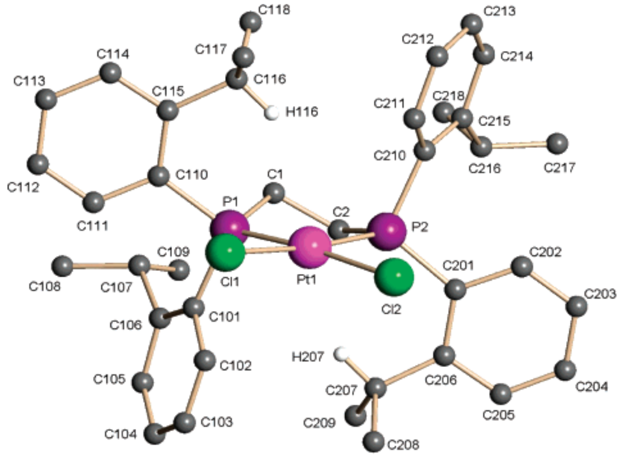

Figure 3. Molecular structure and numbering scheme for [PtCl$_2$(**3c**)]. All but isopropyl tertiary hydrogen atoms have been omitted for clarity. Important molecular dimensions include the following bond lengths (Å), bond angles (deg), and torsion angles (deg): Pt(1)–P(1) = 2.2395(16), Pt(1)–P(2) = 2.2391(17), Pt(1)–Cl(1) = 2.3571(15), Pt(1)–Cl(2) = 2.3706(15); P(1)–Pt(1)–P(2) = 88.02(6), Cl(1)–Pt(1)–Cl(2) = 91.44(6); Pt(1)–P(1)–C(110)–C(115) = 60.4, Pt(1)–P(2)–C(201)–C(206) = 59.6. Deviations from PtP$_2$ plane (Å): Cl(1), 0.224; Cl(2), −0.218.

gave active catalysts with the ligands **1a**–**c**; the results are given in Table 1. It is clear that these systems are active and the activity is a function of the ortho substituent. The activity increases in the order of increasing ligand steric bulk: **2a** < **2b** < **2c** < **2d** (compare entries 1–4 in Table 1), and in this regard, the **2a**–**d** systems resemble the four-membered chelates formed by **1a**–**c**.[3,4] However, the low-molecular-weight, highly branched polymer formed by the **2a**–**d** systems contrasts sharply with the high-molecular-weight, substantially linear material formed by the **1a**–**c** systems. This branching is consistent with the polymer elimination/reinsertion "chain walking" mechanisms that are widely reported for other nickel catalysts.[1] Very similar results are obtained if an alternative activation strategy is adopted using methylalumoxane (MAO) cocatalyst together with a nickel(II) acetylacetonate procatalyst (compare entries 2 and 5 in Table 1). This suggests that the same active site, presumably a cationic alkyl complex, is produced with both of these methods.[5]

In view of the success with the four-membered chelates we decided to extend our study to other chelating diphosphine ligands. However, the five-membered chelates formed by dppe (**3a**) and the six-membered rings formed by dppp (**4a**) were completely inactive under our standard conditions. Moreover, the larger rings are unresponsive to steric effects, complexes of the sterically demanding ligands **3b**,**c** and **4b**,**c** being inactive under our conditions.

In the hope of gaining insight into the reasons for the starkly different catalytic properties of nickel(II) complexes of **2c** and **3c**, we obtained X-ray crystal structures of the model platinum(II) compounds [PtCl$_2$(**2c**)][4] and [PtCl$_2$(**3c**)] (Figures 2 and 3, respectively) as their dichloromethane solvates.[6] In each case the complex has approximate C_2 symmetry. All the isopropyl groups have what is a characteristic conformation for tertiary phosphines carrying an *o*-isopropylphenyl substituent, in

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(3) (a) Cooley, N. A.; Green, S. M.; Wass, D. F.; Heslop, K.; Orpen, A. G.; Pringle, P. G. *Organometallics* **2001**, *20*, 4769. (b) Wass, D. F. WO01/10876 (to BP Chemicals Ltd).

(4) Dossett, S. J.; Gillon, A.; Orpen, A. G.; Fleming, J. S.; Pringle, P. G.; Wass, D. F.; Jones, M. D. *Chem. Commun.* **2001**, 699.

(5) ^{1}H NMR spectroscopy studies indicate that related cationic metal alkyl species are generated in each case for the active ligands **2** and **5** and the inactive **3** when using the ligand + [Ni(COD)$_2$] + H(OEt$_2$)$_2$-BAF activation method. This implies the effects described here are due to intrinsic activity or very short catalyst lifetimes rather than activation problems. See the Supporting Information.

which the tertiary C−H bond lies in the aromatic plane and eclipses the P−C bond (all 15 such groups in our work and the CSD[7] have this conformation). The set of four ortho-substituted aryl rings in [PtCl$_2$(**2c**)] and [PtCl$_2$(**3c**)] have the same conformations, such that both faces of the PtP$_2$Cl$_2$ plane are covered by the isopropyl groups. The principal difference between [PtCl$_2$(**2c**)] and [PtCl$_2$(**3c**)] is the larger bite angle in the latter (76 vs 88°) and the correspondingly smaller space available for substrate binding (inverse cone angle[8] of 125° in [PtCl$_2$(**3c**)] and 133° in [PtCl$_2$(**2c**)]). The electronic changes in the metal−ligand interaction that follow from the change in bite angle may also be important, but we note that the Cl−Pt−Cl angles (91°) and Pt−Cl distances in [PtCl$_2$(**2c**)] and [PtCl$_2$(**3c**)] (ca. 2.36 Å) are almost identical.

It was tempting to conclude that the activity of the systems formed from **1a**−**c** and **2a**−**d** is associated with the smaller bite angles of the four-membered chelates. However, the five-membered nickel(II) chelates formed by the 1,2-phenylene diphosphines **5a**,**b** also give active polymerization catalysts (entries 6−9 in Table 1) and show similar steric activation characteristics: i.e., **5a** < **5b**. The more bulky ligands **5c**,**d** gave polymer and the expected increase in molecular weight, but the activity was very low. This may be associated with problems of coordination with these bulky ligands, leading to low yields of active species; our attempts to coordinate **5c**,**d** to [NiBr$_2$(MeOCH$_2$CH$_2$OMe)] have been unsuccessful. Interestingly, the polymer formed by **5b**−**d** has high molecular weight and low branching: i.e., more akin to the polyethylene formed by the catalysts derived from **1a**−**c** than **2a**−**d**.

Our next hypothesis was that geometric constraint may be a key factor, since the ligands **1**, **2**, and **5** in the active catalyst families all have more rigid ligand structures than the inactive systems **3** and **4**. To test this, we screened ligands **6** and **7**, which have rigid structures combined with larger bite angles,[9] but neither of them gave catalytically active systems under the conditions described in the footnote to Table 1.

In conclusion, we have shown that diphosphine complexes of nickel(II) are active ethylene polymerization and oligomerization catalysts and that activity and polymer structure are acutely sensitive to the structure of the diphosphine ligand used. Variation to ligand backbone and phosphorus substituents allows the synthesis of a wide range of materials, from high-molecular-weight, linear polymers to low-molecular-weight, highly branched oligomers. Although a full rationale remains elusive to date, a number of important ligand factors have emerged. (i) Steric protection of axial coordination sites is beneficial to both activity and polymer molecular weight, as has been observed in nickel diimine catalysts.[1] Sterically demanding ligands are also likely to hinder the formation of multinuclear species in the case of ligand families **1** and **2**. (ii) Small bite angles are favored.[10] (iii) Ligands with rigid backbone structures are favored. Clearly, a combination of these factors is necessary to generate polymerization-active catalysts. Studies to further elucidate structure/activity relationships are ongoing.

Acknowledgment. We thank BP Chemicals Ltd for financial support and the Leverhulme Trust for a research fellowship (P.G.P.).

Supporting Information Available: Text and figures giving experimental details, polymerization procedures, and selected polymer branching analysis, and crystallographic details; full crystallographic data are given as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0494014

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(6) *Crystal structure analyses.* [PtCl$_2$(**2c**)]·CH$_2$Cl$_2$: see ref 4. [PtCl$_2$(**3c**)]·CH$_2$Cl$_2$: C$_{39}$H$_{50}$Cl$_4$P$_2$Pt, $M_r = 917.62$, monoclinic, space group $P2_1/c$ (No. 14), $a = 13.0163(16)$ Å, $b = 13.113(2)$ Å, $c = 23.449(3)$ Å, $\beta = 97.932(15)°$, $U = 3964.2(9)$ Å^3, $Z = 4$, $\mu = 3.916$ mm^{-1}, $T = 173$ K, 6975 unique data, R1 = 0.0384. We note the known structure of [PdCl$_2$(**3c**)] as its acetonitrile solvate (see: Wursche, R.; Klinga, M.; Rieger, B. Private communication to the CSD,[7] refcode KEQHUJ), which has a molecular geometry very similar to that of [PtCl$_2$(**3c**)].

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(8) The inverse cone angle, Ψ, is here defined as the angle of the cone with the metal atom at its apex which circumscribes the cone that touches the van der Waals surfaces of the diphosphine ligand (hydrogen) atoms. Therefore, $\Psi = 2[(180 - 0.25)\Sigma\theta_{\mathrm{Hn}} + \sin^{-1} 1.2/d_{\mathrm{M-H}}]$, where θ_{Hn} = angle (midpoint (P···P)−M−H; $d_{\mathrm{M-H}}$ = metal···hydrogen distance, and the summation is over the four hydrogens which most hinder approach to the metal (for the related accessible molecular surface concept, see: Angermund, K.; Baumann, W.; Dinjus, E.; Fornika, R.; Gorls, H.; Kessler, M.; Kruger, C.; Leitner, W.; Lutz, F. *Chem. Eur. J.* **1997**, *3*, 755).

(9) Van Leeuwen, P. W. N. M.; Dierkes, P. *J. Chem. Soc., Dalton Trans.* **1999**, 1519.

(10) We thank a reviewer for highlighting that small bite angles might also stabilize active Ni(II) species relative to inactive Ni(0) species.