COMMUNICATION

ChemComm
www.rsc.org/chemcomm

New thermally stable cationic η^3-allyl(1,4-diphospha-(1,3)-butadiene)nickel complexes for ethylene polymerization†

Alex Ionkin* and William Marshall
DuPont Central Research & Development, Experimental Station, Wilmington, DE 19880-0328, USA.
E-mail: alex.s.ionkin@usa.dupont.com; Fax: (302) 695-8281

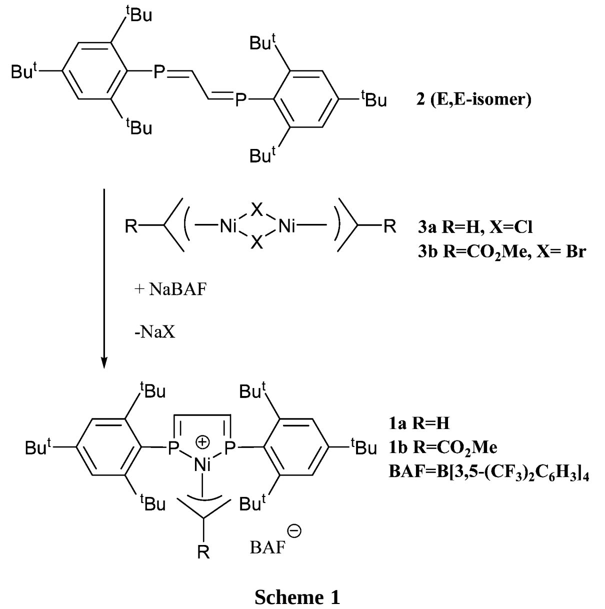
Received (in Corvallis, OR, USA) 13th November 2002, Accepted 17th January 2003
First published as an Advance Article on the web 17th February 2003

Nickel ethylene polymerization catalysts 1a,b bearing a P,P-ligand with two sp²-hybridized phosphorus atoms have been synthesized; their structure and polymerization studies have been reported for the first time.

The search for new homogenous ethylene polymerization catalysts with late transition metals is rapidly moving into the family of unusual sp²-hybridized phosphorus ligands. For example, platinum and palladium complexes active in ethylene polymerization with diphosphinidenecyclobutene ligands were reported recently.[1] 1,4-Diphospha-1,3-butadienes are low-coordinated di-phosphorus analogs of α-diimines, and are a key feature in the discovery of new late transition metal ethylene polymerization catalysts (trademarked the Versipol catalyst system by DuPont).[2] Low-coordinated phosphorus ligands[3] can participate in metal-to-phosphorus π-back-bonding, which could result in more thermally stable catalyst systems then those based on α-diimines.[1]

In this report, we describe the synthetic approach to, structures, and catalytic properties of η^3-allyl(1,4-bis[2,4,6-tri(*tert*-butyl)phenyl]-1,4-diphospha-(1,3)-butadiene)-nickel(1+) tetrakis[3,5-bis(trifluoromethyl)phenyl]borates(1−) **1a,b**. The above complexes were obtained by the reaction of an (*E*,*E*)-stereoisomer of 1,4-bis(2,4,6-tri(*tert*-butyl)phenyl)-1,4-diphospha-1,3-butadiene[4] **2**, π-allylnickel halide dimers **3a,b**[5] and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **4** (Scheme 1). The complexes **1a** and **1b** were isolated as green crystals in 95% and 42% yields after recrystallization from methylene chloride. Both of them were characterized by NMR spectroscopy and elemental analysis.[6]

The X-ray structure of **1a** (Fig. 1)‡ shows the nickel atom has 4-coordinate square planar stereochemistry with the chelating 1,4-diphospha-1,3-butadiene ligand and formally bidentate π-allyl ligand each occupying 2 sites. The quality of the crystals and the resulting structure are poor and only serve to establish the connectivity for this study.



Scheme 1

From the low-resolution X-ray structure it appears that the axis of the allyl group is slightly twisted, distorting the nickel atoms' square planar geometry. The aryl rings are almost perpendicular to the plane of the central ring, although they are shifted up and down from each other (Fig. 1).

The general procedure for ethylene polymerization is as follows. In a nitrogen-purged drybox, a 20 ml glass insert was loaded with the nickel compound (0.001 mmol) and, optionally, specified cocatalyst (*e.g.*, $B(C_6F_5)_3$). Next, the solvent (*p*-xylene (10 ml) in most examples) was added to the glass insert. The glass insert was then loaded in a pressure tube inside the drybox. The pressure tube was then sealed, brought outside the drybox, connected to the pressure reactor, placed under the desired ethylene pressure (600 psig in all cases) and shaken mechanically. After the stated reaction time (18 hours), the ethylene pressure was released and the glass insert was removed from the pressure tube. The polymer was precipitated by the addition of MeOH (~ 20 mL). The polymer was then collected on a frit and rinsed with MeOH. The polymer was transferred to a pre-weighed vial and dried under vacuum overnight. Table 1 summarizes the results for ethylene polymerization catalyzed by nickel complexes **1a,b**.

As seen from sixth column of Table 1, the prepared ethylene polymers have a low degree of branching compared with the α-diimine based catalyst.[2] Judging from DSC results (seventh column), the polymers possess fairly good crystallinity. Remarkably, the nickel catalysts **1a,b** bearing the 1,4-diphospha-1,3-butadiene ligand are thermally stable until 160 °C, which could be tied to the ability of this ligand to participate in metal-to-phosphorus π-back-bonding. Upon increasing the temperature of the polymerization from 60 °C to 160 °C, common trends with α-diimine based catalysts were observed: the productivity and molecular weights (M_w) have a tendency to decrease, but the degree of branching increases. The molecular weights (M_w) of ethylene polymers in Table 1 prepared from nickel catalysts **1a,b** with sp²-hybridized phosphorus ligand

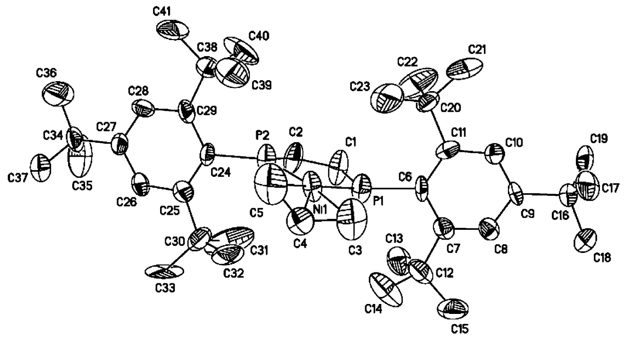


Fig. 1 An ORTEP drawing of the η^3-2-propenyl(1,4-bis[2,4,6-tri(*tert*-butyl)phenyl]-1,4-diphospha-(1,3)-butadiene)nickel(1+) moiety of **1a**. The borate anionic molecule, hydrogen atoms and the disordered allyl position have been omitted for clarity.

DOI: 10.1039/b211252c

---

† This is DuPont Contribution #08295.

Table 1 Ethylene polymerization results catalyzed by η^3-allyl(1,4-bis[2,4,6-tri(*tert*-butyl)phenyl]-1,4-diphospha-(1,3)-butadiene)nickel(1+) tetrakis[3,5-bis(trifluoromethyl)phenyl]borates(1−) **1a,b**

Entry	Catalyst	Temp./°C	Productivity[a]	M_w (M_w/M_n)	^{1}H-NMR branching[b]	m.p./°C (ΔH_f^*/J g^{-1})
1	**1a**	60	38.17	57591 (3.19)	6.63	131.60 (202.0)
2	**1a**	70	30.33	50269 (3.28)	5.21	129.53 (200.7)
3	**1a**	80	21.13	66256 (5.26)	8.16	130.37 (209.0)
4	**1a**	100	15.85	31849 (2.80)	8.91	130.18 (207.9)
5	**1a**	120	15.33	19879 (4.48)	8.62	130.76 (217.2)
6	**1a**	140	14.65	11880 (5.55)	12.30	122.50 (208.6)
7	**1a**	160	7.67	10117 (7.75)	73.60	130.76 (217.2)
8	**1b**	60	35.05	52438 (3.28)	6.80	129.21 (201.7)

[a] kg polymer/g Ni. [b] Total CH_3 per 1000 CH_2. Cocatalyst was $B(C_6F_5)_3$ 20 equiv. in all experiments.

seem to be in line with those from sp^3-hybridized phosphorus-based nickel catalysts.[7,8]

Notes and references

‡ For the crystal structure determination of **1a** a small green wedge shaped crystal with approximate dimensions of 0.10 × 0.08 × 0.01 mm was mounted and run at −100 °C on a Bruker Smart 1K diffractometer. The unit cell parameters were orthorhombic with space group = *P*212121, a = 14.2861(11) Å, b = 18.4281(15) Å, c = 27.872(2) Å, V = 7337.7(10) Å^3, Z = 4, calculated density = 1.396 g cm^{-3} and μ(Mo) = 0.41 mm^{-1}. The resulting refinement based upon F^2 for $C_{73}H_{77}BF_{24}NiP_2$ gave a formula weight = 1541.81. The overall quality of the structure is poor due to the small poorly formed crystallites available and the disordered groups. A treatment of the disorder is described in the CIF file. Merging the 30462 reflections yielded 9002 unique reflections (R_{merge} = 0.10). From the refinement the goodness-of-fit = 1.01, R indices [$I > 4\sigma(I)$] $R1$ = 0.0605, $wR2$ = 0.1280, R indices (all data) $R1$ = 0.1372, $wR2$ = 0.1667, max difference peak and hole = 0.710 and −0.344 e Å^{-3}. All of the hydrogen atoms were idealized using a riding model. CCDC 196917. See http://www.rsc.org/suppdata/cc/b2/b211252c/ for crystallographic data in CIF or other electronic format.

1 S. Ikeda, F. Ohhate, M. Miyoshi, R. Tanaka, T. Minami, F. Ozawa and M. Yoshifuji, *Angew. Chem., Int. Ed.*, 2000, **39**, 4512–4513.

2 S. D. Ittel, L. K. Johnson and M. Brookhart, *Chem. Rev*, 2000, **100**, 169–1203.

3 (*a*) K. D. Dillon, F. Mathey and J. F. Nixon, *Phosphorus: The Carbon Copy*, Wiley, Chichester, 1998, pp. 1–14; (*b*) L. D. Quin, *A Guide to Organophosphorus Chemistry*, Wiley, New York, 2000, pp. 307–345; (*c*) R. Appel, in *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, ed. M. Regitz and O. J. Scherer, Georg Thieme Verlag, Stuttgart, 1990, pp. 157–219.

4 R. Appel, J. Hunerbein and N. Siabalis, *Angew. Chem., Int. Ed.*, 1987, **26**, 779–780.

5 G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kroner, W. Oberkirch, K. Tanaka, E. Steinbucke, D. Walter and H. Zimmermann, *Angew. Chem., Int. Ed.*, 1966, **5**, 151–164.

6 **1a**: green crystals, m.p. 85.9 °C, yield 95%. ^{1}H NMR (500 MHz, CD_2Cl_2) δ = 1.22, 1.30, 1.31, 1.41, 1.49, 1.58 (each s, each 9H, t-Bu), 3.10 (s, broad, 2H, 2-allyl), 4.85 (s, broad, 2H, 2-allyl), 5.26 (s, 1H, central allyl-H), 7.48–8.20 (m, 6H, aromatic and =C–H protons). ^{31}P NMR (500 MHz, CD_2Cl_2) δ = 222.29; elementary analysis calcd. (%) for $C_{73}H_{77}BF_{24}NiP_2$: C 56.87, H 5.03, P 4.02; found: C 56.71, H 5.02, P 4.23. **1b**: green crystals, m.p. 43.2 °C with decomposition, yield 42%. ^{1}H NMR (500 MHz, CD_2Cl_2) δ = 1.01, 1.07, 1.09, 1.22, 1.26, 1.31 (each s, each 9H, t-Bu), 3.30 (s, broad, 2H, 2-allyl), 5.12 (s, broad, 2H, 2-allyl), 7.08–7.62 (m, 4H, aromatic protons). ^{31}P NMR (500 MHz, CD_2Cl_2) δ = 223.07; elementary analysis calcd. (%) for $C_{75}H_{79}BF_{24}NiO_2P_2$: C 56.31, H 4.98, P 3.87; found: C 56.16, H 5.12, P 4.11.

7 N. Cooley, S. Green and D. Wass, *Organometallics*, 2001, **20**, 4769–4771.

8 J. Feldman, E. Hauptman, E. McCord and M. Brookhart, *PCT Int. Appl.*, WO 9847934, 1998.