Regioselective propylene dimerization by tetrahedral (imino)pyridine Co^{II} dichloride complexes activated by MAO

Claudio Bianchini [*], Giuliano Giambastiani [*], Itzel Guerrero Rios, Andrea Meli,
Anna M. Segarra, Alessandro Toti, Francesco Vizza

*Istituto di Chimica dei Composti Organometallici (ICCOM-CNR), Area di Ricerca CNR di Firenze,
via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy*

Abstract

On activation by MAO, tetrahedral Co^{II} dichloride complexes supported by 6-organyl-2-(imino)pyridine ligands generate active catalysts for the dimerisation of propylene to hexenes. The nature of the substituent on the 6-position of the pyridine ring influences both the selectivity and activity of the catalysts. The 6-thienyl complexes $CoCl_2N_2^{2Th}$ and $CoCl_2N_2^{2BT}$ dimerise propylene prevalently to linear hexenes through a propagation pathway involving 1,2-insertion into Co-H, followed by 2,1-insertion and β-hydride elimination. The 6-phenyl complex $CoCl_2N_2^{Ph}$ is much less active and selective producing linear hexenes and methyl branched pentenes in comparable yields. The same activity trend and selectivity is observed for the dimerisation of 1-hexene, which however is one order of magnitude slower as compared to the dimerisation of propylene.
© 2007 Published by Elsevier B.V.

Keywords: Oligomerization; Propene; Regioselectivity; Cobalt; (Imino)pyridine ligands

1. Introduction

Systems comprising late transition metals and (imino)pyridine ligands are receiving considerable attention in homogenous catalysis, especially in C–C bond forming processes. Successful applications span from the polymerization of olefins via either insertion [1–3] or radical reactions [4], to the Suzuki coupling of haloarenes with phenylboronic acid [5], to the production of tailored low-density polyethylene (LDPE) via tandem reactions in conjunction with metallocenes [6], to the copolymerization of CO and olefins [7], to the bis-alkoxycarbonylation of styrene [8]. Tetrahedral (imino)pyridine Co^{II} complexes bearing aromatic substituents in the 6-position of the pyridine ring have been recently reported to oligomerise ethylene to C_4–C_{14} α-olefins in Schulz–Flory distribution with TOFs as high as 1.5×10^6 mol of C_2H_4 converted $(mol\,Co \times h)^{-1}$ [9].

We report here that, upon treatment with MAO in toluene, the tetrahedral (imino)pyridine Co^{II} complexes $CoCl_2N_2^{2Th}$, $CoCl_2N_2^{2BT}$, and $CoCl_2N_2^{Ph}$ (Scheme 1) generate active catalysts for the regioselective dimerisation of propylene to hexenes.

The transition metal-catalysed α-olefin dimerisation is an important process currently employed to produce versatile intermediates and building blocks for the chemical industry, spanning from comonomers for polyethylene to feedstocks for producing surfactans, platicizers, alcohols, pharmaceuticals and gasoline additives [10,11]. Specifically, branched dimers are preferred for the production of fuel additives and synthetic oils [12], while linear dimers find application in the area of fine chemical feedstocks [13].

The dimerisation of α-olefin is typically carried out in homogeneous phase with late-transition metal catalysts, almost exclusively containing nickel, cobalt or iron and either bidentate or tridentate ligands with nitrogen and oxygen donor atoms [12–15]. However, there are a few catalysts known to produce selectively linear olefin dimers with significant turnover frequencies [14–15]. All known cobalt systems contain 2,6-bis(imino)pyridine ligands and show good activities and selectivities in the oligomerisation of propylene, 1-butene and 1-hexene, giving highly linear dimers up to 98% and TOFs as high as several thousands of mol of olefin converted $(mol\,Co \times h)^{-1}$ [14]. The best results, in terms of productivity, have been

* Corresponding authors. Tel.: +39 055 5225280; fax: +39 055 5225203.
  E-mail address: claudio.bianchini@iccom.cnr.it (C. Bianchini).
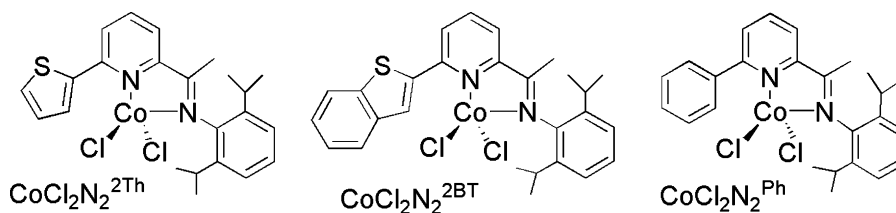
Scheme 1.

reported by Gibson for Co[II] bis(imino)pyridine catalysts stabilized by trifluoromethyl substituents on the aryl groups [14a].

2. Experimental

2.1. Materials and equipments

All air- and/or water-sensitive reactions were performed under a nitrogen in flame-dried flasks using standard Schlenk-type techniques. Anhydrous toluene was obtained by means of a MBraun Solvent Purification Systems. Solid methylaluminoxane (MAO) for oligomerisation was prepared by removing toluene and AlMe$_3$ under vacuum from a commercially available MAO solution (10 wt% solution in toluene, Sigma–Aldrich). The MAO solution was filtered on a D4 funnel and evaporated to dryness at 50 °C under vacuum. The resulting white residue was heated further to 50 °C under vacuum overnight. Modified methylaluminoxane (MMAO) was purchased from Akzo Nobel (7 wt% solution in toluene) and used as received. Literature methods were used to synthesize the tetrahedral cobalt complexes CoCl$_2$N$_2$[2Th], CoCl$_2$N$_2$[2BT], and CoCl$_2$N$_2$[Ph] (N$_2$[org] = 6-(organyl)-2-(imino)pyridine) [9]. 1-Hexene was passed over alumina and distilled under nitrogen before use. All of the other reagents and solvents were used as purchased from commercial suppliers. The GC analyses of the oligomerisation products were performed on a Shimadzu GC-17A gas chromatograph equipped with a flame ionization detector and a Supelco SPB-1 fused silica capillary column (30 m length, 0.25 mm i.d., 0.25 μm film thickness). The yields of dimers, trimers and tetramers were determined by comparing the integrals of the products to those of the internal standard (*n*-heptane) and by assuming equal response factors of the standard and the products. Specific GC analyses for the C$_6$ isomers were performed with a Varian PLOT fused silica capillary column with stationary phase PLOT Al$_2$O$_3$/KCl (50 m, 0.32 mm i.d., 5 μm film thickness). The GC/MS analyses were performed on a Shimadzu QP 5000 apparatus equipped with a column identical with that used for the GC analyses.

2.2. Catalytic reactions

2.2.1. Propylene oligomerisation procedure

2.2.1.1. In toluene (1 bar). A single-necked, round-bottomed flask (50 mL) equipped with a magnetic stirrer and a side gas inlet was heated under vacuum and then cooled to room temperature under nitrogen. Afterwards, the solid precatalyst (7.4 μmol) and toluene (8 mL) were introduced into the flask under a pos-

itive nitrogen flow. The suspension was stirred for 10 min to dissolve the precatalyst and then cooled with an ice-water bath. Propylene was bubbled for 15 min. Afterwards, the flask was close with a stopper fitted with a gas expansion bag as propylene reservoir and allowed to reach room temperature. The run was started by injection of a solution of MAO (1.52 mmol, ca. 200 equiv.) in toluene (2 mL) via a syringe. After the desired reaction period, the reaction was stopped by ventilating propylene under a stream of nitrogen and adding acidic MeOH (5% HCl, 1 mL). The reaction mixture was analyzed by GC using *n*-heptane (60 μL) as GC internal standard.

2.2.1.2. In toluene (10 bar). A 250 mL glass reactor equipped with a mechanical stirrer and an external jacket for the temperature control, was charged with the solid precatalyst (12 μmol) and toluene (26 mL) under nitrogen. The reactor was cooled at −15 °C and the liquid propylene (18.5 g) was transferred from the cylinder into the reactor via a flexible hose. A solution of MAO (7.2 mmol, ca. 600 equiv.) in toluene (4 mL) was injected into the reactor via a syringe. The reactor was rapidly warmed to room temperature and the solution stirred. The reactor internal pressure reached 10 bar. After the desired reaction period, the reactor was depressurized and the reaction was stopped by adding acidic MeOH (5% HCl, 1 mL). Finally, the reactor mixture was cooled to 0 °C and the dissolved propylene was completely ventilated off under vigorous stirring. Afterwards, *n*-heptane (200 μL) was added via syringe into the reactor as the GC internal standard and an aliquot of the reaction mixture was sampled for the GC analyses of the products.

2.2.1.3. In liquid propylene (10 bar). A 250 mL glass reactor equipped with a mechanical stirrer and an external jacket for the temperature control, was charged with the solid precatalyst (12 μmol) under nitrogen. The reactor was cooled at −15 °C and the liquid propylene (45.7 g) was transferred from the cylinder into the reactor via a flexible hose. MMAO (3.6 mmol, ca. 300 equiv., 4 mL) was injected into the reactor via a syringe. The reactor was rapidly warmed to room temperature and the solution stirred. The reactor internal pressure reached 10 bar. After the desired reaction time, the reactor was depressurized and the mixture was quenched by introducing acidic MeOH (5% HCl, 1 mL). Finally, the reactor mixture was cooled at 0 °C and the unreacted propylene was carefully evaporated under vigorous stirring. A solution of *n*-heptane (200 μL) in toluene (30 mL) was added into the reactor as the GC internal standard and an aliquot of the resulting solution was sampled for the GC analyses of the products.

2.2.2. 1-Hexene oligomerisation procedure

A single-necked, round-bottomed flask (50 mL) equipped with a magnetic stirrer and a side gas inlet was heated under vacuum and then cooled to room temperature under nitrogen. Afterwards, a suspension of the precatalyst (7.4 μmol) in either neat 1-hexene (10 mL) or 1-hexene (1.5 mL) in toluene (8.5 mL) was introduced into the flask under a positive nitrogen flow. The suspension was stirred for 10 min to dissolve the precatalyst before injecting a solution of MAO (1.52 mmol, ca. 200 equiv.) in toluene (2 mL) into the flask. All of the runs were terminated after 30 min by addition of acidic MeOH (5% HCl, 1 mL). Afterwards, n-heptane (60 μL) was added via syringe into the flask as a GC internal standard and an aliquot of the reaction mixture was sampled for the GC analyses of the products.

2.2.3. Hydrogenation of the α-olefin oligomerisation products

Hydrogenation of the reaction mixtures were carried out in a 20 mL stainless steel autoclave equipped with a magnetic stirrer at room temperature and 10 bar H_2 pressure for 16 h, using Pd/C 10% (80 mg) as catalyst. GC analysis of the hydrogenated products allowed for the quantification of both linear and branched species.

3. Results and discussion

3.1. Dimerisation of propylene

Upon treatment with MAO in toluene, the complexes $CoCl_2N_2^{2Th}$, $CoCl_2N_2^{2BT}$, and $CoCl_2N_2^{Ph}$ have been found to generate active catalysts for the selective dimerisation of propylene to hexenes. The results of batch reactions catalysed by these catalysts are summarized in Table 1. Since the presence of residual $AlMe_3$ in commercial toluene solutions of MAO may lead to undesired reaction paths [16,17], the oligomerisation reactions were carried out using a freshly prepared toluene solution of solid MAO obtained by removal under reduced pressure of the solvent and volatile impurities from the commercial sample. Under 1 bar propylene pressure (runs 1, 4–5), the TOFs increased in the order $CoCl_2N_2^{Ph} < CoCl_2N_2^{2BT} < CoCl_2N_2^{2Th}$ with the thiophen-2-yl Co^{II} precursor being one order of magnitude more active than the phenyl derivative. The selectivity in C_6 products was generally high, from 83% with the most active system (entry 1) to 96% with the least active, which is consistent with the occurrence of isomerisation only after most of propylene was consumed.

The presence of a thien-2-yl group in the 6-position of the pyridine ring apparently promotes the selective formation of linear dimers. Indeed, a selectivity of 87–88% in linear C_6 products, corresponding to 72–79% of the total product mass, was obtained using either $CoCl_2N_2^{2BT}$ or $CoCl_2N_2^{2Th}$. In contrast, the phenyl derivative $CoCl_2N_2^{Ph}$ gave a high level of methyl branched pentenes with only 52% of linear dimers.

Increasing the pressure of propylene from 1 to 10 bar in the reaction catalysed by $CoCl_2N_2^{2Th}$ (run 2) doubled the activity (TOF 2415 versus 4512) as well as gave a higher selectivity in olefin dimers (82.7 versus 93.3) and in 1-hexene (9.9 versus

Table 1
Dimerisation of propylene[a]

| Entry | Complex | Product mass (g) | TOF[g] | C6 (%) | C9 (%) | C12 (%) | C6 product distribution (%)[b] | | | | | | | Linear dimers of the product mass (%) |
| | | | | | | | Pathway A[c] | | | | | Pathway B[d]/C[e] | Pathway D[f] | |
							Linear dimers	1-Hexene	(E)-2-Hexene	(Z)-2-Hexene	(E+Z)-3-Hexene	Methyl-pentenes[h]	2,3-Dimethyl butenes	
1	$CoCl_2N_2^{2Th}$	0.37	2415	82.7	15.5	1.8	86.9	9.9	46.2	28.8	2.0	13.0	0.1	71.9
2[i]		1.14	4512	93.3	6.1	0.6	86.8	28.5	36.4	21.7	0.2	13.2	0.0	80.9
3[j]		1.24	4912	94.2	5.8	0.0	86.5	27.8	38.1	20.5	0.1	13.5	0.0	81.5
4	$CoCl_2N_2^{2BT}$	0.20	1289	89.7	9.5	0.8	88.4	17.5	34.8	35.2	0.9	11.5	0.1	79.3
5	$CoCl_2N_2^{Ph}$	0.04	225	96.4	3.5	0.1	52.3	19.2	23.4	7.8	1.9	47.2	0.5	50.4

[a] Reaction conditions: complex 7.4 μmol, propylene 1 bar, toluene 10 mL, MAO 200 equiv., 30 min, 25 °C.
[b] Products quantified by GC using n-heptane as internal standard.
[c] Propylene 1,2-insertion followed by propylene 2,1-insertion.
[d] Propylene 1,2-insertion, followed by propylene 1,2-insertion.
[e] Propylene 2,1-insertion, followed by propylene 2,1-insertion.
[f] Propylene 2,1-insertion followed by propylene 1,2-insertion.
[g] TOF: mol of C_3H_6 converted (mol Co)$^{-1}$ h^{-1}.
[h] 4-Methyl-pent-1-ene (E+Z)-4-methyl-pent-2-ene, 2-methyl-pent-1-ene, and 2-methyl-pent-2-ene; total amount determined after hydrogenation of final reaction mixture using 10% Pd/C and 10 bar of H_2.
[i] Reaction conditions: complex 12.0 μmol, propylene 18.5 g (10 bar), toluene 30 mL, MAO 600 equiv., 30 min, 25 °C.
[j] Reaction conditions: complex 12.0 μmol, propylene 45.7 g (10 bar), MMAO 300 equiv., 30 min, 25 °C.

28.5). As expected, the higher concentration of propylene was found to disfavour competing paths like the isomerisation of 1-hexene and the formation of trimers.

Almost identical results were obtained when the reaction was carried out in liquid propylene (run 3) using MMAO in the place of MAO which is poorly soluble in hydrocarbon solvents. The very small increase in productivity on going from toluene solution to neat propylene may be explained by the non-dependence of the dimerisation rate on propylene at high propylene concentration [12e], which suggests the migratory insertion of an alkyl olefin intermediate as the rate-determining step. Overall, the catalytic activity of $CoCl_2N_2^{2BT}$ and $CoCl_2N_2^{2Th}$ lies in the range of well-performing Co^{II} catalysts, being clearly surpassed by the o-trifluromethyl substituted 2,6-bis(imino)pyridine catalysts described by Gibson [14a].

The specific steps leading to the formation of various hexene isomers are reported in Scheme 2. The isomer distribution depends on several factors, which include the alternative migration of either n-propyl or isopropyl groups and the way this migration occurs (either 1,2- or 2,1-), and finally the regioselectivity of the β-H elimination steps when two possibilities exist for the latter (paths A and C). Since 3-hexenes account only for 2% of the total product and 2-methyl-2-pentene and 2,3-dimethyl-2-butene are practically absent, some mechanistic conclusions can be drawn from the quantitative analysis of the primary products. For the thien-2-yl catalysts $CoCl_2N_2^{2Th}$ and $CoCl_2N_2^{2BT}$, path A, involving 2,1-insertion of the n-propyl complex, is the major process for the dimerisation, accounting for 87–88% of the linear dimers (1-hexene, cis-2-hexene, and trans-2-hexene). Path C, involving 2,1-insertion of the isopropyl complex, accounts for the formation of all of the other

products, i.e., the branched pentenes 4-methyl-1-pentene, cis-4-methyl-2-pentene, and trans-4-methyl-2-pentene. Indeed, both 2-methyl-1-pentene (path B) and 2,3-dimethyl-1-butene (path D) were produced only in trace amounts. Overall, the thien-2-yl catalysts promote the insertion of the second propylene molecule exclusively in the 2,1-fashion.

Like the thien-2-yl catalysts, $CoCl_2N_2^{Ph}$ operates through paths A and C, yet it is much less active and selective producing linear hexenes (path A) and methyl branched pentenes (path C) in comparable yields. The lower selectivity may be ascribed to the reduced regioregularity of the first olefin insertion step as a consequence of the much weaker stereochemical control exerted by the 6-phenyl ring on the metal centre during olefin insertion [9a]. Indeed, a recent study has demonstrated that MAO converts the high-spin tetrahedral precursors into low-spin square-planar Co^{II} species with two nitrogen atoms from the (imino)pyridine ligand, a carbon atom from a methyl group, released by MAO, and a fourth weakly bound ligand provided by the organyl group in the 6-position of the pyridine ring (Scheme 3) [9a].

The fastening/unfastening of the sulfur atom in the thien-2-yl complexes was suggested, on one hand, to stabilize the electron-deficient transition state for migratory insertion, on the other hand to retard chain transfer by destabilize the transition state to α-olefin elimination. A similar role, yet not as efficacious as that exerted by the sulfur atom, was also hypothesized for the agostic C_{phenyl}–H···Co interaction (Scheme 3). Indeed, while $CoCl_2N_2^{2Th}$ and $CoCl_2N_2^{2BT}$ generate catalysts for the production of C_4–C_{14} α-olefins, only butenes are obtained with $CoCl_2N_2^{Ph}$, which is also one order of magnitude less active than the 2-thienyl precursors [9]. Since the three Co^{II} catalysts examined in this work have shown a similar activity trend in
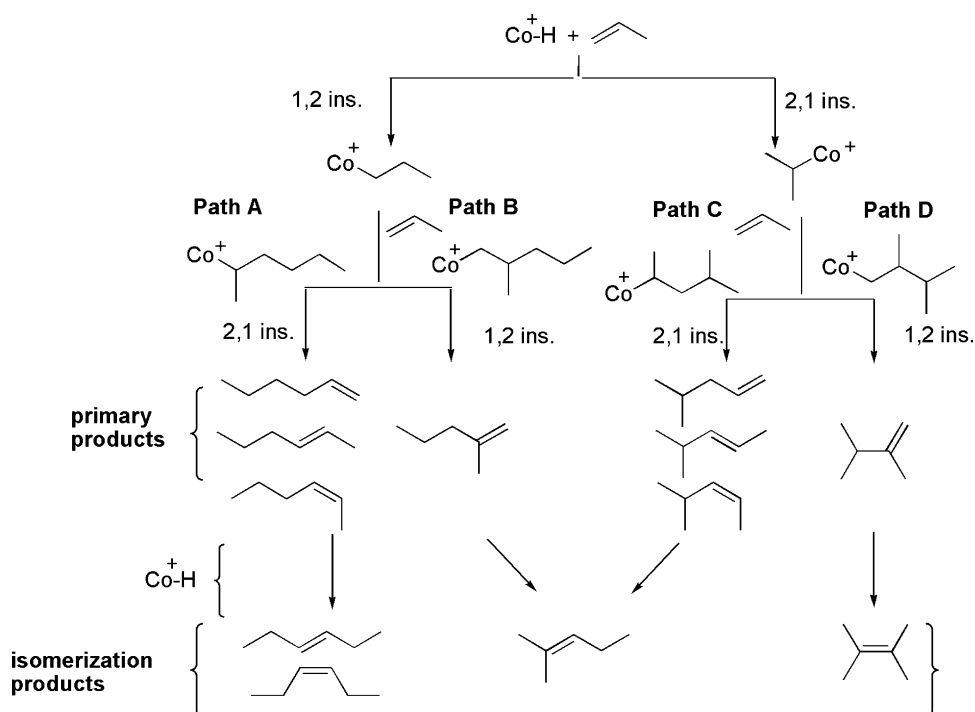
Scheme 2. Propylene dimerization pathways and isomerization of primary products.
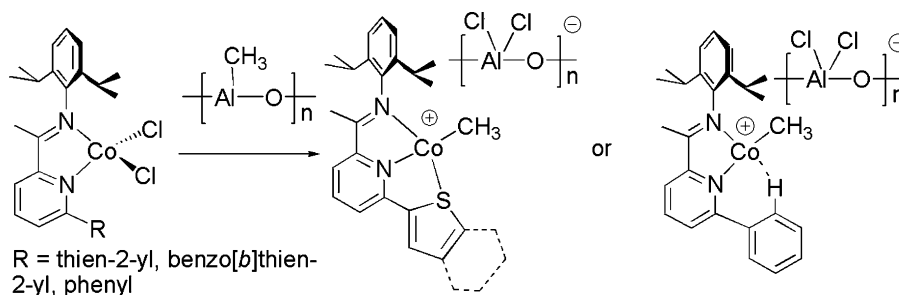
Scheme 3.

the dimerisation of propylene, one may reasonably extend these mechanistic considerations to the present reactions and, hence, conclude that the sulfur atom of the 2-thienyl substituent contributes to increase both the stability and steroselectivity of the square-planar Co–H or Co-alkyl species acting as an hemilable ligand.

Finally, it is worth mentioning that $CoCl_2N_2^{2BT}$ and $CoCl_2N_2^{2Th}$ produced also small amounts of linear trimers as shown by GC/MS analyses of the C_9 fractions obtained after hydrogenation of the final catalytic mixtures. Indeed, the C_9 fractions obtained with the thien-2-yl catalysts contained more than 80% linears nonenes. This is a clear indication that the C_9 byproducts were formed by a "step growth" mechanism [14c] rather than to a "chain growth" mechanism, which inevitably would lead to the formation of methyl-branched isomers (Scheme 4). According to the step growth mechanism, 1-nonene is the result of the reaction of n-hexenyl complexes

with propylene, while 4-nonene is formed by the coupling of n-propenyl species with 1-hexene.

To the best of our knowledge, both the linearity of the dimers and the selectivity in 1-hexene obtained with the precursors $CoCl_2N_2^{2BT}$ and $CoCl_2N_2^{2Th}$ have only one precedent in the literature [14c].

3.2. Dimerisation of 1-hexene

In some reactions catalysed by $CoCl_2N_2^{2Th}$, $CoCl_2N_2^{2BT}$ and $CoCl_2N_2^{Ph}$, propylene was replaced by 1-hexene (Table 2) with the aim of supporting the mechanism proposed for the former substrate as well as verifying the potential of the present catalysts for the oligomerisation/dimerisation of higher α-olefins [14a,15,18]. Under comparable experimental conditions, all catalysts gave C_{12} dimers in rather modest yields, however. The 1-hexene dimerisation process was
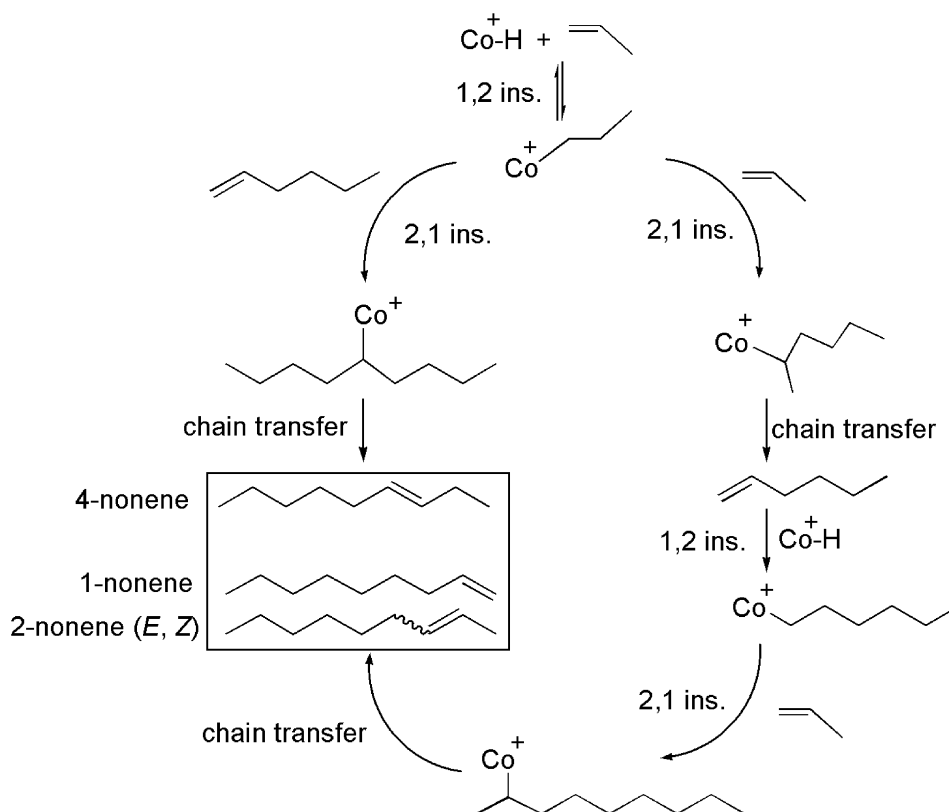
Scheme 4. Proposed mechanism of step growth for linear propylene trimers.

Table 2
The isomerisation and dimerisation data of 1-hexene[a,b]

Precatalyst	C6 (mL)	C6 (g)	Solvent	Time (h)	Isom.[c] (%)	Conv. (%)	Product mass (g)	C12 sel. (%)	g (g Co)^-1 h^-1	mol C6 (mol)^-1 h^-1	g (mmol)^-1 h^-1	D/I
CoCl2N2^2Th	10	6.78		0.5	6.84	2.89	0.20	99.0	905	634	53	0.42
	10	6.78		20	36.33	20.40	1.38	99.0	160	112	9	0.56
	1.5	1.02	Toluene	0.5	7.69	2.21	0.02	100	104	73	6	0.29
CoCl2N2^2BT	10	6.78		0.5	4.50	2.82	0.19	99.3	884	619	52	0.63
	10	6.78		20	30.29	18.76	1.27	98.9	147	103	9	0.62
	1.5	1.02	Toluene	0.5	2.50	0.91	0.01	100	43	30	3	0.36
CoCl2N2^Ph	10	6.78		0.5	2.30	0.28	0.02	100	88	61	5	0.12
	10	6.78		20	27.92	4.02	0.27	100	32	22	2	0.14
	1.5	1.02	Toluene	0.5	4.49	0.49	<0.01	100	23	16	1	0.11

[a] Reaction conditions: catalyst 7.4 μmol, solvent 30 mL, MAO 200 equiv., 25 °C.
[b] Products quantified by GC using *n*-heptane as internal standard.
[c] (*E*)-2-hexene ≥ (*Z*)-2-hexene ≫ (*E* + *Z*)-3-hexene.

accompanied by appreciable isomerisation to a mixture of internal isomers ((*E*)-2-hexene ≥ (*Z*)-2-hexene ≫ (*E* + *Z*)-3-hexene). Higher yields and higher dimerisation/isomerisation (*D/I*) ratios were obtained performing the reactions in neat 1-hexene rather than in toluene solution. As observed for the oligomerisation of propylene, the CoCl$_2$N$_2$^{2Th}/MAO system generated the most active catalyst with TOFs ranging from 73 in toluene, at relatively low 1-hexene concentration, to 634 in neat 1-hexene. On the other hand, irrespective of the catalyst, the dimerisation rates of 1-hexene were at least one order of magnitude slower than those of propylene under comparable reaction conditions (Table 1). The GC and NMR analysis of the C$_{12}$ olefin products revealed the selective formation of linear internal olefins (>90%), which was confirmed by the analysis of the hydrogenated reaction mixtures (10 bar H$_2$ pressure, Pd/C 10% catalyst). These data strongly suggest that the dimerisation of both 1-hexene and propylene occurs with a very similar mechanism, involving a cobalt(II) hydride initiator and two consecutive (1,2-/2,1-) insertions, followed by chain termination via β-H transfer. In the light of the present data, one may also conclude that the re-incorporation of higher olefins is a disfavored process for catalytic systems comprising 6-organyl-2-(imino) pyridine Co^{II} dihalides activated by MAO.

4. Conclusions

The catalytic dimerisation of propylene to hexenes has been achieved by activation with MAO of tetrahedral (imino)pyridine Co^{II} dichloride complexes containing an aromatic substituent in the 6-position of the pyridine ring. The nature of this substituent influences both the selectivity and activity of the catalysts. The 6-thienyl complexes CoCl$_2$N$_2$^{2Th} and CoCl$_2$N$_2$^{2BT} dimerise propylene prevalently to linear hexenes through a propagation pathway involving 1,2-insertion into Co–H, followed by 2,1-insertion and β-hydride elimination, while the 6-phenyl complex CoCl$_2$N$_2$^{Ph} is much less active and selective, yielding linear hexenes and methyl branched pentenes in comparable yields. On the basis of previous studies, it is suggested that the sulfur atom of the 2-thienyl substituent contributes to increase both the stability and regioselectivity of Co–H initiators as well as propagating Co-alkyl species.

References

[1] L.K. Johnson, J. Feldman, K.A. Kreutzer, S.J. McLain, A.M.A. Bennett, E.B. Coughlin, D.S. Donald, L.T. Jennings Nelson, A. Parthasarathy, X. Shen, W. Tam, Y. Wang (DuPont), U.S. Patent 5,714,556 (1998).

[2] (a) R. Chen, S.F. Mapolie, J. Mol. Catal. A: Chem. 193 (2003) 33;
(b) A. Koppl, H.G. Alt, J. Mol. Catal. A: Chem. 154 (2000) 45;
(c) X. Tang, W.-H. Sun, T. Gao, J. Hou, J. Chen, W. Chen, J. Organomet. Chem. 690 (2005) 1570;
(d) W.-H. Sun, X. Tang, T. Gao, B. Wu, W. Zhang, H. Ma, Organometallics 23 (2004) 5037;
(e) G.J.P. Britovsek, S.P.D. Baugh, O. Hoarau, V.C. Gibson, D.F. Wass, A.J.P. White, D.J. Williams, Inorg. Chim. Acta 345 (2003) 279;
(f) S.P. Meneghetti, P.J. Lutz, J. Kress, Organometallics 18 (1999) 2734;
(g) J.M. Benito, E. de Jesus, F.J. de la Mata, J.C. Flores, R. Gomez, P. Gomez-Sal, Organometallics 25 (2006) 3876.

[3] (a) T.V. Laine, M. Klinga, M. Leskelä, Eur. J. Inorg. Chem. (1999) 959;
(b) T.V. Laine, K. Lappalainen, J. Liimatta, E. Aitola, B. Löfgren, M. Leskelä, Macromol. Rapid Commun. 20 (1999) 487;
(c) T.V. Laine, U. Piironen, K. Lappalainen, M. Klinga, E. Aitola, M. Leskelä, J. Organomet. Chem. 606 (2000) 112.

[4] (a) D.M. Haddleton, C. Waterson, P.J. Derrick, C.B. Jasieczek, A.J. Shooter, Chem. Commun. (1997) 683;
(b) G. Tian, H.W. Boone, B.M. Novak, Macromolecules 34 (2001) 7656;
(c) V.C. Gibson, R.K. O'Reilly, D.F. Wass, A.J.P. White, D.J. Williams, Dalton Trans. (2003) 2824.

[5] C. Bianchini, G. Grenoble, W. Oberhauser, S. Parisel, F. Zanobini, Eur. J. Inorg. Chem. (2005) 4794.

[6] C. Bianchini, M. Frediani, G. Giambastiani, W. Kaminsky, A. Meli, E. Passaglia, Macromol. Rapid. Commun. 26 (2005) 1218.

[7] (a) Z. Jang, S.E. Adams, A. Sen, Macromolecules 27 (1994) 2694;
(b) C.R. Barr, M.C. Jennings, R.J. Puddephatt, Organometallics 20 (2001) 3459;
(c) J.M. Benito, E. de Jesus, F.J. de la Mata, J.C. Flores, R. Gomez, Organometallics 25 (2006) 3045.

[8] C. Bianchini, H.-M. Lee, G. Mantovani, A. Meli, W. Oberhauser, New J. Chem. 26 (2002) 387.

[9] (a) C. Bianchini, D. Gatteschi, G. Giambastiani, I. Guerrero Rios, A. Ienco, F. Laschi, C. Mealli, A. Meli, L. Sorace, A. Toti, F. Vizza, Organometallics 26 (2007) 726;
(b) C. Bianchini, G. Giambastiani, G. Mantovani, A. Meli, D. Mimeau, J. Organomet. Chem. 689 (2004) 1356;
(c) C. Bianchini, G. Mantovani, A. Meli, F. Migliacci, F. Laschi, Organometallics 22 (2003) 2545.

[10] (a) Y. Chauvin, H. Olivier, in: B. Cornils, W. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, vol. 1, VCH, New York, 1996, p. 258;
(b) J. Skupinska, Chem. Rev. 91 (1991) 613.

[11] (a) U. Englert, R. Haerter, D. Vasen, A. Salzer, E.B. Eggeling, D. Vogt, Organometallics 18 (1999) 4390;
(b) M. Matsuno, M. Kudoh, H. Imai (Nippon Oil Company) U.S. Patent 4533781 (1985);
(c) H. Sato, T. Nogushi, S. Yasui, Bull. Chem. Soc. Jpn. 66 (1993) 3069.

[12] (a) S. Wu, S. Lu, J. Mol. Catal. A: Chem. 197 (2003) 51;
(b) S. Wu, S. Lu, Appl. Catal. A: Gen. 246 (2003) 295;
(c) C. Carlini, M. Marchionna, A.M. Raspolli Galletti, G. Sbrana, J. Mol. Catal. A: Chem. 169 (2001) 19;
(d) H. Sato, H. Tojima, K. Ikimi, J. Mol. Catal. A: Chem. 144 (1999) 285;
(e) S.A. Sveja, M. Brookhart, Organometallics 18 (1999) 65.

[13] (a) B. Ellis, W. Keim, P. Wasserscheid, Chem. Commun. (1999) 337;
(b) P. Wasserscheid, M. Eichmann, Catal. Today 66 (2001) 309.

[14] (a) K.P. Tellmann, V.C. Gibson, A.J.P. White, D.J. Williams, Organometallics 24 (2005) 280;
(b) B.L. Small, R. Schmidt, Chem. Eur. J. 10 (2004) 1014;
(c) B.L. Small, Organometallics 22 (2003) 3178;
(d) N. Ajellal, M.C.A. Kuhn, A.D.G. Boff, M. Hörner, C.M. Thomas, J.-F. Carpentier, O.L. Casagrande Jr., Organometallics 25 (2006) 1213.

[15] B.L. Small, A.J. Marcucci, Organometallics 20 (2001) 5738.

[16] (a) E.Y.-X. Chen, T.J. Marks, Chem. Rev. 100 (2000) 1391;
(b) V. Busico, R. Cipullo, F. Cutillo, N. Friederichs, S. Ronca, B. Wang, J. Am. Chem. Soc. 125 (2003) 12402.

[17] (a) D.-J. Byun, S.Y. Kim, Macromolecules 33 (2000) 1921;
(b) G.J.P. Britovsek, S.A. Cohen, V.C. Gibson, P.J. Maddox, M. van Meurs, Angew. Chem. Int. Ed. 41 (2002) 489;
(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, D.J. Williams, J. Am. Chem. Soc. 121 (1999) 8728.

[18] (a) J. Zhang, H. Gao, Z. Ke, F. Bao, F. Zhu, Q. Wu, J. Mol. Catal. A: Chem. 231 (2005) 27;
(b) M.E. Bluhm, C. Folli, D. Pufky, M. Kroger, O. Walter, M. Doring, Organometallics 24 (2005) 4139.