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Screw Sense Selective Polymerization of Achiral Isocyanides catalysed by Complexes of Nickel(ii) and Optically Active Amines

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Polymerization of t-butyl and t-pentyl isocyanide by nickel(ii) in the presence of optically active amines yields helical polymers with an enantiomeric excess of up to 61%.

Poly(isocyanides) [poly(iminomethylene)] are rigid, highly isotactic polymers.1,2 They consist of right-handed (P) and left-handed (M) helices and, therefore, are chiral. Poly(isocyanides) are prepared from isocyanides by the catalytic action of nickel(ii) salts [reaction (1)].1 Mechanistic studies have shown that the polymerization reaction starts by attack of a nucleophile (Nu) on the square-planar complex Ni(CNR)2 [reaction (2)].1 In the resulting complex the carbon atom of C(Nu)NR has enhanced nucleophilicity and is now able to attack one of its neighbouring, co-ordinated, isocyanide ligands. Once started, the polymerization proceeds in the same direction through a series of consecutive insertion reactions.2,5c Such a behaviour could be attributed to a preferred binding of two molecules of either diene or dienophile. The results demonstrate the delicate geometric requirements to be fulfilled when a macrocycle is used to bind two different substrates within the cavity.

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References
11 (a) M. H. Abraham, J. Am. Chem. Soc., 1979, 101, 5477; (b) ibid., 1982, 104, 2085, and references cited therein; (c) unpublished results.
Figure 1. C.d. spectra of poly(t-butyl isocyanides): (A) optically pure (M)-polymer, (B) polymer sample containing 61% e.e. of (P)-helices (Table 1, run 4). The additional bands at 260 nm are caused by the phenyl rings of the 1-phenylethylamine end groups.

Table 1. Screw sense selective polymerization of t-butyl and t-pentyl isocyanide by nickel(II) and optically active initiators.

<table>
<thead>
<tr>
<th>Entry</th>
<th>R in RNC</th>
<th>Initiator</th>
<th>[α]D20 (°)</th>
<th>E.e. (%c)</th>
<th>Screw sense</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bu</td>
<td>(S)-(+)</td>
<td>-3.5</td>
<td>7</td>
<td>P</td>
</tr>
<tr>
<td>2</td>
<td>Bu</td>
<td>t-Pro</td>
<td>3.7</td>
<td>36</td>
<td>M</td>
</tr>
<tr>
<td>3</td>
<td>Bu</td>
<td>t-Phenylalaninol</td>
<td>21.8</td>
<td>37</td>
<td>M</td>
</tr>
<tr>
<td>4</td>
<td>Bu</td>
<td>(S)-(−)</td>
<td>-28.7</td>
<td>61</td>
<td>P</td>
</tr>
<tr>
<td>5</td>
<td>Bu</td>
<td>(S)-(−)-CH(Ph)MeNH2</td>
<td>-25.8</td>
<td>54</td>
<td>P</td>
</tr>
<tr>
<td>6</td>
<td>Pr</td>
<td>(S)-(−)</td>
<td>-9.7</td>
<td>5</td>
<td>P</td>
</tr>
<tr>
<td>7</td>
<td>Pr</td>
<td>(S)-(−)-CH(Ph)MeNH2</td>
<td>-6.9</td>
<td>6</td>
<td>P</td>
</tr>
</tbody>
</table>

Note: a Catalyst: Ni(BuNC)4(CIO4)2. b In CHCl3, c 0.5—1.0. c Enantiomeric excess calculated by comparing the [α]D values in the c.d. spectra of the samples with the [α]D value of optically pure (M)-(+)-(BuNC)4, see ref. 5. d Determined from the c.d. spectrum of the polymer samples, see ref. 5. e Catalyst: Ni(Pn'NC)4(CIO4)2. f Optical rotation is lower than expected from the e.e. value probably owing to an end group effect. g Optical rotation and c.d. spectrum of optically pure polymer are unknown.

We explain our results in the following way. Adding the optically active amine to Ni(CNR)2+)2 leads to a complex of type (1).† This reaction probably proceeds via co-ordination of the amine to the nickel centre, whereupon this nucleophile attacks one of the co-ordinated isocyanide ligands. Complexes similar to (1) derived from palladium, platinum, and molybdenum have been described before. In the first propagation step C1 attacks one of its neighbouring carbon atoms, for instance C2 or C3. When this attack takes place on C2 and proceeds in the direction C1 → C2 → C3 a right-handed helix is formed. When it occurs on C3 and subsequently on C4, C5, etc., a left-handed helix is formed. For achiral nucleophiles the attack of C3 on C2 and on C4 have equal probabilities, and a racemic mixture of left-handed and right-handed helices is obtained. In contrast, for chiral nucleophiles of the type used here, the direction of attack will depend on the position and the steric requirements of the substituents at the chiral carbon centre. In case of (S)-1-phenylethylamine and (S)-s-butyramine, polymers with an excess of right-handed screws are formed. This suggests that in the transition state of the first propagation step the phenyl and ethyl groups at the chiral centre are preferentially orientated

n R−N=C NiII + Ni(CNR)4+ → [R−N−C]+ (1)

Ni(CNR)4+ + Nu → Ni(CNR)3(C(Nu)NR)2+ (2)

t-Butyl isocyanide and t-pentyl (Pr) isocyanide3 were polymerized with a nickel complex prepared by adding 1 equiv. of an optically active amine (Table 1) to Ni(CNR)4+ (ClO4)2 (R = Bu3 or Prn).‡ 1.0 mol% of nickel catalyst was used. The reaction time varied between one day and one week. After work-up, polymer samples with Mw = 2200—3400 (end group determination by 1H n.m.r.) were obtained, which showed optical rotations and c.d. spectra characteristic for right-handed or left-handed helices (Table 1, Figure 1). The extent of asymmetric induction was calculated by comparing the c.d. spectra of the polymer samples with the c.d. spectra of optically pure (M)-(+)-(t-butyl isocyanide). The enantiomeric excess (e.e.) varied between 7 and 61% (Table 1). The highest value was obtained with (S)-(−)-1-phenylethylamine as the initiator and the lowest with (S)-(−)-s-butyramine (Table 1, entries 4 and 1).

† In a typical experiment (S)-(-)-l-phenylethylamine (1.15 mmol, [α]D20 40.3° (neat)) was added to a solution of Ni(Pn'NC)4(CIO4)2 (1.15 mmol)4 in CH2Cl2 (45 ml). After evaporation in vacuo a solid complex was obtained for which we propose the structure Ni(CNPr)4(C[NH(Me)Ph]NHPnt)(ClO4)2: [α]D20 +9.8° (c 0.3, CHCl3), fast-atom bombardment mass spectrum (matrix: glycerol, MeOH, H2O) m/z 666 (M−ClO4), 569 (M−ClO4−C10H15NC)−, 505 (M−2ClO4−C10H15NC+Cl)−, 437 (M−2ClO4−2C2H3NC)−, 311 (M−2ClO4−3C2H3NC+Cl)−, and 276 (M−2ClO4−3C2H3NC+2Cl)−; i.r. (CH2Cl2): 3290 (NH), 2246, 2247, and 2195 (co-ordinated NC); 1586, 1569, and 1537 (N=C−C=N) cm−1; 1H n.m.r. (CDCl3) δ 7.0—7.5 (m, 5H, ArH) and 0.2—3.0 (m, 50H, remaining H). t-Butyl isocyanide (9.1 mmol) was stirred with a sample of this complex (0.09 mmol, 1.0 mol%) at 25°C for 4 days. The volatile components were then removed in vacuo and the residue was treated with methanol (10 ml). The solid that precipitated was collected by filtration and washed with methanol to remove the nickel salt and oligomeric products. After drying in vacuo the polymer was obtained as pale yellow solid (0.28 g, 37%). [α]D20 −25.8° (c 0.15, CHCl3), i.r. (KBr) 1630 cm−1; 1H n.m.r. (CDCl3) δ 1.32 (s, Bu3), 7.1 (m, ArH) from initiator.

reactions around the nickel(II) centre. These insertion reactions may proceed in either a clockwise or counter-clockwise direction around this centre. In this way, both right-handed and left-handed helices will be formed. We report here that by using an optically active nucleophile, preferentially one type of helix is formed.

n R−N=C NiII + Ni(CNR)4+ → [R−N−C]+ (1)

Ni(CNR)4+ + Nu → Ni(CNR)3(C(Nu)NR)2+ (2)

t-Butyl isocyanide and t-pentyl (Prn) isocyanide were polymerized with a nickel complex prepared by adding 1 equiv. of an optically active amine (Table 1) to Ni(CNR)4+. 1.0 mol% of nickel catalyst was used. The reaction time varied between one day and one week. After work-up, polymer samples with Mw = 2200—3400 (end group determination by 1H n.m.r.) were obtained, which showed optical rotations and c.d. spectra characteristic for right-handed or left-handed helices (Table 1, Figure 1). The extent of asymmetric induction was calculated by comparing the c.d. spectra of the polymer samples with the c.d. spectra of optically pure (M)-(+)-(t-butyl isocyanide). The enantiomeric excess (e.e.) varied between 7 and 61% (Table 1). The highest value was obtained with (S)-(−)-1-phenylethylamine as the initiator and the lowest with (S)-(−)-s-butyramine (Table 1, entries 4 and 1).
towards the nickel. Consequently, the reaction occurs in the direction of C5, which becomes the sterically least hindered reaction path. The markedly higher enantiomeric excess obtained in the reaction with (S)-1-phenylethylamine could indicate that there is an additional stabilizing interaction between the phenyl ring of this amine and the nickel lone pair.

In the case of L-prolinol and L-phenylalaninol, it is not clear which group actually carries out the nucleophilic attack. It could involve either the amino or the alcohol function. The remaining functional group could co-ordinate as a second ligand to the nickel centre. From the observed screw sense (M-screw, Table 1) we are led to believe that the alcohol function is the nucleophile and the amino function the co-ordinating ligand. Experiments are currently being carried out to verify this.

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The Preparation and Structures of Metallathietane-3-oxides and -3,3-dioxides of Platinum and Palladium: the Crystal Structures of trans-2,4-Dibenzoyl-1,1-bis(triphenylphosphine)platinathietane-3-oxide and trans-2,4-Dibenzoyl-1,1-bis(triphenylphosphine)platinathietane-3-dioxide

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High yields of platinathietane-3-oxides and metallathietane-3,3-dioxides may be obtained by treatment of [MC2L2] with [RCH2SO(O)2CH2R] (n = 1, R = COPh; n = 2, R = COPh or CO2Me) and silver(i) oxide; single crystal X-ray studies on the title complexes establish the presence of puckered metallacycles, the sulphinyl oxygen of the platinathietane-3-oxide adopting an equatorial environment.

The utility of silver(i) oxide in the synthesis of an n1-oxo-dimethylenemethane complex via the ketone (1) led us to investigate reactions of related compounds, e.g. (2) and (3) in a metallasualitydacyclicacetic acid. Treatment of the sulfoxide (2) with cis-[PtCl2L2] (L = PPh3, PMePh2, or PMe2Ph) and silver(i) oxide in refluxing dichloromethane afforded the air-stable metallathietane-3,3-dioxide complexes (5a–c). A series of platina- and pallada-thietane-3,3-dioxides (5a–l) were also formed in quantitative yield via reactions of [MC2L2] (M = Pt or Pd, L = PPh3, PMePh2, PMe2Ph, PEt3, or PBn3) with the sulphone (3a) and silver(i) oxide. Similarly treatment of [MCl2(PPh3)2] (M = Pt or Pd) with the dimethyl ester of sulphonyldiacetic acid, in the presence of silver(i) oxide, afforded the metallathietane-3,3-dioxide complexes (5m) and (5n).

The synthesis of the metallathietane-3-oxide complexes (4a–c) provides a very convenient route to the first examples of the metallacyclic ring system M–C–S(O)–C and this is particularly noteworthy since our attempts to generate a source of the dianionic species [PhCH(S)(O)CHPh]2– via (PhCH2)2SO and BuLi and use this reagent in metallathietane-3-oxide synthesis have not been successful. In contrast the sulphine dianion [PhCH(S)(O)CHPh]2– is available and can be used in metallacyclesulphone synthesis. In previous studies on metallacyclobutan-3-ones of PtII and PdII the presence of highly puckered metallacyclic rings and transannular M···CO interactions has been established. The availability of platinathietane-3-oxide complexes (4) afforded the opportunity to investigate the conformation of this ring system and in particular to determine the competing conformational requirements of an oxygen atom and a non-bonding sulphur electron pair in a metallacyclosulphone. Accordingly a single crystal X-ray structure determination of (4a) was carried out together with that of the metallacyclic sulphone (5a) for comparative purposes.

References

+ Selected n.m.r. spectroscopic data (J in Hz); (4a): 1H(300 MHz, CDCl3, room temp.), δ 7.52–6.79 (m, 40H, Ph), 5.05{d, 1H, H(1)}, 2J[Pt(1)H(1)] 10.31, 2J[Pt(1)H(2)] 77.3, and 4.65 (d, 1H, H(2)), 1J[Pt(1)H(2)] 10.05, 1J[Pt(1)H(3)] 48.8, 31P(1H) (24 MHz, dichloromethane, relative to 85% H3PO4, second order AB spin system), 8 17.3 (d, P(1), 1J[Pt(1)P(2)] 2920, 1J[Pt(2)P(1)] 19.5), and 12.6 (d, P(2), 1J[Pt(2)P(2)] 2783, 1J[Pt(1)P(2)] 19.5).

‡ Crystal data: Crystals of (4a) and (5a) were grown slowly from dichloromethane–light petroleum. Data were collected at 293 K using Mo-Kα X-radiation, λ = 0.71069 Å, on a Stoe STADI-2 Weissenberg diffractometer. (4a): C24H18O2P2S2-2CH2Cl2, M = 1173.8, triclinic, space group P1, a = 13.819(3), b = 12.940(4), c = 19.24(1) Å, α = 118.0(1), β = 55.5(1), γ = 113.48(5)°, U = 2464.66 Å3, Z = 2, Dc = 1.36 g cm−3, μ(Mo-Kα) = 30.60 cm−1; final R 0.0487 (Re, 0.0512) for 7864 independent reflections (I ≥ 2σ(I)) in the range 7 < 2θ < 55°. (5a): C31H24O2P2S2-2CH2Cl2, M = 1189.8, triclinic, space group P1, a = 20.835(2), b = 10.626(2), c = 12.577(4) Å, α = 109.6(1), β = 105.8(1), γ = 91.3(1)°, U = 2501.97 Å3, Z = 2, Dc = 1.36 g cm−3, μ(Mo-Kα) = 30.16 cm−1; final R 0.0595 (Re, 0.0580) for 5553 independent reflections (I ≥ 2σ(I)) in the range 7 < 2θ < 55°. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

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1791