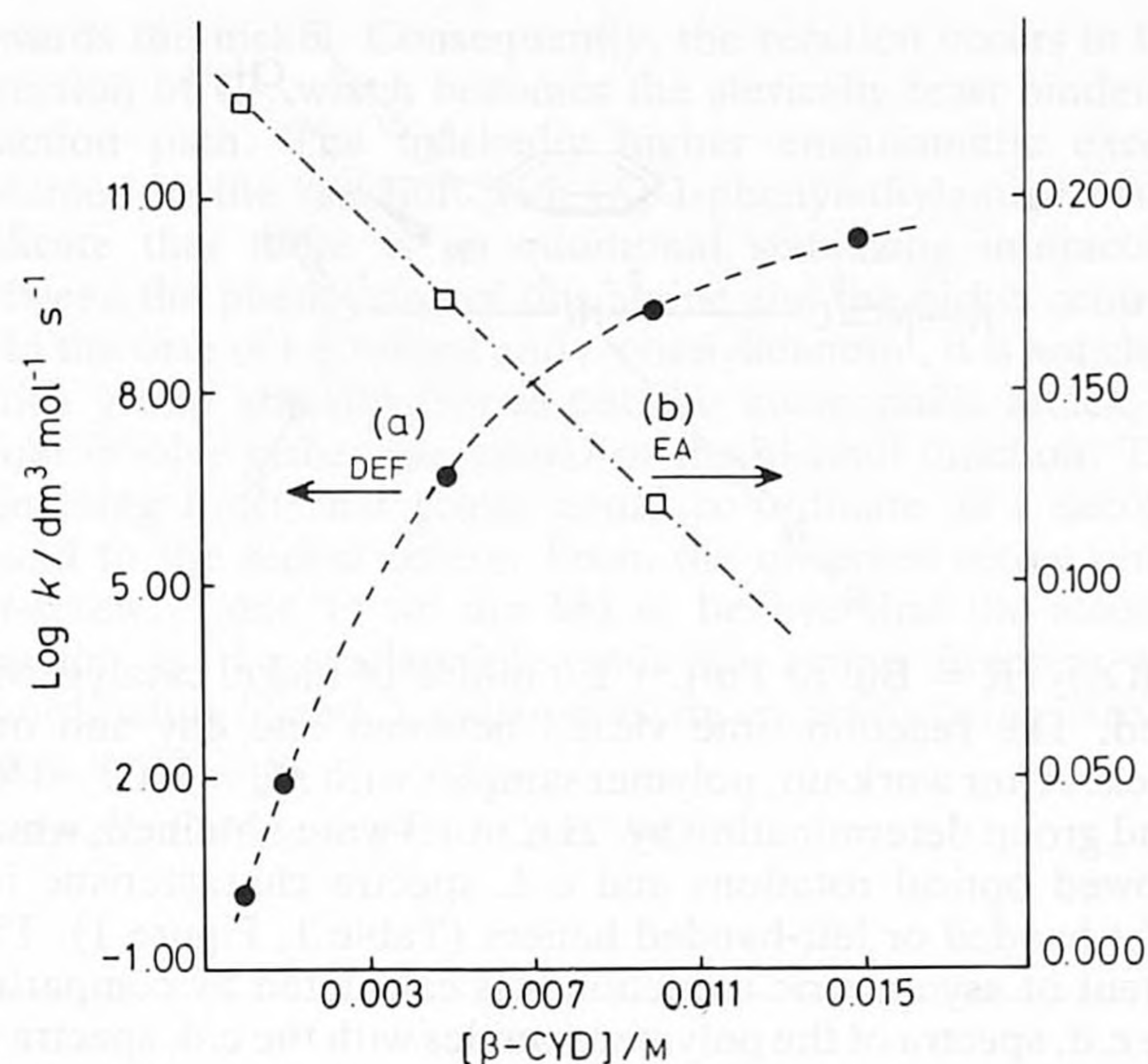Figure 3. Rate constants k_2 of the reaction (a) DEF + CP, (b) EA + CP (all at 20.0 °C, in water, 0.1 vol % dioxane) vs. [β-CYD] in mol^{-1} dm^{-3}.

tion of enzyme–analogue saturation kinetics with a Diels–Alder reaction, indicating the formation of ternary complexes. A full kinetic analysis must await an evaluation of the additional ternary and possibly also binary complexation constants between the host and diene as well as dienophile alone. Based on our experience with a related complex system,[6] these constants cannot be extracted from saturation kinetics alone but require independent measurements by spectroscopic methods. If one takes an association constant for the ternary complex [β-CYD·DEF·CP] of $K \sim 10^4$ dm^3 mol^{-1} from comparison with related cyclodextrins[13] as a conservative limit, the observed rates (Figure 3) would indicate a catalysed reaction with at least $k_{cat.} \sim 10^{-1}$ s^{-1}.‡

The reaction between ethyl acrylate (EA) and cyclopentadiene in the presence of β-cyclodextrin strikingly shows a rate

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‡ This estimate is derived from the assumption that with 0.15 M β-CYD the uncatalysed reaction is negligible (see Figure 3). The initial rate with [β-CYD] = 0.15 M and [DEF] = [CP] = 10^{-4} M is $v =$ [DEF$_o$][CP$_o$]$k_{obs.}$ = 10^{-7} which is also equal to v: $k_{cat.}$[Tern] = $v =$ 10^{-7}. The concentration of the ternary complex [Tern] at the concentrations given above is 10^{-7} M with $K = 10^4$ and, e.g., 10^3 (by mass law), which gives $k_{cat.}$ values of 10^{-1} s^{-1} or 1 s^{-1}, respectively.

decrease (Figure 3), reminiscent of some earlier observations.[2c,5a] 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.

References

1 For paper 7 of our series on Host–Guest Chemistry see: H.-J. Schneider and A. Junker, *Chem. Ber.*, 1986, **119**, 2815.
2 (a) R. Breslow, U. Maitra, and D. Rideout, *Tetrahedron Lett.*, 1983, **24**, 1901; (b) R. Breslow and U. Maitra, *ibid.*, 1984, **25**, 1239; (c) D. C. Rideout and R. Breslow, *J. Am. Chem. Soc.*, 1980, **102**, 7817.
3 P. A. Grieco, P. Galatsis, and R. F. Spohn, *Tetrahedron*, 1986, **42**, 2847; S. D. Larsen and P. A. Grieco, *J. Am. Chem. Soc.*, 1985, **107**, 1768, and earlier papers cited therein.
4 A. Lubineau and Y. Queneau, *Tetrahedron Lett.*, 1985, **26**, 2653; see also A. Lubineau, *J. Org. Chem.*, 1986, **51**, 2142.
5 (a) D. D. Sternbach and D. M. Rossana, *J. Am. Chem. Soc.*, 1982, **104**, 5853; (b) D. R. Williams, R. D. Gaston, and I. B. Horton, III, *Tetrahedron Lett.*, 1985, **26**, 1391.
6 H.-J. Schneider and R. Kramer, unpublished results.
7 H.-J. Schneider, K. Philippi, and J. Pöhlmann, *Angew. Chem.*, 1984, **96**, 907; *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 908.
8 J. A. Berson, Z. Hamlet, and W. A. Mueller, *J. Am. Chem. Soc.*, 1962, **84**, 297.
9 J. Sauer, H. Wiest, and A. Mielert, *Chem. Ber.*, 1964, **97**, 3183.
10 For empirical solvent parameters see, *e.g.*, C. Reichardt, 'Solvent Effects in Organic Chemistry,' Verlag Chemie, Weinheim, 1979.
11 (a) M. H. Abraham, *J. Am. Chem. Soc.*, 1979, **101**, 5477; (b) *ibid.*, 1982, **104**, 2085, and references cited therein; (c) unpublished results. We sincerely thank Dr. Abraham for a fruitful exchange of ideas and for allowing us to use *Sp* values prior to publication.
12 (a) H.-J. Schneider and K. Philippi, *Chem. Ber.*, 1984, **117**, 3056. For reviews on related azacyclophanes and their use as enzyme analogues see (b) K. Odashima and K. Koga, in: 'Cyclophanes,' vol. II, Academic Press Inc., New York, 1983, p. 626 ff; (c) H.-J. Schneider, R. Busch, R. Kramer, U. Schneider, and I. Theis, Advances in Chemistry, American Chemical Society, Washington D.C., in the press.
13 See M. L. Bender and M. Komiyama, 'Cyclodextrin Chemistry,' Springer Verlag, Berlin, 1978.

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(iminomethylenes)] 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)$_4$$^{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
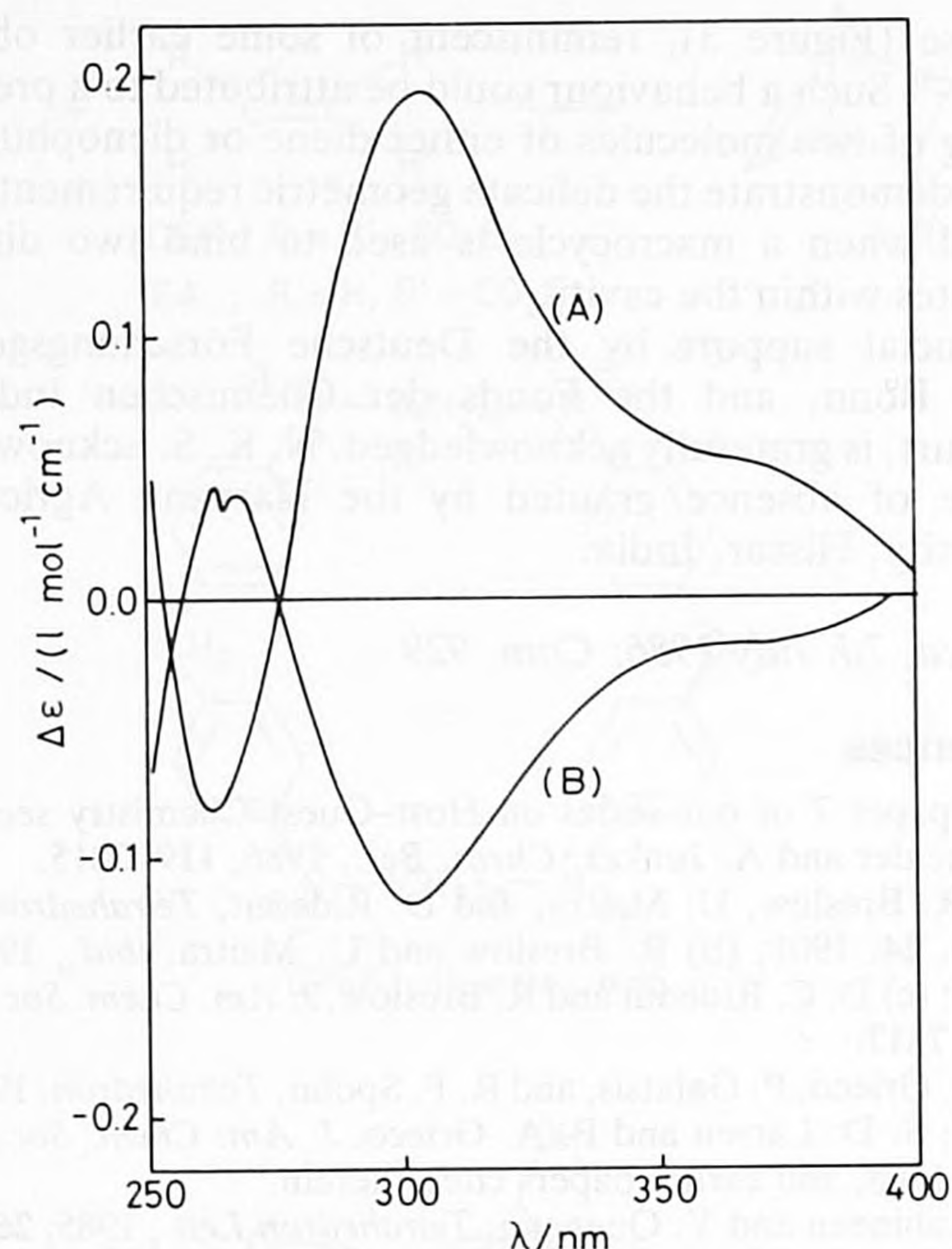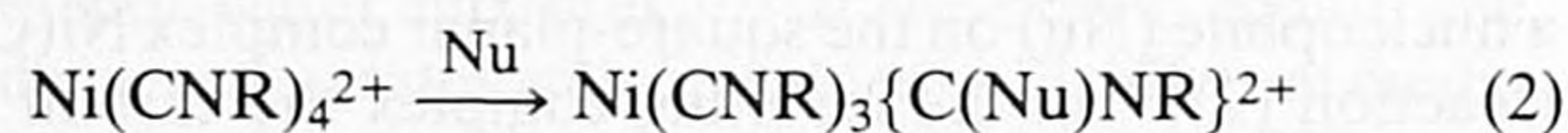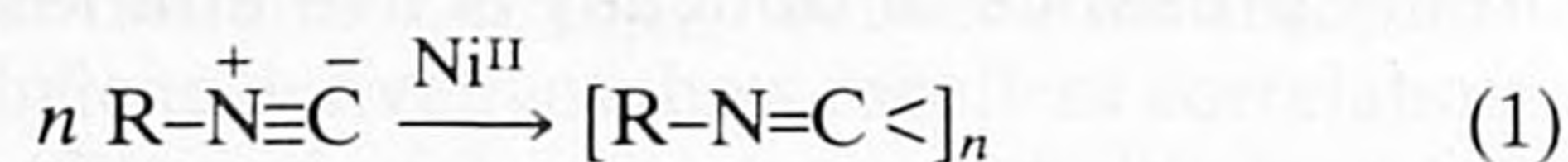
Figure 1. C.d. spectra of poly(t-butyl isocyanides): (A) optically pure (*M*)-polymer, (B) polymer sample containing 61% e.e. of (*P*)-helices (Table 1, run 4). The additional bands at 260 nm are caused by the phenyl rings of the 1-phenylethylamine end groups.

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

Entry	R in RNC	Initiator[a]	$[\alpha]_D^{20/\circ}$ [b]	E.e.,%[c]	Screw sense[d]
1	Bu^t	(*S*)-(+)-Bu^{s}NH$_2$	−3.5	7	*P*
2	Bu^t	L-Prolinol	3.7[f]	36	*M*
3	Bu^t	L-Phenylalaninol	21.8	37	*M*
4	Bu^t	(*S*)-(−)-CH(Ph)MeNH$_2$	−28.7	61	*P*
5	Bu^t	(*S*)-(−)-CH(Ph)MeNH$_2$[e]	−25.8	54	*P*
6	Pn^t	(*S*)-(−)-CH(Ph)MeNH$_2$	−9.7	g	*P*
7	Pn^t	(*S*)-(−)-CH(Ph)MeNH$_2$[e]	−6.9	g	*P*

[a] Catalyst: Ni(Bu^{t}NC)$_4$(ClO$_4$)$_2$. [b] In CHCl$_3$, *c* 0.5—1.0. [c] Enantiomeric excess calculated by comparing the $\Delta\varepsilon$ values in the c.d. spectra of the samples with the $\Delta\varepsilon$ value of optically pure (*M*)-(+)-(Bu^{t}NC)$_n$, see ref. 5. [d] Determined from the c.d. spectrum of the polymer samples, see ref. 5. [e] Catalyst: Ni(Pn^{t}NC)$_4$(ClO$_4$)$_2$. [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.

reactions around the nickel(II) centre. These insertion reactions may proceed in either a clock-wise or counter-clock-wise 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.

$$n\ R-\overset{+}{N}\equiv\overset{-}{C}\ \xrightarrow{\text{Ni}^{II}}\ [R-N=C<]_n \qquad (1)$$

$$\text{Ni(CNR)}_4^{2+} \xrightarrow{\text{Nu}} \text{Ni(CNR)}_3\{\text{C(Nu)NR}\}^{2+} \qquad (2)$$

t-Butyl isocyanide and t-pentyl (Pn^t) isocyanide[3] were polymerized with a nickel complex prepared by adding 1 equiv. of an optically active amine (Table 1) to Ni(CNR)$_4$-
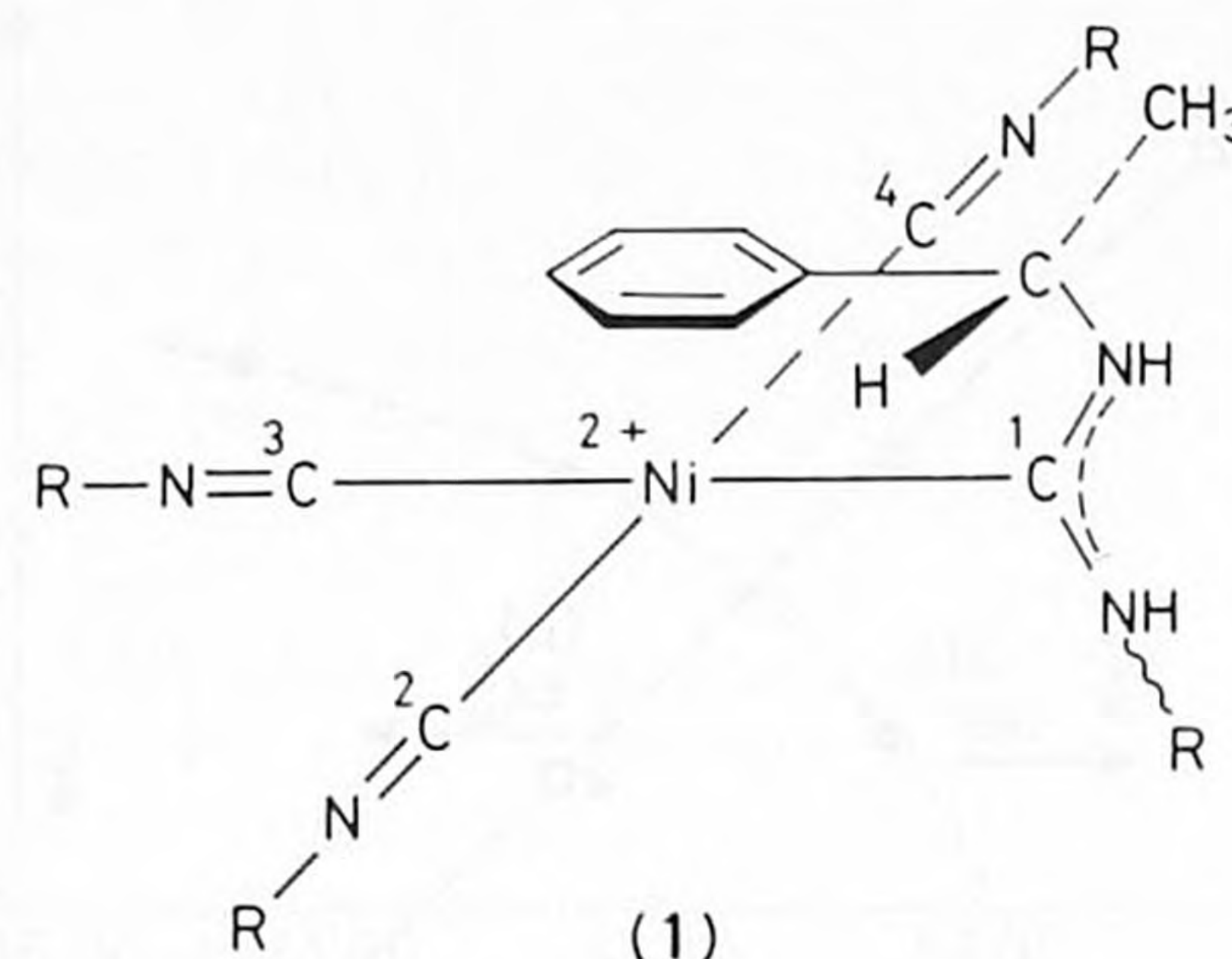
(ClO$_4$)$_2$ (R = Bu^t or Pn^t).[4†] 1.0 mol% of nickel catalyst was used. The reaction time varied between one day and one week. After work-up, polymer samples with M_n = 2200—3400 (end group determination by ^{1}H n.m.r.) were obtained, which showed optical rotations and c.d. spectra characteristic 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).[5] 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-butylamine (Table 1, entries 4 and 1).

We explain our results in the following way. Adding the optically active amine to Ni(CNR)$_4^{2+}$ 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.[6] Complexes similar to (**1**) derived from palladium, platinum, and molybdenum have been described before.[6] In the first propagation step C^1 attacks one of its neighbouring carbon atoms, for instance C^2 or C^4. When this attack takes place on C^2 and proceeds in the direction C$^1 \rightarrow$ C$^2 \rightarrow$ C^3 a right-handed helix is formed.[5] When it occurs on C^4 and subsequently on C^3, C^2, *etc.* a left-handed helix is formed. For achiral nucleophiles the attack of C^1 on C^2 and on C^4 have equal probabilities, and a racemic mixture of left-handed and right-handed helices is obtained.[5] 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-butylamine, 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

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† In a typical experiment (*S*)-(−)-1-phenylethylamine {1.15 mmol, $[\alpha]_D^{20}$ 40.3° (neat)} was added to a solution of Ni(Pn^{t}NC)$_4$(ClO$_4$)$_2$ (1.15 mmol)[4] in CH$_2$Cl$_2$ (45 ml). After evaporation *in vacuo* a solid complex was obtained for which we propose the structure Ni(CNPn^t)$_3${C[NH(Me)Ph]NHPn^t}(ClO$_4$)$_2$: $[\alpha]_D^{20}$ +9.8° (*c* 0.3, CHCl$_3$), fast-atom bombardment mass spectrum (matrix: glycerol, MeOH, HCl) *m/z* 666 (*M* − ClO$_4$), 569 (*M* − ClO$_4$ − C$_5$H$_{11}$NC)$^+$, 505 (*M* − 2ClO$_4$ − C$_5$H$_{11}$NC + Cl)$^+$, 373 (*M* − 2ClO$_4$ − 2C$_5$H$_{11}$NC)$^+$, 311 (*M* − 2ClO$_4$ − 3C$_5$H$_{11}$NC + Cl)$^+$, and 276 (*M* − 2ClO$_4$ − 3C$_5$H$_{11}$NC)$^+$; i.r. (CH$_2$Cl$_2$): 3290 (NH), 2246, 2247, and 2195 (co-ordinated NC); 1586, 1569, and 1537 (N—C—N) cm^{-1}; ^{1}H n.m.r. (CDCl$_3$) 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%); $[\alpha]_D^{20}$ −25.8° (*c* 0.15, CHCl$_3$), i.r. (KBr) 1630 cm^{-1}; ^{1}H n.m.r. (CDCl$_3$) δ 1.32 (s, Bu^t), 7.1 (m, ArH from initiator).

towards the nickel. Consequently, the reaction occurs in the direction of C^2, 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 centre.

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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References

1 W. Drenth and R. J. M. Nolte, *Acc. Chem. Res.*, 1979, **12**, 30.
2 F. Millich, *Macromol. Rev.*, 1980, **15**, 207.
3 R. E. Schuster, J. E. Scott, and J. Casanova, *Org. Synth.*, 1966, **46**, 75.
4 R. W. Stephany and W. Drenth, *Recl. Trav. Chim. Pays-Bas*, 1972, **91**, 1453.
5 A. J. M. van Beijnen, R. J. M. Nolte, A. J. Naaktgeboren, J. W. Zwikker, and W. Drenth, *Macromolecules*, 1983, **16**, 1679.
6 (a) J. S. Miller and A. L. Balch, *Inorg. Chem.*, 1972, **11**, 2069; (b) K. P. Wagner, P. M. Treichel, and J. C. Calabrese, *J. Organomet. Chem.*, 1974, **71**, 299; (c) E. M. Badley, J. Chatt, R. L. Richards, and G. A. Sim, *Chem. Commun.*, 1969, 1322; (d) P. Domiano, A. Musatti, M. Nardelli, and G. Predieri, *J. Chem. Soc., Dalton Trans.*, 1975, 2165; (e) R. D. Adams and D. F. Chodosh, *J. Am. Chem. Soc.*, 1976, **98**, 5391.

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-3,3-dioxide

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High yields of platinathietane-3-oxides and metallathietane-3,3-dioxides may be obtained by treatment of [MCl$_2$L$_2$] with [RCH$_2$S(O)$_n$CH$_2$R] (n = 1, R = COPh; n = 2, R = COPh or CO$_2$Me) 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 η^3-oxodimethylenemethane complex *via* the ketone (1)[1] led us to investigate reactions of related compounds, *e.g.* (2) and (3) in metallacyclic synthesis. Treatment of the sulphoxide (2) with cis-[PtCl$_2$L$_2$] (L = PPh$_3$, PMePh$_2$, or PMe$_2$Ph) and silver(I) oxide in refluxing dichloromethane afforded the air-stable platinathietane-3-oxide complexes (4a—c) in quantitative yield.† A series of platina- and pallada-thietane-3,3-dioxides (5a—l) were also formed in quantitative yield *via* reactions of [MCl$_2$L$_2$] (M = Pt or Pd, L = PPh$_3$, PMePh$_2$, PMe$_2$Ph, PMe$_3$, PEt$_3$, or PBu$^n_3$) with the sulphone (3a) and silver(I) oxide. Similarly treatment of [MCl$_2$(PPh$_3$)$_2$] (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 [PhCHS(O)CHPh]$^{2-}$ *via* (PhCH$_2$)$_2$SO and Bu^{n}Li and use this reagent in metallathietane-3-oxide synthesis have not been successful. In contrast

the sulphone dianion [PhCHS(O)$_2$CHPh]$^{2-}$ is available and can be used in metallacyclosulphone synthesis.[2]

In previous studies on metallacyclobutan-3-ones of Pt^{II} and Pd^{II} the presence of highly puckered metallacyclic rings and transannular M · · · CO interactions has been established.[1,3,4] 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 metallacyclosulphoxide. Accordingly a single crystal X-ray structure determination of (4a) was carried out together with that of the metallacyclic sulphone (5a) for comparative purposes.‡