J. Org. Chem. 1988, 53, 182-185

Notes

Conformational Studies by Dynamic NMR. 34.[1] Stereomutation and Torsional Processes in Aromatic Tertiary Amines

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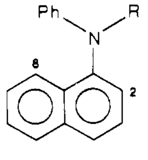
Received May 21, 1987

In sufficiently hindered aromatic amines the dynamic plane containing the rapidly inverting nitrogen atom is twisted with respect to the plane of the aromatic ring.[2] As a consequence, 1-naphthylamines, having different substituents at the N atom, give rise to a pair of enantiomeric conformers. At low temperatures the rate of exchange between these conformers is slow and in the case of derivatives containing prochiral probes[3] (e.g., ethyl or isopropyl groups) the geminal nuclei (i.e., the methylenic hydrogens of the ethyl moiety or the methylic hydrogens of the isopropyl moiety) become anisochronous, thus yielding different NMR signals.[4] Line shape analysis of these signals[5] affords the activation energy for the enantiomerization process.

If a phenyl group is bonded to the N atom a second motion, corresponding to the Ph–N torsional process, can be detected in addition to enantiomerization. In fact in derivatives of general structure



1: R = Me
2: R = Et
3: R = *i*-Pr

the enantiomerization process can be represented as indicated in Scheme I.

This process corresponds, in practice, to a rotation about the naphthyl–N bond and involves the passage from a twisted conformer A (represented as perpendicular for simplicity) to its enantiomer B, via a transition state where the dynamic plane of the N atom is coplanar to that of the naphthalene ring. In addition, it is also possible to detect the restricted rotation about the phenyl–N bond that involves the passage from the planar (or quasi-planar) topomer C to topomer C′ via a perpendicular transition state (Scheme II).[6]

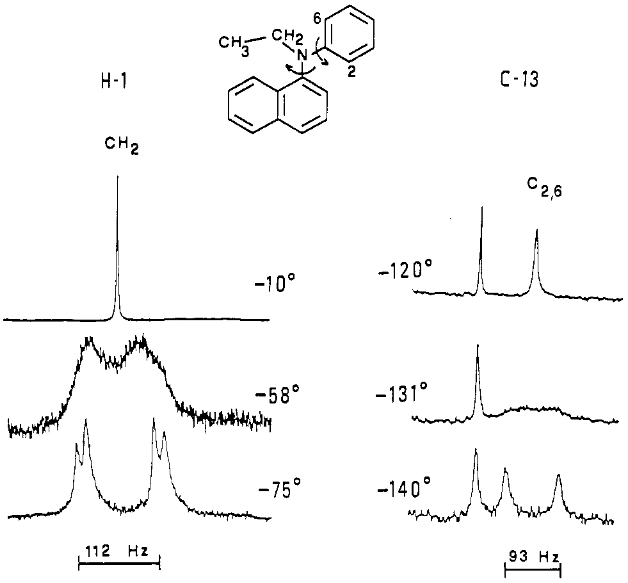
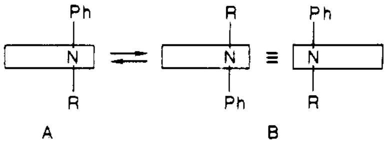
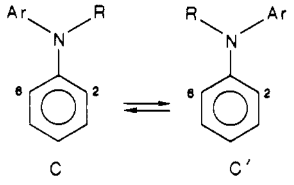


Figure 1. Left-hand side: NMR signal (^{1}H, 300 MHz) of the methylenic hydrogens of **2** taken in CD_2Cl_2 at various temperatures. The splitting due to the methylic hydrogens was eliminated by homonuclear decoupling. The hydrogens become anisochronous at −75 °C owing to the slow enantiomerization process described in Scheme I. Right-hand side: NMR signals (^{13}C, 25.16 MHz) of two lines in the aromatic region of **2**, taken in Me_2O at various temperatures. Whereas one of the two lines remains unchanged, that corresponding to the pair of ortho carbons of the phenyl ring (i.e., C-2, C-6) is split below −131 °C. The effect is due to the slow torsional process described in Scheme II.

Scheme I



Scheme II



Ar = 1-naphthyl

In order to follow the enantiomerization process (Scheme I) it is necessary to have a prochiral probe such as the ethyl group in **2** or the isopropyl group in **3**. The Ph–N rotation (Scheme II) can be observed on the other hand by following the ^{13}C NMR signals of the two ortho carbons (C-2 and C-6) of the phenyl group.[5]

The results of the experiments that allowed the detection of these two motions are reported in Figure 1 for the case of derivative **2**. On the left-hand side the proton signal (300 MHz) of the methylenic hydrogens, recorded while

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[1] Part 33. Casarini, D.; Lunazzi, L.; Macciantelli, D. *J. Org. Chem.*, in press.

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[3] (a) Jennings, W. B. *Chem. Rev.* **1975**, *75*, 307. (b) Reisse, J.; Ottinger, B.; Bickart, P.; Mislow, K. *J. Am. Chem. Soc.* **1978**, *100*, 911.

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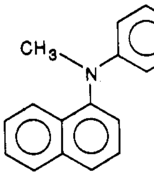
Table I. Free Energies of Activation (kcal mol^{-1}) and Chemical Shift Differences ($\Delta\nu$) Observed in Derivatives 1–4^a

compd	motion	$\Delta G^\ddagger$	$\Delta\nu_1$ Hz
1	rotation	7.1 (–120)	91.5 (–135)
2	rotation	6.5_5 (–131)	93 (–140)
	enantiom	10.2 (–58)	112 (–75)
3	rotation	7.8_5 (–104)	108 (–120)
	enantiom	11.0 (–39)	147 (–75)
4	enantiom	8.3_5 (–87, –99)	165 (–110)

[a] For the rotational barriers the shift difference is that of the ortho carbons at 25.16 MHz (solvent, dimethyl ether). For the enantiomerization barriers the shift difference is that of the appropriate anisochronous protons (see text) at 300 MHz (solvent, CD_2Cl_2). The temperatures (in °C) are given in parentheses for each value. The error[5] in $\Delta G^\ddagger$ is ±0.15 kcal mol^{-1}.

decoupling the triplet of the methylic hydrogens, is reported at three selected temperatures. At –75 °C the enantiomerization is slow enough so as to transform the singlet of the methylenic hydrogens into an AB spectrum, having a chemical shift difference of 112 Hz and J_{AB} = –14.5 Hz. On the right-hand side the two ortho carbons of the phenyl group (C-2 and C-6) display, at –140 °C, a pair of signals separated by 93 Hz (at 25.16 MHz), owing to the fact that the N–Ph rotation is now "frozen". The activation energies corresponding to these processes were obtained by line shape simulation and are collected in Table I.

It is obvious, however, that the enantiomerization process cannot be determined in the case of 1 (R = Me) since a suitable prochiral probe is not available.[7] To overcome this difficulty derivative 4 was prepared.



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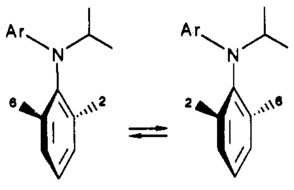
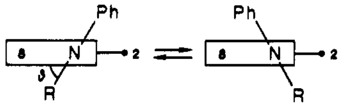
The ethyl group in the meta position of the phenyl ring acts as a prochiral probe and the corresponding barrier for the enantiomerization is expected to be essentially equal to that of 1. The value obtained from derivative 4 (Table I) will be thus considered as a substitute for the unknown value of 1.

The torsional barrier about the Ph–N bond decreases in 2 (R = Et) with respect to 1 (R = Me): a result expected for situations having coplanar ground states and perpendicular transition states.[8–10] The steric effects in fact destabilize a planar conformation more than a perpendicular one. Contrary to expectation, the barrier of 3 (R = *i*-Pr) is larger than those of 2 and 1. This might be taken as an indication that the steric demand is increased so much when R is an isopropyl group as to reverse the situation of the phenyl group, such that in the ground state it is forced to align itself, contrary to the case of 1 and 2, perpendicular[11] to the dynamic plane of the aminic nitrogen (Scheme III). The transition state would then become planar, rather than perpendicular, and this might explain why derivative 3 does not follow the expected decreasing trend of the $\Delta G^\ddagger$ values as observed for 1 and 2. Although direct evidence in favor of this hypothesis is not available, there are many examples where a similar reversal in the conformational symmetry due to steric demand has been unambiguously detected.[5,12–15]

Scheme III



Scheme IV



I II

The barriers for the enantiomerization process on the other hand were found to increase regularly with the increasing bulkiness of R. The corresponding $\Delta G^\ddagger$ values are in fact 8.3_5, 10.2, and 11.0 kcal mol^{-1} when R is Me, Et, and *i*-Pr (i.e., derivatives 4, 2, and 3) respectively. This trend is typical of systems having a twisted ground state and a planar transition state:[5,15] the steric effects destabilize, in fact, the planar transition state more than the twisted ground state. However, the difference between the barriers of 2 and 4 (i.e., for the case R = Et and R = Me) is twice as large (1.85 kcal mol^{-1}) as the difference (0.8 kcal mol^{-1}) between the barriers of 3 and 2 (i.e., for the case R = *i*-Pr and R = Et). This observation is quite surprising as the isopropyl group is expected to have, with respect to the ethyl group, at least an equal and possibly a larger steric effect than that of the ethyl with respect to the methyl group.

In order to explain this result it has to be considered that the conformation of the ground state for each of the enantiomers A or B of Scheme II is better described by an equilibrium between the pair of nonequivalent conformers I and II shown in Scheme IV.

The barrier for this process is too low to be detected by NMR, and therefore the spectrum observed at low temperature represents the average between the spectra of conformers I and II. The angle ϑ should increase with the bulkiness of the R group, thus making the ground state less stable, since the conjugation between the nitrogen and

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(7) Attempts at detecting at low-temperature separate NMR signals for the two enantiomeric conformers in a chiral environment failed. The chiral Pirkle's alcohol [(–)-2,2,2-trifluoro-1-(9-anthryl)ethanol: $ArCHOHCF_3$, with Ar = 9-anthryl] which had allowed the discrimination of two such conformers in analogous alkylnaphthylamines,[4] did not produce any effect in the present situation. Most likely the *N*-phenyl derivatives, being less basic than the analogous *N*-alkyl derivatives, do not associate sufficiently with the chiral alcohol to give separate spectra for the two enantiomeric conformers at low temperature. Also the use of an optically active acid, such as (–)-α-methoxy-α-(trifluoromethyl)phenylacetic acid, failed to induce the chiral discrimination between the enantiomeric conformers of 1.

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(11) Owing to the molecular asymmetry and to the fact that the enantiomerization has a higher barrier than the Ph–N rotation, the two ortho carbons can be diastereotopic at low temperature even if the phenyl ring adopts a perpendicular arrangement (Scheme III) with respect to the dynamic plane of the aminic nitrogen.

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Table II. Results of the Differential NOE Experiments in Derivatives 1–3 at Room Temperature in CCl_4 (300 MHz)

		obsd NOE,[a] %	
compd	irradiated protons	H-2	H-8
1 (R = Me)	NCH_3	6.9	8.7
	ortho	4.8	3.0
2 (R = Et)	NCH_2	7.5	9.5
	ortho	4.3	2.8
3 (R = *i*-Pr)	NCH	<1	<1
	ortho	2.0	1.0

[a] The error is about ±0.5%.

the naphthalene ring becomes even less efficient. As a consequence the variations in the enantiomerization barriers for molecules having R groups of increasing bulkiness is the result of a balance between the steric effect of R on the twisted ground state (that would reduce the barrier) and the effect on the planar transition state (that would increase the barrier). It could thus be argued that when R = ethyl (in **2**) the angle ϑ might be essentially equal to the case of R = methyl (in **4**) so that the variation in the bulkiness of R (which changes from methyl to ethyl) would only contribute by increasing the energy of the transition state, hence the observed barrier. On the other hand when R is the bulkier isopropyl group (in **3**) the effect on the ground state of **3** might not be negligible with respect to **2** and would thus contribute to reduce the enhancement of the barrier of **3**, so that such an enhancement is smaller than expected. In order to substantiate this interpretation with direct experimental evidence, nuclear Overhauser enhancement (NOE) experiments were carried out on **1**–**3**.

In the case of molecules having analogous structures, the larger the observed NOE effect is, the smaller the distance is between the protons involved in the experiment.[16] Saturation of the ortho protons in the phenyl group and saturation of the NCH_n protons in the alkyl groups (n = 1, 2, 3 respectively in **3**, **2**, **1**) was found to produce an enhancement of the signals of H-2 and H-8 in the naphthalene ring. The results are collected in Table II. When the corresponding NOE relationships are compared (see Table II), the effects measured in **1** are equal, within the errors, to those measured in **2** (e.g., $6.9 \simeq 7.5$ and $4.8 \simeq 4.3$) thus indicating that the corresponding interprotonic distances and hence the ϑ values are very similar. On the contrary the NOE values measured in **3** are much smaller than the corresponding values in **1** and **2**. This suggests that the corresponding distances are larger and, therefore, that the ϑ value in **3** is larger than in **1** or **2**. The NOE experiments, apparently, support the hypothesis that the reduced difference of the $\Delta G^{\ddagger}$ values between **3** and **2** with respect to the difference between **2** and **1** should be attributed to a larger value of the twist angle ϑ in the conformational ground state of **3**.

Experimental Section

Materials. Melting points are uncorrected. NMR spectra were taken at 60 MHz.

***N*-Methyl *N*-phenyl-1-naphthylamine (1).** To a cooled (−30 °C) solution containing *N*-phenyl-1-naphthylamine (4 g, 18.3 mmol) in anhydrous ether (20 mL) was added dropwise a 1.5 M cyclohexane/ether solution of phenyllithium (15 mL, 22.5 mmol). The reaction was then allowed to reach room temperature, and 1.7 mL (27 mmol) of methyl iodide was added, leaving the system to react overnight under stirring. The mixture was treated with water and the organic layer washed to neutrality, dried, and concentrated. The crude produce (4.8 g) was purified through a silica column (eluent petroleum ether/ether, 95:5), and 3.5 g of **1** (yield 82%) was recovered: ^1H NMR (CCl_4) δ 3.3 (3 H, s, NCH_3), 6.5 (3 H, m, Ar), 6.8–8.0 (9 H, m, Ar); mass spectrum, *m/e* 233 (M^+). Anal. Calcd for $C_{17}H_{15}N$: C, 87.55% H, 6.44; N, 6.01. Found: C, 87.1; H, 6.8; N, 5.7.

***N*-Ethyl-*N*-phenyl-1-naphthylamine (2).** The reaction was the same as for **1**, using as alkylating agent BF_4OEt_3 (yield 59%): ^1H NMR (CCl_4) δ 1.2 (3 H, t, CH_3CH_2), 3.7 (2 H, q, CH_2CH_3), 6.3–8 (12 H, m, Ar); mass spectrum, *m/e* 247 (M^+). Anal. Calcd for $C_{18}H_{17}N$: C, 87.45; H, 6.88; N, 5.67. Found: C, 87.9; H, 7.1; N, 5.5.

***N*-Isopropyl-*N*-phenyl-1-naphthylamine (3).** In an autoclave were introduced 5 g (22.8 mmol) of *N*-phenyl-1-naphthylamine, 10 mL (130 mmol) of isopropyl alcohol and 0.5 g (2 mmol) of iodine. After the introduction of 50 atm of nitrogen, the system was left for 30 h at 160 °C (the pressure rose to 90 atm). The excess alcohol was distilled off and the residue passed through a silica column (eluent, petroleum ether/ether, 9:1) to yield 0.3 g of **3** (yield 5%): ^1H NMR (CCl_4) δ 1.2 (6 H, d, CH_3CH), 4.5 (1 H, sept, $CHMe_2$), 6.3–8.2 (12 H, m, Ar); mass spectrum *m/e* 261 (M^+). Anal. Calcd for $C_{19}H_{19}N$: C, 87.36; H, 7.28; N, 5.36. Found: C, 87.1; H, 7.6; N, 5.7.

***N*-Methyl-*N*-(3-ethylphenyl)-1-naphthylamine (4)** was prepared as **1**, but with *n*-butyl lithium and *N*-(3-ethylphenyl)-1-naphthylamine. The crude product was purified on SiO_2 (eluent, petroleum ether/ethyl alcohol, 97:3), the yield being 40%: ^1H NMR (CCl_4) δ 1.15 (3 H, t, CH_3CH_2), 2.5 (2 H, q, CH_2CH_3), 3.3 (3 H, s, NMe), 6.2–8.0 (11 H, m, Ar); mass spectrum, *m/e* 261 (M^+). Anal. Calcd for $C_{19}H_{19}N$: C, 87.36; H, 7.28; N, 5.36. Found: C, 86.8; H, 6.9; N, 5.0.

***N*-(3-Ethylphenyl)-1-naphthylamine.** A mixture of 1-naphthylamine (7.4 g, 51.7 mmol), 3-ethylaniline (10 g, 82 mmol) and iodine (0.1 g) was allowed to react at 230 °C for 13 h. The residue was purified on a silica column (petroleum ether/ether, 97:3) and 11 g of the pure product (yield 85%) were obtained: ^1H NMR (CCl_4) δ 1.15 (3 H, t, CH_3CH_2), 2.5 (2 H, q, CH_2CH_3), 5.8 (1 H, br s, NH), 6.6–8.1 (11 H, m, Ar).

NMR Measurements. The low-temperature ^{13}C NMR experiments were carried out at 25.16 MHz (Varian XL-100 equipped with a ^{19}F external lock device). The temperature was measured before or after each acquisition (a few hundred transients were collected) by replacing the sample into the probe with a thermocouple or a thermistor. The samples were prepared by connecting the 10-mm tubes to a vacuum line and condensing the gaseous solvent (dimethyl ether) with liquid nitrogen. The tubes were then sealed off in vacuo and allowed to reach room temperature: they were subsequently inserted into the precooled probe of the spectrometer.

The low-temperature ^1H NMR experiments were carried out at 300 MHz (Bruker CXP-300), and the temperatures were measured by substituting the samples with a tube containing methanol whose chemical shift difference is calibrated with the temperature.

The nuclear Overhauser enhancement experiments were also run at 300 MHz by preirradiating the desired signals for 15–20 s and acquiring the spectrum with the decoupler turned off, so that coupled spectra were obtained. A control experiment was created by setting the irradiation away from any signal. The acquisitions were carried out in groups of eight for each irradiated signal, each group being preceded by two dummy scans. Each transient was separated by a relaxation delay of 20 s, a period more than three times longer than the maximum T_1 of H-2 or H-8. The cycle was repeated eight times, thus resulting in 64 accumulations for each spectrum. The FID's, acquired with 16K (3000 Hz sweep width), were Fourier transformed with 32K (zero-filling) and with a line broadening of 4–5 Hz. The spectra obtained in this way were subtracted from the control, yielding the NOE difference spectrum. The decoupler was set at the minimum value required to saturate the irradiated signal (40–50 db below 0.2 W). The samples (the solvent was CCl_4 containing acetone-d_6 for deuterium locking) were carefully degassed with nitrogen, and the level of the liquid in the tube was kept at the minimum (0.25 mL) required for an acceptable resolution.

Acknowledgment. We thank Dr. J. E. Anderson (University College, London) for helpful discussions which

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were made possible by a NATO Research Grants Programme. The work was carried out with the financial support of the Ministry of Public Education, Rome.

Registry No. **1**, 34160-17-3; **2**, 110972-21-9; **3**, 110972-22-0; **4**, 110972-23-1; *N*-phenyl-1-naphthylamine, 90-30-2; *N*-(3-ethylphenyl)-1-naphthylamine, 95275-66-4; 1-naphthylamine, 134-32-7; 3-ethylaniline, 587-02-0.

Nickel-Catalyzed Codimerization of 1,3-Cyclohexadiene and Vinyltrimethylsilane. Effects of Organophosphorus Ligands

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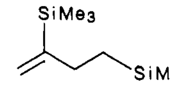
Received October 30, 1986

Recent progress achieved by using organosilicon compounds has offered several new aspects to synthetic organic chemistry.[1] One of them is the use of vinylsilane as a masked carbonyl functionality[2] and as a possibility for generation of α-silyl carbanions through the addition of different types of carbanionic species on the activated double bond.[3] Another interesting feature in respect to synthesis results from the electrophilic substitution reactions.[4] Recently, we reported a high enantioselectivity (93% ee) in the asymmetric hydrovinylation of 1,3-cyclohexadiene catalyzed by the Ni(COD)$_2$–AlEt$_2$Cl–(2*R*,3*R*)-threophos system.[5] The catalytic cyclodimerization of 1,3-dienes with miscellaneous olefins is an attractive route to interesting synthons. Unfortunately, this reaction fails in more general cases.[6,7] Miller et al.[8] was the first to report the codimerization of ethylene and 1,3-cyclohexadiene catalyzed by nickel complexes and we describe herein that Ni(COD)$_2$–AlEt$_2$Cl–L (in 1/6/2 molar ratio) modified with suitable organophosphorus P(III) ligands L is able to catalyze a codimerization reaction between 1,3-cyclohexadiene (**1**) and vinyltrimethylsilane (VTMS **2**) (**1**/**2**/Ni = 50/50/1) in toluene solution at 50 °C. As shown in Table I and Scheme I, after 48 h of reaction, the expected compound 3-[1-(trimethylsilyl)vinyl]cyclohexene (**3**) and the oligomer byproducts 2,4-bis(trimethylsilyl)-1-butene (**4**) and (*E*)- and (*Z*)-1,4-bis(trimethylsilyl)-3-butene (**5**, **6**) were formed. The latter compounds have been already obtained by the oligomerization of VTMS catalyzed by the catalytic system prepared from AlEt$_3$ reduction of nickel acetylacetonate Ni(acac)$_2$ in the presence of triphenylphosphine with dichloroethylene as solvent;[9] these products probably result from isomerization of (*Z*)- and (*E*)-1,4-bis(trimethylsilyl)-1-butenes (**7**, **8**), previously prepared in the VTMS dimerization by using NiCl$_2$–Al$_2$Et$_3$Cl$_3$–PPh$_3$ as the catalytic system.[9] Under our catalytic conditions the compounds **5** and **6** are the minor products. The major byproduct resulting from homoligomerization of VTMS is compound **4**. Unlike the Ni(0)-catalyzed cooligomerization of VTMS with 1,3-dienes such as butadiene[10,11] and isoprene,[12] the compounds **3** and **4** result from the C–C bond formation between the α-carbon of VTMS and either 1,3-cyclohexadiene or VTMS, whatever the nature of the ligand (see Table I). Such an addition was observed in accordance with our results in the cooligomerization of butadiene–VTMS over a nickel chloride catalytic system in the presence of an organoaluminum Lewis acid and triphenylphosphine.[13] Indeed, we never observed the inverse addition with the formation of 3-[2-(trimethylsilyl)vinyl]cyclohexene (**9**).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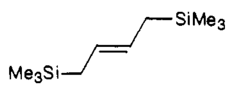
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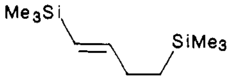
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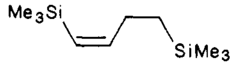
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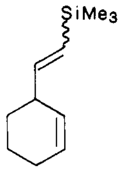
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It can be seen from Table I that the nature of the phosphorus ligand and the P/Ni ratio strongly affect both catalytic activity and product selectivity. The ligand is essential for the formation of **3** (run 5) as is the organoaluminum Lewis acid, without which the reaction fails to give any of the desired products. The best results are obtained with triethyl phosphite (run 10) and bis(dimethylamino)phenylphosphine (run 13) as ligands and with a P/Ni ratio of 2/1 and AlEt$_2$Cl/Ni(COD)$_2$ ratio of 6/1 at 50 °C.[16] The chelating 1,2-bis(diphenylphosphino)ethane inhibits the catalyst activity for L/Ni = 2 and 1 and becomes only active with a L/Ni = 0.5. Such an effect has already been observed with chelating

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0022-3263/88/1953-0185$01.50/0 © 1988 American Chemical Society