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Titanocene-Catalyzed Coupling of Aromatic Amides in the Presence of Organosilanes: A Novel Route to Vicinal Diamines and a New Class of Amine-Substituted Oligomers

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The title reaction has been surveyed for a number of substrates with differing substitution patterns. With a few exceptions, the methodology provides a one-pot synthesis of the 1,2-diamines from widely available and inexpensive starting materials, and in high yields. In addition, the coupling of 1,4- and 1,3-bis-(*N*,*N*,*N*′,*N*′-tetraalkyl)arylenediamides is shown, under the same experimental conditions, to yield oligomers: $R_2NC(O)C_6H_4CH(NR_2)$-$[CH(NR_2)C_6H_4CH(NR_2)]_n$-$CH(NR_2)C_6H_4C(O)$-$NR_2$ (R = methyl and ethyl; n = 0 to ca. 5). The chemical structures of these unprecedented oligomers are determined by comparison of NMR and MS spectra to those of vicinal diamines, prepared from the analogous *N*,*N*-dialkylbenzamides. The origin of the limitation of oligomer chain length is probably due to a specific effect of the internal benzylic amine group, since the substrate 4-$Me_2NCH_2C_6H_4C(O)NMe_2$ was found to be uniquely unreactive compared to the other 4-substituted *N*,*N*-dialkylbenzamides investigated. *N*-Methylphthalimide was briefly studied as a monomer and analysis by MS showed that oligomers are formed. Attempts to fully characterize these polymers were unsuccessful.

Introduction

Chiral vicinal diamines are of great importance, as they are found in a variety of compounds that display a broad spectrum of pharmaceutical activity.[1] They are also used increasingly as stereoselective auxiliaries, or as metal ligands in catalytic asymmetric synthesis.[1e] The regio- and stereoselective synthesis of vicinal diamines is an active and challenging topic in organic chemistry because of the importance of such derivatives[2a,b] in coordination chemistry[2c,d] and medicinal chemistry.[2e] Despite the existence of many synthetic approaches[3] and useful methodologies,[4] there is still a need for better and more general methods based on simple and inexpensive starting materials.

In a preliminary communication we reported a novel reduction−deoxygenation coupling of aromatic amides in the presence of a stoichiometric amount of organosilane, catalyzed by $[Cp_2TiX_2]$ (Cp = η^5-cyclopentadienyl; X = Me or F).[5a,b] To our knowledge, such a reaction had not been previously reported, although there is a very extensive literature on noncatalytic, titanium-mediated coupling of carbonyl[6a] and imine[6b] compounds in the presence of strong reducing agents.[6a] The intramolecular coupling of 1,2-acylamido compounds to indoles and pyrroles has also been extensively studied.[7]

The catalytic coupling reaction described above has proven to be very useful for the synthesis of a wide range of ring-functionalized 1,2-diarylbis(1,2-*N*,*N*-dialkylamino)ethanes, but so far it has shown little, or no, regio- or enantioselectivity. Nevertheless, because the reactants are generally widely available and inexpensive, the chemistry certainly warrants further exploration. The present paper gives a full report on our work to date.

An interesting feature of the catalytic coupling reaction is that some of the simple *N*,*N*-dialkylbenzamides we have studied give essentially quantitative yields of vicinal

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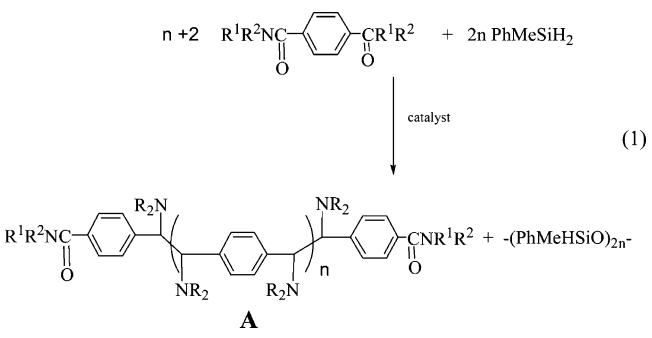
diamines. A C−C bond-forming reaction with this kind of efficiency is of interest as a source of new polymer chemistry. We have therefore studied the coupling of a number of bifunctional arylene diamides with a view to making polymers of the structure **A** as shown in (1). The synthesis of such polymers by other known routes would be at best difficult and costly.



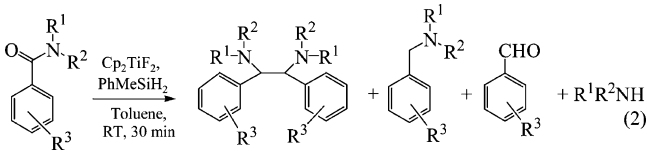
(1)

A

Polymers such as **A** are interesting both in their own right and as potential precursors for a novel class of polyconjugated polymers. They could, in principle, be transformed into amine-substituted polyarylenevinylenes by classical autoxidation, catalytic dehydrogenation, or dehydroamination reactions.

Results

Reactions of Monoamides. The effects of a number of chemical and physical variables on the outcome of the reactions of several aryl monoamides were investigated [eq 2 and Tables 1 and 2].



(2)

At 80 °C, most benzamides yield the 1,2-diamines with high chemoselectivity, but with low diastereoselectivity. However, Some aromatic amides, notably nicotinamides, also undergo to a significant extent the additional side reactions shown in (2), even when the reaction is carried out at 80 °C. At 25 °C, the C−N bond cleavage and the C═O reduction reactions become more important in most cases (Table 2). Replacement of one of the *N*-alkyl groups with a phenyl group does not seriously alter the course of the reaction, although there is a slight reduction in the yield of diamines. Replacement of both alkyl groups with phenyl effectively closes down the coupling reaction. In all of the cases studied, cleavage of the $C(O)NPh_2$ bond to give high yields of Ph_2NH was the main reaction. As previously noted, reactions of amides with unsubstituted N−H bonds, using the conditions described above, are too slow to be of interest.

Characterization was greatly aided by the presence of the chiral centers in the products. The spectra of a mixture of diastereoisomers of **1** (Table 1) and of the separated diastereomers of the same product are shown in Figure 1, parts a−c. The presence of the couplings of the pairs of inequivalent, diastereotopic hydrogens in the *diethyl*amino products, **1**, and its absence in the *dimethyl*amino product (**16**, Table. 1) is clearly diagnostic

TABLE 1. Results for Titanocene-Catalyzed Reductive Coupling of Amides at 80 °C with 10% Catalyst

compd no.	R^1	R^2	R^3	method[a]	ratio (meso:rac)[b]	yield[c] (%)
1	Et	Et	H	A	52:48	92
				B	52:48	80
2	Et	Et	4-Cl	A	53:47	93
3	Et	Et	3-Cl	A	52:48	86
4	Et	Et	4-F	A	51:49	93
5	Et	Et	3-F	A	52:48	87
6	Et	Et	4-CF_3	A	53:47	96
7	Et	Et	3-CF_3	A	51:49	84
8	Et	Et	2-CF_3	A	49:51	72
9	Et	Et	4-OCH_3	A	56:44	94
10	Et	Et	4-Me	A	62:28	91
11	Et	Et	3-Me	A	52:48	73
12	Et	Et	4-CN	A	49:51	44
13	Et	Et	4-NMe_2	A	48:52	44
14	Me	Ph	H	A	50:50[e]	77[d]
15[f]			*N*,*N*-diethyl-2-naphthamide	A	54:46	83
16	Me	Me	H	A	52:48	84
				B	52:48	80
17	Me	Me	4-Cl	A	49:51	88
18	Me	Me	3-Cl	A	53:47	62
19	Me	Me	4-F	A	52:48	86
20	Me	Me	3-F	A	51:49	81
21	Me	Me	4-CF_3	A	51:49	87
22	Me	Me	3-CF_3	A	52:48	84
23	Me	Me	2-CF_3	A	60:40	66
24	Me	Me	4-Me	A	57:43	63
25	Me	Me	3-Me	A	54:46	59
26	Me	Me	4-CH_2NMe_2	A		NR[h]
				B		NR[h]
27[g]	**27**[g]		*N*,*N*-diethyl-nicotinamide	A	57:43	27

[a] See Experimental Section. [b] Ratios of isomers are calculated after isolation, or by ^1H NMR analysis. [c] Yields are given for isolated compounds. [d] *N*-Methyl-*N*-benzylaniline is one of the products (8%). [e] Isomers were not separated. [f] *N*,*N*-Diethyl-2-naphthylamine is formed as a side product (9%). [g] 3-(*N*,*N*-Diethylaminomethyl)pyridine is also formed (25%). [h] NR = no reaction.

TABLE 2. Results for $[Cp_2TiF_2]$-Catalyzed Reductive Coupling of Aromatic Monoamides at 25 °C with 10% Catalyst

			ratio of products (%)		
R^1	R^2	R^3	diamines (meso:rac)	mono-amines	aldehyde
Me	Me	H	81.3 (54:46)	2.0	16.7
Et	Et	H	97.7 (60:40)		2.3
Et	Et	4-Cl	44.8 (53:47)	29.9	25.3
Et	Et	4-OMe	100 (53:47)		
Me	Ph	H	14.7 (55:45)	44.2	41.1
Et	Et	4-CF_3	55.9 (53:47)	20.6	23.5
Et	Et	4-Me	100 (50:50)		
N,*N*-diethyl-2-naphthamide			51.2 (48:52)	39.6	9.2
N,*N*-diethyl-nicotinamide			43.5 (56:44)	34.1	22.4

of the C−C coupling product in the case of ethyl-substituted substrates. In the *diethyl*amino products, the two diastereotopic hydrogens of the methylene group have different chemical shifts and they couple to give a widely separated pair of doublets. Each of these doublets is in turn spilt by the methyl group to give two pairs of overlapping quartets, with a characteristic pseudosextet appearance. This pattern is observed for all of the 1,2-diethylamino products listed in Table 1. In the 1,2-dimethylamino products, the *N*-methyl protons all appear

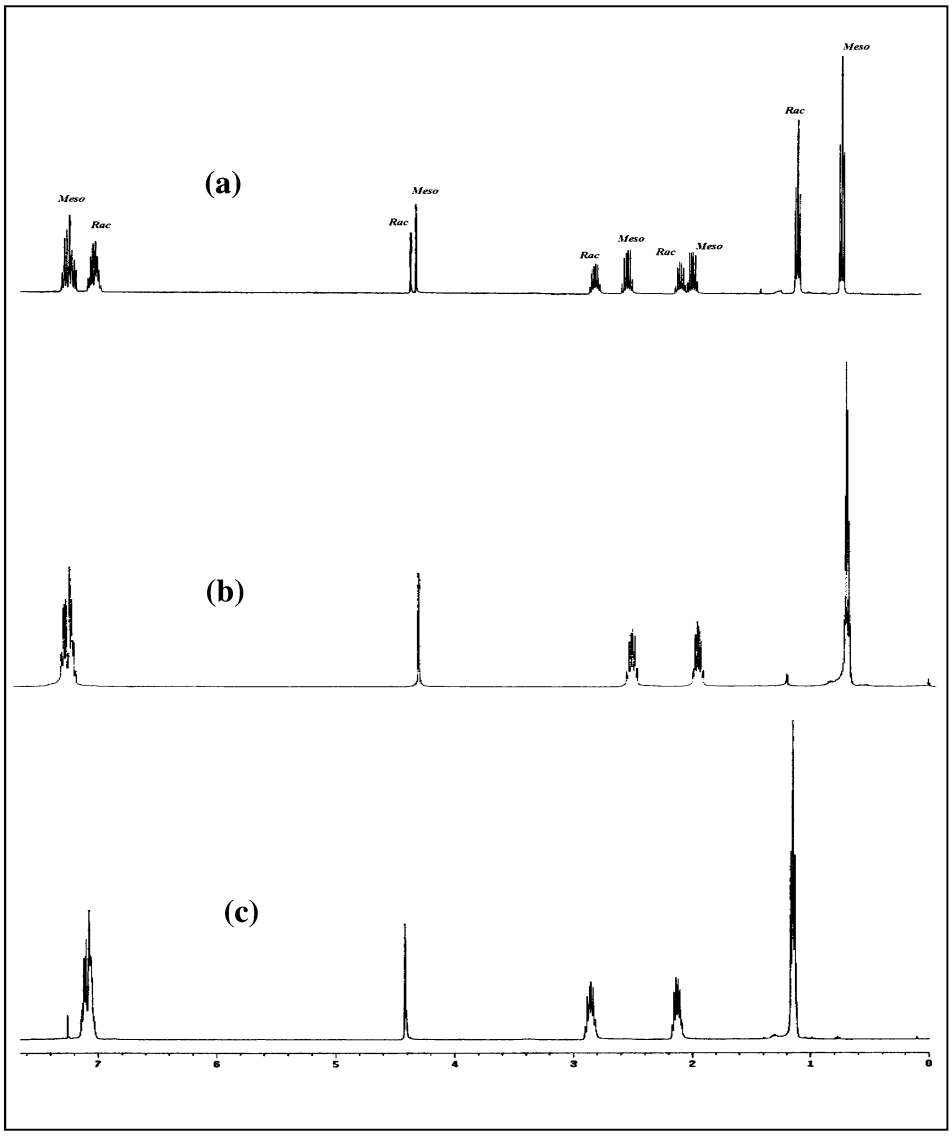


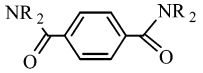
FIGURE 1. ^{1}H NMR spectra of (a) a mixture of the diastereomers of 1,2-diphenyl-1,2-*N*,*N*-diethylaminoethane, (b) the pure meso isomer, and (c) the pure rac isomer (in $CDCl_3$ at room temperature).

as two sharp singlets, characteristic of the two diastereomers, and in the same chemical shift relationship as found with the analogous diethylamide dimers.

The yields of coupling products are, in general, very good to excellent. Exceptions to this are the substrates where the phenyl ring is substituted in the 2-position, *N*,*N*-diethylnicotinamide and 4-dimethylaminomethyl-*N*,*N*-dimethylbenzamide (**9**, **23**, **26**, and **27** in Table 1).

In the cases of the 2-substituted substrates, there is a considerable reduction in the rates of all of the reactions represented in (2), suggesting a general interference in the binding of the substrate to the catalyst. A similar effect was observed in the hydrosilation of 2-substituted pyridines.[8] In the case of *N*,*N*-diethylnicotinamide, the reaction proceeds effectively in terms of conversion of substrate, but the reduction of the 3-diethylamido function to 3-dimethylaminomethyl proceeds at about the same rate as coupling. The remainder of the substrate in this case is converted to a mixture of products that were not isolated and characterized, but which clearly result from hydrosilation/reduction of the pyridine nucleus.[8] The case of 4-dimethylaminomethyl-*N*,*N*-dimethylbenzamide is special and will be discussed below in relation to the polymerization of 1,4-arylenediamides.

Reactions of *N*,*N*,*N*′,*N*′-Tetraalkylterephthaldiamides. To test the concept of applying reaction 2 to the synthesis of polymers we have studied the polymerization of *N*,*N*,*N*′,*N*′-tetraalkylterephthaldiamides, **29**. The reac-



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tions were run at 80 °C, to minimize side reactions. The progress of the reaction was followed by removing the reaction mixture and analyzing the product by ^{1}H NMR.

A typical ^{1}H NMR spectrum of an oligomeric product, as described above, is shown in Figure 2a, along with the room temperature spectrum of the monomer, Figure 2b.

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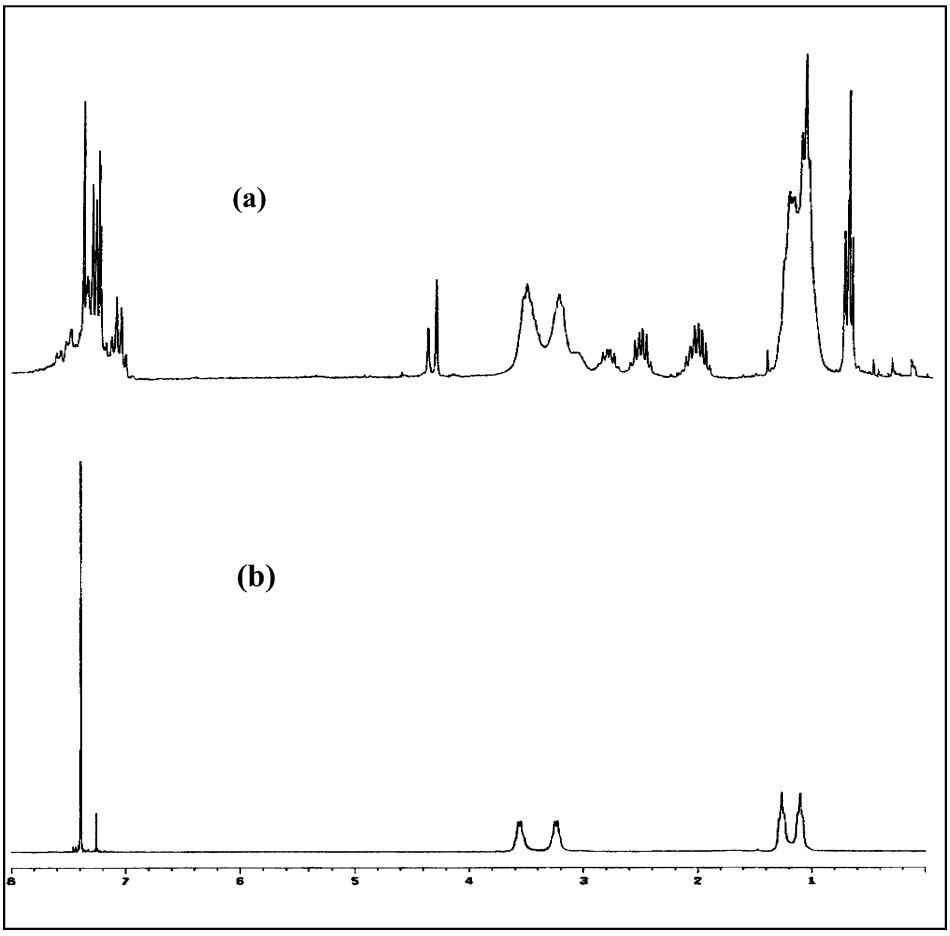


FIGURE 2. ^{1}H NMR spectra of (a) *N*,*N*,*N*′,*N*′-tetraethylterephthaldiamide coupling product and (b) *N*,*N*,*N*′*N*′-tetraethylterephthaldiamide (in $CDCl_3$ at room temperature).

It is clear from Figure 2a that coupling has taken place, but that there is still a considerable concentration of unreacted amide end groups. The ratio of the integrals for the methylene protons of the terminal $-C(O)N(CH_2CH_3)_2$ groups to those of the internal $>CH(NCH_2CH_3)$ groups indicates an average degree of polymerization (DP_n) for this sample of ca. 1.5. The relative simplicity of the spectrum also indicates the presence of low molecular weight material. The methyl resonances of the terminal $>C(O)N(CH_2CH_3)_2$ groups (3.0−3.6 ppm) are broad and lacking in any fine structure, due to the restricted rotation about the $>C(O)-N$ bond at room temperature (also seen in the monomer), while the methylenes of the internal $>CH[N(CH_2CH_3)_2]$ groups appear as sharp overlapping multiplets in the range 2.0−3.0 ppm. The methine protons of the $>CH(NCH_2CH_3)_2$ groups of the two diasteroisomers appear as two quite sharp singlets at 4.38 and 4.43 ppm, as in the case of the benzamide dimers. The multiplicities of the methylene resonances of the $>CH(NCH_2CH_3)_2$ groups are similar to, but more complex than, those of the simple dimers, indicative of the presence of more than one species. The two resonances of the methine protons are due to the diastereomers, but unlike the methylene resonances, the chemical shift differences are less sensitive to the DP_n and the peaks are broadened but not split. The purified product, whose NMR properties are described in the previous paragraph, was also analyzed by MS. Measurements were taken in both EI and CI modes as well as MALDI. All three methods supported the same conclusions.

The CI-MS spectrum of this sample is shown in Figure 3. The salient features of the spectrum are (i) the absence of monomer, (ii) the presence of a series of peaks corresponding to oligomers + H up to $n = 5$, and possibly up to $n = 7$, (iii) the characteristic loss of a diethylamine from each oligomer, (iv) a strong peak due to the end group, $Et_2N(CO)C_6H_4C^+H(NEt_2)$ and the presence of a peak due to the loss of this group from each *n*-mer, and (v) the absence of significant peaks which could signify structural anomalies in the oligomer molecules.

The spectroscopic data clearly show that oligomerization has taken place to produce a polymeric species with the structure **A**, such as shown in (1). It is also clear, however, that the yield of polymer is low and only a low DP_n is achieved. Reactions were also carried out over much longer times (up to 36 h), and with higher catalyst concentration, with no significant improvement in either yield, or increase in DP_n. These facts suggest that the reaction is limited either by catalyst deactivation, or by the intercession of the side reactions shown in (2). The latter explanation is unlikely, since the known side reactions, i.e., reduction of $C(O)NR_2$ to CH_2NR_2, and cleavage of the C−N bond of the amide function, would give oligomeric species with masses quite easily distinguishable from those of the pristine oligomers, contrary

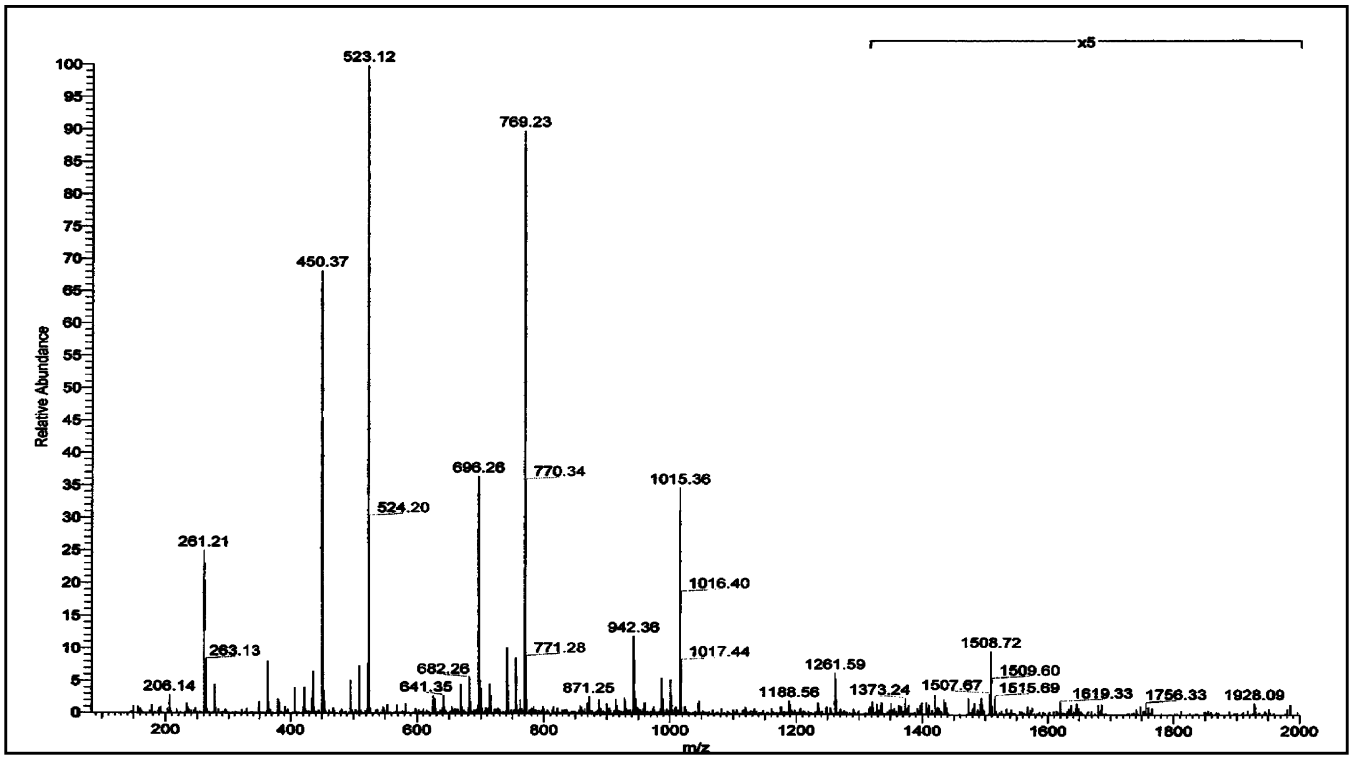


FIGURE 3. The CI-MS spectrum of the *N*,*N*,*N*′,*N*′-tetraethylterephthaldiamide coupling product. The peaks at M^+ 523, 769, 1015, and 1261 amu correspond to $DP_n = 2$, 3, 4, and 5, respectively.

to the MS evidence. A decline in catalyst activity is therefore a more likely explanation.

The coupling of benzamides, under conditions identical with those used in the current polymerization experiments, shows no serious decline of catalytic activity over the course of the reaction. Nor does depletion in reactant concentrations seriously impair the yields of products. These facts point to the source of the problem of DP_n limitation as being either a specific electronic effect, characteristic of the 4-$CH(NR_2)C_6H_4C(O)NR_2$ end group of the oligomers, or an inhibition of catalyst by the product.

A qualitative comparison of the relative reactivities of $PhC(O)NMe_2$ and $Me_2NCH_2C_6H_4C(O)NMe_2$ indicated that the rate of reaction of $PhC(O)NMe_2 \gg$ the rate of reaction of $Me_2NCH_2C_6H_4C(O)NMe_2$.

Furthermore, the attempted coupling of samples of isolated and purified oligomers, to give a product of higher DP_n, was unsuccessful. It may therefore be concluded that the inhibition of polymerization is most likely a consequence of the generation of the $-C_6H_4CH(NEt)_2-$ function in the product of the initiation step. The specific nature of the inhibition remains to be determined.

Reactions of Other Diamides. The reactions of *N*,*N*,*N*′,*N*′-tetramethylisophthaldiamides and *N*-methylphthalimide were also studied and were found to give the same types of products as the terephthaldiamides. The conversions were, however, even lower than those with the terephthaldimides and the reactions were not studied in detail. A few results of such reactions are shown in Table 3.

TABLE 3. Results for Titanocene-Catalyzed Oligomerization of Aromatic Amides at 80 °C with 10% Catalyst

substrate	reaction time (h)	yield (%)	highest obsd (DP_n)[c]
N,*N*,*N*′,*N*′-tetraethyl-terephthaladiamide	24	33[a]	5
N,*N*,*N*′,*N*′-tetramethyl-terephthaladiamide	18	37[b]	3
N,*N*,*N*′,*N*′-tetramethyl-isophthaladiamide	18	43[b]	3
N-methylphthalimide	18	52[b]	7

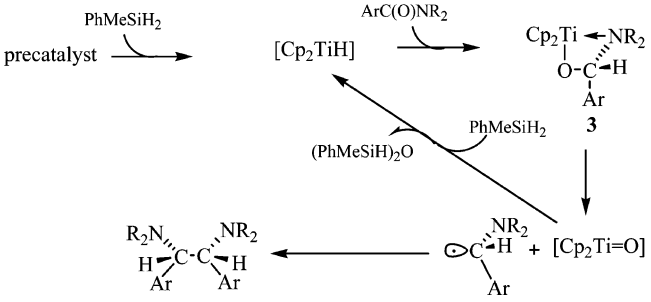
[a] Polymer purified by precipitation from cyclohexane. [b] Polymer purified by precipitation from ether. [c] Based on CI-MS analysis.

Discussion

Reaction 2 provides a fairly general route for the synthesis of 1,2-(dialkyldiamino)-1,2-diarylethanes. The positive aspects of the chemistry are (i) the commercial availability, or easy synthesis of a wide range of amide substrates at low to moderate cost, (ii) commercially available catalyst materials, and (iii) one pot reactions at acceptable rates and with simple workup. The most serious limitations of the reaction are the lack of diastereo- and enantioselectivity. Our attempts to control the stereochemical outcome of the reaction by steric modification of the basic titanocene structure have all led to a reduction, or shutting down, of catalyst activity. We therefore consider it unlikely that a solution to the lack of stereocontrol will be found with titanocene-based catalysts. A more profitable approach might be to investigate some of the new mono-η^5-cyclopentadienyl titanium or cyclopentadiene-free catalysts that have recently been developed for other catalyses.[9,10]

Our studies of terephthaldiamide coupling reactions have established the principle that this type of reaction may be applied to the synthesis of unusual polymers in a simple one-pot reaction. However, the chemistry with

SCHEME 1. A [Cp_2TiH]-Mediated Reaction Sequence for the Generation of $Ar(NR_2)CH•$ Radicals



titanocene-based catalysts is also seriously limited by the apparent product inhibition of reaction beyond low molecular weight oligomers.

Reaction Mechanism

It was proposed earlier that the coupling reaction 2 is most likely free radical in nature.[5] The major justification for this hypothesis is the very low sensitivity of the diastereoselectivity of the reactions to wide variations in substrate electronic and steric properties. A second justification is the fact that the coupling reaction supercedes the other reactions shown in (2) at higher temperatures, a behavior that is expected for a thermolytic process. The proposed sequence of steps leading to the formation of the necessary free radicals is shown in Scheme 1. In this scheme the organosilane serves as a source of hydride ligand. There is ample evidence for the formation of TiH complexes by reaction of organosilanes with the titanocene precatalysts used in the current reactions.[11] Addition of $Ti^{III}-H$ across the C=O bond of the amide substrate results in species **3**, a sterically hindered alkoxy−titanium(III) complex. The tendency of the O−C bond of this species to undergo homolysis is enhanced by steric hindrance within the bulky ligand and also by the stabilization of the resulting C radical by electron delocalization through the N−C−Ar moiety. There is abundant precedent for this type of radical stabilization.[12] A further factor favoring the C−O bond rupture is the formation of the Cp_2Ti=O moiety. Although this compound has not been isolated, it is certainly a plausible reactive intermediate. Convincing evidence for the transitory existence of $(Me_5C_5)_2Ti$=O has been reported.[13] This species can be regarded as either a Ti(IV) oxo complex ("titanyl") or a titanium(III)-coordinated oxy radical complex ($Ti^{III}-O^{•}$). Thus, the bond breaking is assisted by stabilizing effects at both the C atom and the O atom.

The recycling of the titanyl species in Scheme 1 may occur by a number of steps, some of which may also be free radical in nature, and some of which may involve σ-bond metathesis. The overall exchange of O between Ti and Si is plausible, since facile metathesis of OR groups between Ti−OR and Si−H is well-known, as also is exchange of fluoride between Ti−F and Si−H.[14]

Conclusions

It has been established that the titanocene-catalyzed reactions of hydrosilanes with aromatic carboxamides provide a versatile route for the synthesis of substituted vicinal diamines. The reaction provides a simple one-pot synthesis from cheap and widely available starting materials. The utility of the chemistry is limited by the lack of control over stereochemistry of the reaction. The proposed free radical process for the coupling reaction is probably responsible for the relative insensitivity of the reaction to attempts to influence the stereochemical outcome.

We have established, in principle, that the coupling reaction can be used to generate concatenated vicinal diamines, but a strong inhibitory effect of the product's 4-dialkylaminomethyl group on the coupling of chain end amide groups precludes the buildup of polymers with molecular weights of practical interest. There is a possibility that this limitation could be overcome with more active catalysts.

Experimental Section

All amides used in this work were synthesized by reacting the respective acid chlorides with appropriate amines according to literature methods (for *N*,*N*-dimethylbenzamides,[15] *N*,*N*-diethylbenzamides,[16a] *N*,*N*-diphenylbenzamides,[16b] and phthalic acid diamides[17]). The amides were characterized by ^{1}H NMR, IR, and mass spectral data. Where possible, the melting points were determined and compared with literature values. Cp_2TiF_2 and Cp_2TiMe_2 were prepared by literature procedures.[18,19] The identities of all the products listed in Tables 1 and 2 were determined from their ^{1}H and ^{13}C NMR spectra, and where possible by comparison to literature data.[20]

The following general procedures were used:

Method A. Reactions at 80 °C: *N*,*N*′-Diethylbenzamide (177 mg, 1 mmol), [Cp_2TiF_2] (21 mg, 0.1 mmol), methylphenylsilane (0.28 mL, 2 mmol), and toluene (1 mL) were heated at 80 °C for 1 h in a Schlenk tube. After the reaction mixture had cooled to room temperature, ether (20 mL) was added and the solution was extracted with 1 M HCl solution. The acid

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extract was neutralized with 3 M KOH and extracted with ether. The ether layer was dried with anhydrous $MgSO_4$ and evaporated to give analytically pure *N*,*N*,*N*′,*N*′-tetraethyl-1,2-diphenylethylenediamine. The *rac*-*N*,*N*,*N*′,*N*′-tetraethyl-1,2-diphenylethylenediamine was separated from the residual meso isomer on a silica gel column with use of a 10% ethyl acetate:hexane mixture as an eluent.

Reactions at 25 °C: [Cp_2TiF_2] (21 mg, 0.1 mmol) and methylphenylsilane (0.28 mL, 2 mmol) were heated at 80 °C for 10 min to effect activation (reduction) of the precatalyst. The green solution was cooled to room temperature, and further aliquots of methylphenylsilane (0.28 mL, 2 mmol) and *N*,*N*-diethylbenzamide (177 mg, 1 mmol) dissolved in toluene-(0.5 mL) were added. The reaction was monitored by TLC, and the ratios of the products were calculated from their ^{1}H NMR spectra.

Method B. [Cp_2TiMe_2] was used instead of [Cp_2TiF_2].

Typical Procedure for the *N*,*N*-Diphenylbenzamide Coupling Reaction. *N*,*N*-Diphenylbenzamide (1.365 g, 0.005 mol), [Cp_2TiF_2] (0.1084 g, 0.0005 mol), methylphenylsilane (1.224 g, 0.01 mol), and toluene (8 mL) were heated at 80 °C for 4 h in a Schlenk tube under nitrogen. After the reaction mixture had cooled to room temperature, ether (75 mL) was added and the solution was extracted with 3 M HCl solution. The acid extract was neutralized with 5 M KOH and extracted with ether. The ether layer was dried with anhydrous $MgSO_4$ and evaporated to give a brown solid. (yield 0.61 g.)

Typical Procedure for Diamide Polymerization. *N*,*N*,*N*′,*N*′-tetraethylterephthalimide (1.38 g, 0.005 mol), [Cp_2TiF_2] (0.1084 g, 0.0005 mol), methylphenylsilane (1.224 g, 0.01 mol), and toluene (5 mL) were heated at 80 °C for 24 h in a Schlenk tube under nitrogen. After the reaction mixture had cooled to room temperature, ether (50 mL) was added and the solution was extracted with 1 M HCl solution. The acid extract was neutralized with 3 M KOH and extracted with ether. The ether layer was dried with anhydrous $MgSO_4$ and evaporated to give a brown-yellow solid. This solid was dissolved in cyclohexane (10 mL) and left overnight at 5 °C. Precipitated solid was filtered off and the cyclohexane solution was evaporated to give a glassy brown amorphous solid (yield 0.455 g).

Specroscopic Data for 1,2-Diamines. *N*,*N*,*N*′,*N*′-Tetraethyl-(1,2-diphenyl)-ethylenediamine (1): ^{1}H NMR ($CDCl_3$) (meso) δ 0.73 (t, J = 6.8 Hz, 12H), 1.97 (q, J = 6.4 Hz, 4H), 2.53 (q, J = 6.0 Hz, 4H), 4.32 (s, 2H), 7.20−7.32 (m, J = 6.4 Hz, 8H); (rac) δ 1.14 (t, J = 7.2 Hz, 12H), 2.13 (q, J = 6.4 Hz, 4H), 2.86 (q, J = 5.2 Hz, 4H), 4.41 (s, 2H), 7.05−7.13 (m, J = 4 Hz, 8H). ^{13}C NMR ($CDCl_3$) (meso) δ 14.07, 43.83, 64.35, 126.43, 127.30, 129.80, 138.58; (rac) δ 14.41, 43.36, 64.16, 126.52, 127.61, 129.52, 138.37.

***N*,*N*,*N*′,*N*′-Tetraethyl-1,2-bis(4-chlorophenyl)ethylenediamine (2):** Mp 141−143 °C. ^{1}H NMR ($CDCl_3$) (meso) δ 0.74 (t, J = 6.8 Hz, 12H), 1.96 (q, J = 6.4 Hz, 4H), 2.51 (q, J = 7.2 Hz, 4H), 4.27 (s, 2H), 7.17 (s, 4H), 7.29 (s, 4H); (rac) δ 1.27 (t, J = 7.2 Hz, 12H), 2.24 (q, J = 6.4 Hz, 4H), 2.97 (q, J = 5.6 Hz, 4H), 4.48 (s, 2H), 7.12 (s, 4H), 7.27 (s, 4H). ^{13}C NMR ($CDCl_3$) (meso) δ 14.01, 43.75, 63.76, 127.59, 130.87, 132.19, 136.77; (rac) δ 14.30, 43.26, 63.60, 128.06, 130.56, 132.34, 136.61.

***N*,*N*,*N*′,*N*′-Tetraethyl-1,2-bis(3-chlorophenyl)ethylenediamine (3):** Mp 132−134 °C. ^{1}H NMR ($CDCl_3$) ! δ 0.72 (t, J = 7.2 Hz, 12H), 1.87 (q, J = 6.4 Hz, 4H), 2.32 (q, J = 5.8 Hz, 4H), 4.21 (s, 2H), 7.07−7.23 (m, J = 4.2 Hz, 8H); (rac) δ 1.31 (t, J = 7.2 Hz, 12H), 2.31 (q, J = 6.2 Hz, 4H), 2.99 (q, J = 6.0 Hz, 4H), 4.38 (s, 2H), 6.89−7.21 (m, J = 3.8 Hz, 8H). ^{13}C NMR ($CDCl_3$) (meso) δ 43.11, 63.02, 126.87, 127.67, 129.44, 136.63; (rac) δ 42.97, 62.91, 127.99, 131.56, 132.66, 137.02.

***N*,*N*,*N*′,*N*′-Tetraethyl-1,2-bis(4-fluorophenyl)ethylenediamine (4):** ^{1}H NMR ($CDCl_3$) (meso) δ 0.75 (t, J = 9.2 Hz, 12H), 1.99 (q, J = 8.4 Hz, 4H), 2.51 (q, J = 9.6 Hz, 4H), 4.27 (s, 2H), 7.03 (s, 4H), 7.13 (s, 4H); (rac) δ 1.14 (t, J = 8.8 Hz, 12H), 2.09 (q, J = 8.0 Hz, 4H), 2.82 (q, J = 8.8 Hz, 4H), 4.34 (s, 2H), 6.82 (s, 4H), 6.98 (s, 4H). ^{13}C NMR ($CDCl_3$) (meso) δ 43.79, 63.97, 124.66, 124.54, 129.57, 142.62; (rac) δ 43.29, 63.62, 124.88, 124.98, 129.24, 142.19.

***N*,*N*,*N*′,*N*′-Tetraethyl-1,2-bis(3-fluorophenyl)ethylenediamine (5):** Mp 126−128 °C. ^{1}H NMR ($CDCl_3$) (meso) δ 0.81 (t, J = 6.8 Hz, 12H), 1.87 (q, J = 6.8 Hz, 4H), 2.53 (q, J = 5.4 Hz, 4H), 4.29 (s, 2H), 7.02 (m, J = 6.4 Hz, 4H), 7.39 (m, J = 6.4 Hz, 4H); (rac) δ 1.31 (t, J = 7.2 Hz, 12H), 2.21 (q, J = 6.2 Hz, 4H), 2.99 (q, J = 5.4 Hz, 4H), 4.42 (s, 2H), 6.97−7.27 (m, J = 5.6 Hz, 8H).

***N*,*N*,*N*′,*N*′-Tetraethyl-1,2-bis(4-trifluoromethylphenyl)-ethylenediamine (6):** ^{1}H NMR ($CDCl_3$) (meso) δ 0.67 (t, J = 9.2 Hz, 12H), 1.92 (q, J = 9.6 Hz, 4H), 2.47 (q, J = 10.0 Hz, 4H), 4.35 (s, 2H), 7.30 (s, 4H), 7.53 (s, 4H); (rac) δ 1.12 (t, J = 9.6 Hz, 12H), 2.08 (q, J = 8.6 Hz, 4H), 2.83 (q, J = 6.8 Hz, 4H), 4.46 (s, 2H), 7.13 (s, 4H), 7.37 (s, 4H). ^{13}C NMR ($CDCl_3$) (meso) δ 13.94, 43.77, 63.96, 124.34, 128.63, 129.05, 129.7, 142.23; (rac) δ 14.27, 43.30, 63.72, 124.78, 124.83, 129.4, 141.94.

***N*,*N*,*N*′,*N*′-Tetraethyl-1,2-bis(3-trifluoromethylphenyl)-ethylenediamine (7):** Mp 121−123 °C. ^{1}H NMR ($CDCl_3$) (meso) δ 0.69 (t, J = 8.8 Hz, 12H), 1.87 (q, J = 8.8 Hz, 4H), 2.54 (q, J = 6.4 Hz, 4H), 4.38 (s, 2H), 7.23 (m, J = 3.6 Hz, 4H), 7.39 (m, J = 3.4 Hz, 4H); (rac) δ 1.26 (t, J = 8.4 Hz, 12H), 2.11 (q, J = 8.6 Hz, 4H), 2.92 (q, J = 8.6 Hz, 4H), 4.46 (s, 2H), 6.99−7.27 (m, J = 6.4 Hz, 8H).

***N*,*N*,*N*′,*N*′-Tetraethyl-1,2-bis(2-trifluoromethylphenyl)-ethylenediamine (8):** Mp 104−106 °C. ^{1}H NMR ($CDCl_3$) (meso) δ 0.76 (t, J = 6.8 Hz, 12H), 2.01 (q, J = 6.6 Hz, 4H), 2.54 (q, J = 5.4 Hz, 4H), 4.41 (s, 2H), 7.32−7.73 (m, J = 3.8 Hz, 8H); (rac) δ 1.13 (t, J = 7.2 Hz, 12H), 2.10 (q, J = 6.4 Hz, 4H), 2.82 (q, J = 5.8 Hz, 4H), 4.46 (s, 2H), 7.12−7.40 (m, J = 2.8 Hz, 8H).

***N*,*N*,*N*′,*N*′-Tetraethyl-1,2-bis(4-methoxyphenyl)ethylenediamine (9):** ^{1}H NMR ($CDCl_3$) (meso) δ 0.68 (t, J = 7.6 Hz, 12H), 1.90 (q, J = 6.0 Hz, 4H), 2.46 (q, J = 5.6 Hz, 4H), 3.73 (s, 6H), 4.17 (s, 2H), 6.79 (s, 4H), 7.10 (s, 4H); (rac) δ 1.11 (t, J = 9.2 Hz, 12H), 2.05 (q, J = 6.4 Hz, 4H), 2.80 (q, J = 6.0 Hz, 4H), 3.68 (s, 6H), 4.30 (s, 2H), 6.66 (s, 4H), 6.98 (s, 4H). ^{13}C NMR ($CDCl_3$) (meso) δ 14.12, 43.81, 55.31, 63.67, 112.62, 130.68, 158.15; (rac) δ 14.39, 43.29, 55.17, 63.49, 112.94, 130.39, 130.63, 158.01.

***N*,*N*,*N*′,*N*′-Tetraethyl-1,2-bis(4-methylphenyl)ethylenediamine (10):** ^{1}H NMR ($CDCl_3$) (meso) δ 0.77 (t, J = 9.6 Hz, 12H), 2.00 (q, J = 8.0 Hz, 4H), 2.36 (s, 6H), 2.55 (q, J = 9.6 Hz, 4H), 4.31 (s, 2H), 7.11−7.17 (m, J = 8.0 Hz, 8H); (rac) δ 1.13 (t, J = 9.6 Hz, 12H), 2.06 (q, J = 9.6 Hz, 4H), 2.20 (s, 6H), 2.80 (q, J = 9.6 Hz, 4H), 4.36 (s, 2H), 6.91−6.98 (m, J = 4.8 Hz, 8H). ^{13}C NMR ($CDCl_3$) (meso) δ 14.12, 21.40, 43.85, 63.87, 128.04, 129.69, 135.37, 135.69; (rac) δ 14.41, 21.24, 43.31, 63.53, 128.35, 129.38, 135.07, 135.77.

***N*,*N*,*N*′,*N*′-Tetraethyl-1,2-bis(3-methylphenyl)ethylenediamine (11)**: Mp 72−74 °C. ^{1}H NMR ($CDCl_3$) (meso) δ 0.75 (t, J = 7.2 Hz, 12H), 1.98 (q, J = 7.2 Hz, 4H), 2.37 (s, 6H), 2.53 (q, J = 7.2 Hz, 4H), 4.29 (s, 2H), 7.13−7.24 (m, J = 5.6 Hz, 8H); (rac) δ 1.30 (t, J = 7.2 Hz, 12H), 2.07 (q, J = 6.4 Hz, 4H), 2.21 (s, 6H), 2.78 (q, J = 7.2 Hz, 4H), 4.33 (s, 2H), 6.91−7.28 (m, J = 4.4 Hz, 8H).

***N*,*N*,*N*′,*N*′-Tetraethyl-1,2-bis(4-cyanophenyl)ethylenediamine (12).** ^{1}H NMR ($CDCl_3$) (meso) δ 0.76 (t, J = 6.8 Hz, 12H), 2.01 (q, J = 6.4 Hz, 4H), 2.58 (q, J = 6.4 Hz, 4H), 4.36 (s, 2H), 7.28−7.59 (m, J = 4.8 Hz, 8H); (rac) δ 1.14 (t, J = 7.2 Hz, 12H), 2.16 (q, J = 6.8 Hz, 4H), 2.92 (q, J = 5.4 Hz, 4H), 4.43 (s, 2H), 7.08−7.46 (m, J = 4.2 Hz, 8H).

***N*,*N*,*N*′,*N*′-Tetraethyl-1,2-bis(4-*N*,*N*-dimethylaminophenyl)ethylenediamine (13):** ^{1}H NMR ($CDCl_3$) (meso) δ 0.78 (t, J = 6.8 Hz, 12H), 1.99 (q, J = 7.8 Hz, 4H), 2.48 (q, J = 7.8 Hz, 4H), 2.89 (s, 6H), 4.22 (s, 2H), 6.69−7.14 (m, J = 4.8 Hz, 8H); (rac) δ 1.11 (t, J = 6.4 Hz, 12H), 2.21 (q, J = 6.8 Hz, 4H), 2.96 (q, J = 6.4 Hz, 4H), 2.64 (s, 12H), 4.28 (s, 2H), 6.43−6.94 (m, J = 6.6 Hz, 8H).

1,2-Bis(*N*-methyl-*N*-phenylamino)-1,2-phenylethane (14): ^{1}H NMR ($CDCl_3$) δ 2.72 (s, 6H), 2.70 (s, 6H), 5.45 (s, 2H), 5.40 (s, 2H), 6.63, 6.72, 6.88, 7.12, 7.28 (m, 20H).

1,2-Bis(diethylamino)-1,2-bis(2-naphthyl)ethane (15): ^{1}H NMR ($CDCl_3$) (meso) δ 0.68 (t, J = 9.2 Hz, 12H), 2.00 (q, J = 8.8 Hz, 4H), 2.56 (q, J = 8.8 Hz, 8H), 4.58 (s, 2H), 7.36−7.81 (m, J = 4.8 Hz, 8H); (rac) δ 1.18 (t, J = 9.6 Hz, 12H), 2.18 (q, J = 8.4 Hz, 4H), 2.92 (q, J = 9.6 Hz, 8H), 4.71 (s, 2H), 7.26−7.68 (m, J = 4.6 Hz, 8H). ^{13}C NMR ($CDCl_3$) (meso) δ 14.19, 43.93, 64.38, 125.37, 125.72, 126.55, 127.77, 128.16, 128.60, 132.70, 133.28, 136.47; (rac) δ 14.48, 43.67, 64.89, 125.02, 125.98, 126.41, 127.20, 128.19, 128.66, 133.21, 137.02.

***N,N,N′,N′*-Tetramethyl-1,2-diphenylethylenediamine (16)**: ^{1}H NMR ($CDCl_3$) (meso) δ 1.96 (s, 6H), 4.13 (s, 2H), 7.23−7.41 (m, J = 2.8 Hz, 8H); (rac) δ 2.24 (s, 6H), 4.23 (s, 2H), 6.98−7.13 (m, J = 1.6 Hz, 8H). ^{13}C NMR ($CDCl_3$) (meso) δ 40.96, 68.62, 127.11, 127.66, 129.56, 135.16; (rac) δ 41.04, 68.06, 126.83, 127.48, 130.13, 133.96.

***N,N,N′,N′*-Tetramethyl-1,2-bis-(4-chlorophenyl)-ethylenediamine (17):** Mp 140−142 °C. ^{1}H NMR ($CDCl_3$) (meso) (mp 140−142 °C) δ 1.95 (s, 12H), 4.06 (s, 2H), 7.13 (s, 4H), 7.33 (s, 4H); (rac) δ 2.25 (s, 12H), 4.21 (s, 2H), 6.89 (s, 4H), 7.11 (s, 8H). ^{13}C NMR ($CDCl_3$) (meso) δ 41.08, 78.29, 129.59, 131.61, 133.10; (rac) δ 41.89, 78.37, 129.02, 130.99, 133.43.

***N,N,N′,N′*-Tetramethyl-1,2-bis(3-chlorophenyl)ethylenediamine (18):** Mp 176−178 °C. ^{1}H NMR ($CDCl_3$) (meso) (mp 176−178 °C) δ 1.98 (s, 12H), 4.05 (s, 2H), 7.08−7.32 (m, J = 4.0 Hz, 8H); (rac) δ 2.55 (s, 12H), 4.17 (s, 2H), 6.84−7.19 (m, J = 5.6 Hz, 8H). ^{13}C NMR ($CDCl_3$) (meso) δ 41.94, 77.79, 126.03, 130.34, 134.45, 136.28; (rac) δ 41.04, 77.51, 125.98, 128.04, 130.63, 134.11, 136.83.

***N,N,N′,N′*-Tetramethyl-1,2-bis(4-fluorophenyl)ethylenediamine (19):** Mp 107−109 °C. ^{1}H NMR ($CDCl_3$) (meso) δ 1.95 (s, 12H), 4.06 (s, 2H), 7.02 (s, 4H), 7.15 (s, 4H); (rac) δ 2.23 (s, 12H), 4.18 (s, 2H), 6.76 (s, 4H), 7.05 (s, 4H). ^{13}C NMR ($CDCl_3$) (meso) δ 42.48, 78.54, 116.04, 129.82, 130.69, 156.11; (rac) δ 41.91, 78.66, 115.69, 129.42, 130.42, 157.33.

***N,N,N′,N′*-Tetramethyl-1,2-bis(3-fluorophenyl)ethylenediamine (20):** Mp 99.5−101 °C. ^{1}H NMR ($CDCl_3$) (meso) δ 1.98 (s, 12H), 4.07 (s, 2H), 6.99−7.35 (m, J = 4.0 Hz, 8H); (rac) δ 2.25 (s, 12H), 4.17 (s, 2H), 6.65−7.12 (m, J = 4.6 Hz, 8H). ^{13}C NMR ($CDCl_3$) (meso) δ 42.41, 78.89, 117.62, 129.78, 130.41, 156.87; (rac) δ 41.89, 79.46, 115.69, 129.82, 130.77, 158.02.

***N,N,N′,N′*-Tetramethyl-1,2-bis(4-trifluoromethylphenyl)-ethylenediamine (21):** Mp 154−156 °C. ^{1}H NMR ($CDCl_3$) (meso) δ 1.98 (s, 12H), 4.20 (s, 2H), 7.15−7.46 (m, J = 5.2 Hz, 8H); (rac) δ 2.29 (s, 12H), 4.31 (s, 2H), 7.09−7.36 (m, J = 4.8 Hz, 4H). ^{13}C NMR ($CDCl_3$) (meso) δ 41.48, 78.43, 124.27, 125.94, 128.72, 138.02; (rac) δ 41.11, 78.62, 123.97, 124.62, 125.82, 128.44, 139.14.

***N,N,N′,N′*-Tetramethyl-1,2-bis(3-trifluorophenyl)ethylenediamine (22):** Mp 147−149 °C. ^{1}H NMR ($CDCl_3$) (meso) δ 1.98 (*s*, 12H), 4.21 (s, 2H), 7.21−7.57 (m, J = 4.0 Hz, 8H); (rac) δ 2.29 (*s*, 12H), 4.31 (s, 2H), 7.14−7.32 (m, J = 4.6 Hz, 8H).

***N,N,N′,N′*-Tetramethyl-1,2-bis(2-trifluorophenyl)ethylenediamine (23):** Mp 79−81 °C. ^{1}H NMR ($CDCl_3$) (meso) δ 2.13 (*s*, 12H), 4.52 (s, 2H), 7.29−7.66 (m, J = 4.4 Hz, 8H); (rac) δ 2.41 (s, 12H), 4.94 (s, 2H), 6.98−7.33 (m, J = 4.2 Hz, 8H).

***N,N,N′,N′*-Tetramethyl-1,2-bis(4-methylphenyl)ethylenediamine (24):** ^{1}H NMR ($CDCl_3$) (meso) δ 0.75 (t, J = 6.6 Hz 12H), 4.29 (s, 2H), 2.38 (s, 6H), 7.02−7.16 (m, J = 2.6 Hz, 8H); (rac) δ 1.08 (t, J = 6.8 Hz, 12H), 4.33 (s, 2H), 2.34 (s, 6H), aromatic, 6.82−6.86, 7.16−7.20 (m, J = 6.8 Hz, 8H). ^{13}C NMR ($CDCl_3$) (meso) δ 24.37, 41.16, 78.30, 128.14, 129.23, 134.72; (rac) δ 25.2, 41.88, 79.02, 127.94, 129.43, 133.71.

***N,N,N′,N′*-Tetramethyl-1,2-bis(3-methylphenyl)ethylenediamine (25):** Mp 142−144 °C. ^{1}H NMR ($CDCl_3$) (meso) δ 0.73 (t, J = 6.6 Hz, 12H), 4.25 (s, 2H), 2.37 (s, 6H), 7.12−7.24 (m, J = 2.6 Hz, 8H); (rac) δ 1.11 (t, J = 7.2 Hz, 12H), 4.37 (s, 2H), 2.39 (s, 6H), 6.73−7.19 (m, J = 7.2 Hz, 8H).

***N,N,N′,N′*-Tetraethyl-1,2-bis(3-pyridylyl)ethylenediamine (27):** ^{1}H NMR ($CDCl_3$) (meso) δ 0.69 (t, J = 6.8 Hz, 12H), 1.95 (q, J = 6.2 Hz, 4H), 2.47 (q, J = 6.2 Hz, 2H), 4.29 (s, 2H), 7.18 (m, J = 4.6 Hz, 2H), 7.55 (s, 2H), 8.44 (m, J = 7.2 Hz, 4H); (rac) δ 0.77 (t, J = 7.2 Hz, 12H), 2.11 (q, J = 6.6 Hz, 4H), 2.58 (q, J = 8.6 Hz, 4H), 4.37 (s, 2H), 7.27 (m, 2H), 7.61 (m, 2H), 8.52 (s, 4H). ^{13}C NMR ($CDCl_3$) (meso) δ 43.83, 62.25, 122.73, 133.37, 136.59, 148.26, 150.92.

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Supporting Information Available: Copies of ^{1}H NMR spectra for meso and rac isomers of compounds **2**, **9**, **14**, **15**, and **16** and ^{13}C NMR spectra of meso and rac isomers of compounds **6**, **10**, and **16**. This material is available free of charge via the Internet at http://pubs.acs.org.

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