$[PtCl_3(C_2H_4)]^-[AmH]^+$ Complexes Containing Chiral Secondary Amines: Use as Chiral Derivatizing Agents for the Enantiodiscrimination of Unsaturated Compounds by ^{195}Pt NMR Spectroscopy and NMR Stereochemical Investigation

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Ionic complexes $[PtCl_3(C_2H_4)]^-[AmH]^+$, containing chiral secondary amines, constitute a versatile class of chiral derivatizing agents (CDAs) for the enantiomeric purity determination of chiral unsaturated compounds via ^{195}Pt NMR spectroscopy. The NMR conformational analysis allows us to search for the stereochemical basis of their enhanced versatility.

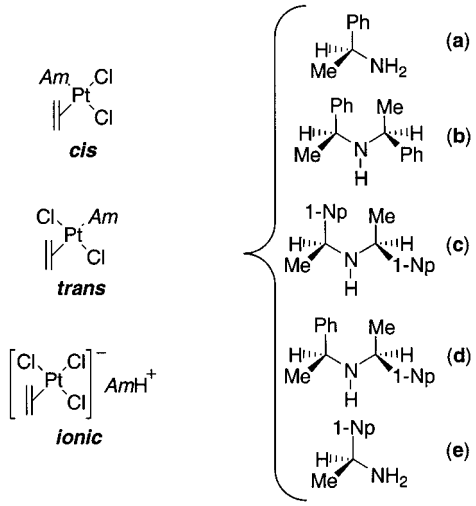
Introduction

The heightened interest in asymmetric syntheses raises the need for efficient, versatile and practical solutions for determining the enantiomeric composition of the products.

In the area of nonchiroptical techniques, NMR methods based on the use of a chiral auxiliary to convert the enantiomeric mixture into diastereoisomeric derivatives and on the detection of their anisochronous resonances represent one of the most popular choices.[1] Three classes of chiral auxiliaries for NMR spectroscopy have been developed, chiral derivating agents (CDAs)[1,2] employed to convert the enantiomeric pair into a diastereoisomeric mixture by a chemical transformation and chiral solvating agents (CSAs)[1,3] and chiral lanthanide shift reagents (CLSRs)[1,4] which form diastereoisomeric adducts by noncovalent interactions.

Both organic[1,2] and organometallic[1,5] CDAs have been proposed: the former compounds have found extensive applications in the analyses of chiral substrates endowed with polar functionalities, the latter compounds have received more limited attention even if they have interesting potentialities. In fact, their use can involve the simple coordination of π-moieties of the chiral substrates to the metal as a derivatization process opening the way to the analyses of compounds devoid of polar functionalities, such as the simple olefins or aromatic hydrocarbons. The use of organometallic platinum CDAs also gives the interesting possibility of detecting the diastereotopic species by the simple analyses of the resonances of their ^{195}Pt nuclei (I = 1/2, natural abundance 33.8%).

Chart 1



In the past years, we have proposed the use as CDAs of *cis*-[5f,g] (*cis*-**a**) and *trans*-dichloro(ethylene)(amine)-platinum(II)[5h,i] (*trans*-**a**) (Chart 1), containing the chiral

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Scheme 1

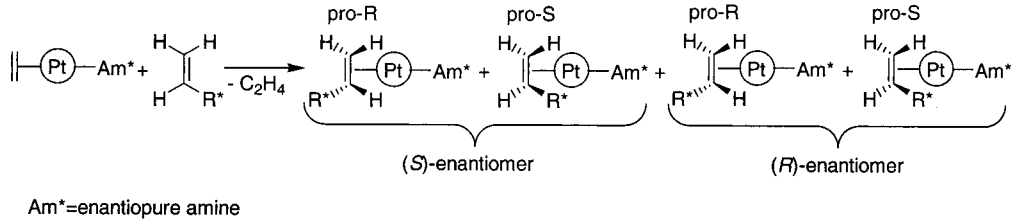
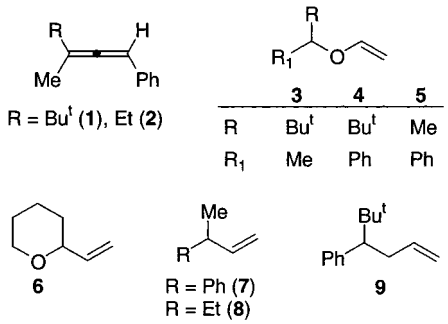


Chart 2



primary amine (*S*)-1-phenylethylamine (**a**), in the analyses of chiral unsaturated compounds. Even though the cis complex showed a very large applicability to the analyses of unsaturated ethers, its synthesis is time-consuming and proceeds with satisfactory yields only in the case of primary amines. The applicability of the *trans*-**a** was rather limited. Their use[5f−i] is based on the fast exchange of the ethylene with the enantiomeric mixture, the coordination of which occurs by the two prochiral faces of the double bond (Scheme 1). Therefore, each enantiomer can originate a maximum number of two diastereoisomers, the ratio of which reflects the diastereoselectivity in the complexation. When the diastereoisomers formed by the two enantiomers produce distinct ^{195}Pt NMR resonances, the comparison between their integrated areas directly gives the enantiomeric purity of the complexed substrates.

More recently, we have shown[6] the great potentialities of the ionic organometallic CDA $[PtCl_3(C_2H_4)]^-[AmH]^+$ *ionic*-**b** (Chart 1), containing the chiral secondary amine (1*S*,1′*S*)-bis(1-phenylethyl)amine (**b**), which was remarkably more versatile than *cis*-**a** or *trans*-**a**. Indeed, it discriminates trisubstitued allenes, unsaturated ethers, and simple olefins also.

Keeping in mind the aforementioned results, we have prepared the new ionic organometallic complexes *ionic*-**c** and *ionic*-**d** (Chart 1), respectively, containing the chiral secondary amines (1*S*,1′*S*)-bis[1-(1-naphthyl)ethyl]amine (**c**) and (1*S*,1′*S*)-N-[1′-(1-naphthyl)ethyl]-1-phenylethylamine (**d**), to investigate the effect of structural changes in the ammonium cation on the efficiency and versatility of CDAs for the ^{195}Pt NMR enantiodiscrimination of several classes of chiral unsaturated compounds **1**−**9** (Chart 2). Their enantiodiscriminating capabilities have also been compared to those of the trans-covalent CDAs *trans*-**b**−**d**, containing the corresponding secondary amines, as well as the complexes *ionic*-**e** and *trans*-**e**, where the primary amine (*S*)-1-(1-naphthyl)ethylamine (**e**) has been employed (Chart 1). Furthermore, with the aim of having some insight into the stereochemical basis of the enantiodiscriminating capabilities of these new ionic and covalent CDAs, their conformation has been investigated by NMR methods.[7]

Results and Discussion

Synthesis and Characterization of the Amine Ligands. The employed procedure[8] for the diastereoselective syntheses of chiral secondary amines **b**−**d**, having two chiral centers directly bound to the same nitrogen, involves the condensation reaction between an enantiomerically pure chiral primary amine and a prochiral ketone to give the syn/anti mixture of the imines, followed by catalytic hydrogenation (Pd/C 10%) (Scheme 2). The hydrogenation product is constituted by a mixture of two diastereoisomeric amines (ca. 90:10), from which the prevalent species is isolated by simple crystallization of the hydrochloride derivatives **b**′−**d**′. The crystallized products **b**′ and **c**′ were obtained as optically active (*S*,*S*)-stereoisomers. The absolute configuration of **d**′ has been established by determining the relative stereochemistry of the two chiral moieties (*S*)-1-phenylethyl and 1-(1-naphthyl)ethyl by NOE measurements, to obtain the spatial proximity constraints between them. The detected effects (Supporting Information, Figure S1), indicated in Figure 1 by arrows, demonstrated that the two methine protons are cis each other, with the methine of the 1-(1-naphthyl)ethyl moiety mainly directed toward the peri proton H_8 and in spatial proximity of the phenyl group of the other unit. The methine group of the 1-phenylethyl fragment is directed toward the H_2 proton of the naphthyl ring. The absolute configuration of the 1-phenylethyl group is prefixed and *S*, so the *S* absolute configuration must be assigned to the other chiral fragment.

Synthesis and Characterization of the CDAs. Ionic and covalent CDAs *ionic*-**b**−**e** and *trans*-**b**−**e** (Chart 1) have been prepared starting from Zeise's salt $[PtCl_3(C_2H_4)]^-K^+$ following the procedures described in ref 6. The complexes have been employed without further purification.

The CDAs have been characterized by ^{1}H and ^{13}C NMR spectroscopy in $CDCl_3$ as solvent: the ^{1}H characterization in some cases required the comparison between the 2D NOESY and 2D DQF−COSY maps and the ^{13}C spectra have been attributed by bidimensional heteronuclear correlation HETCOR. The ^{1}H NMR spectra of the ionic complexes *ionic*-**b**−**d** (Supporting Information, Figure S2) show the signals arising from the amine portion, very similar to those of the hydrochloride amine. For *ionic*-**b**−**c** the methyl, methine and aromatic protons of the two chiral residues are isochronous. The well recognizable

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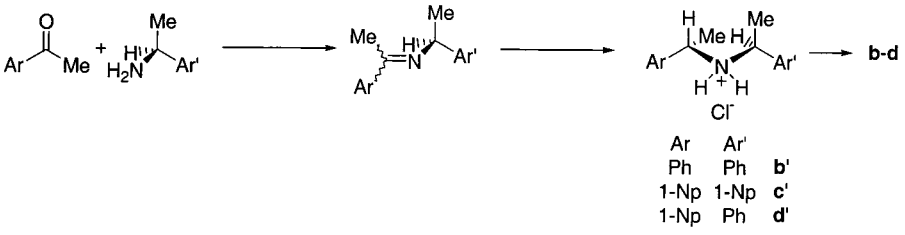
Scheme 2



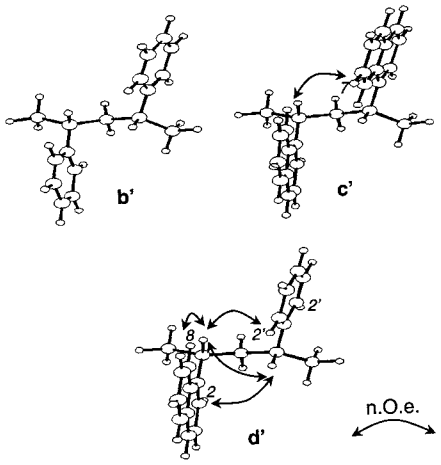


Figure 1. Representation of the ammonium cation of **b′**−**d′**.

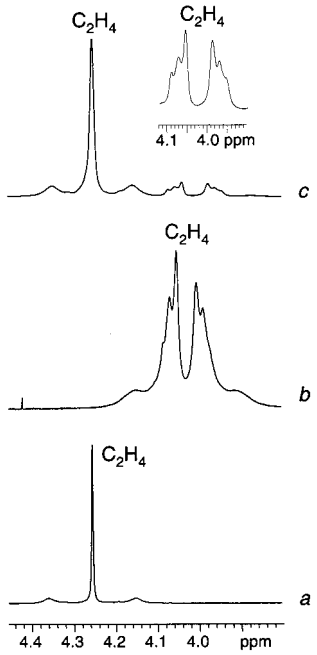


Figure 2. ^1H NMR spectral regions (300 MHz, $CDCl_3$, 25 °C) corresponding to the ethylene resonances of trans-covalent complexes: (a) *trans*-**b**, (b) *trans*-**c**, and (c) *trans*-**d**.

ethylene resonance is a sharp singlet accompanied by the satellites which result from the coupling with ^{195}Pt. For all ionic complexes ethylene protons behave as a simple A4 system, indicating the free rotation of the coordinated ethylene.[9] Very different spectral patterns have been observed for the covalent complexes *trans*-**b**−**d**: in *trans*-**b** or *trans*-**c** the coordination of the nitrogen makes anisochronous the two amine methyl, methine and aromatic groups. However, the coordinated ethylene maintains the A4 pattern in *trans*-**b** (Figure 2a) and produces a symmetrical multiplet corresponding to an AA′BB′ system in *trans*-**c** (Figure 2b), to indicate that ethylene is freely rotating in the former and its rotation is restricted (at room temperature) in the latter. In both cases the amine proton shows coupling to platinum. A very complicated spectrum is obtained for *trans*-**d**, showing simultaneous presence of two main species in a ratio 80:20, the prevailing one having the ethylene in free rotation (A4 system) and the minor one having it in hindered rotation (AA′BB′) (Figure 2c). These two species reasonably are due to the fact that, in this case, the nitrogen is chiral and its coordination generates two diastereoisomers corresponding to the two sets of signals. Accordingly, the platinum spectrum of each ionic complex *ionic*-**b**−**d**, and covalent *trans*-**b**−**c** shows a single absorption, whereas the complex *trans*-**d** shows two signals at −2909.6 ppm and −2916.6 ppm, corresponding to the two diastereoisomers.

Use of CDAs. The enantiodiscrimination experiments involve the displacement of the coordinated ethylene in the CDAs by the unsaturated chiral substrates (Scheme 1). This reaction can be very easily performed by dissolving a mixture of the CDA and of the substrate in the deuterated solvent (C_6D_6). By using a small excess of the CDA (CDA/substrate = 1:0.8) the fast exchange reaction occurs without detectable kinetic resolution phenomena. The diastereoisomeric mixtures are directly analyzed by ^{195}Pt NMR spectroscopy and the magnitudes of unequivalences ($\Delta\delta$, differences between the chemical shifts of the diastereoisomers containing the two enantiomers) measured in the spectra reflect the enantiodiscriminating capabilities of the CDAs used. Due to the possibility to have four or two signals in the spectra, two unequivalences values must be defined, calculated as differences between the ^{195}Pt NMR chemical shifts of the more ($\Delta\delta_1$) and less ($\Delta\delta_2$) abundant diastereoisomers formed by the two enantiomers (Table 1). The data reported in Table 1 summarize the results obtained in the use of the complexes *ionic*-**b**−**d** as CDAs for the unsaturated chiral substrates **1**−**9** (Chart 2) and demonstrate that the nature of the amine hydrochloride strongly affects the unequivalences.

The diastereoisomeric mixtures originated by complexation of the trisubstituted allene **1** always produce two signals, each due to one enantiomer and the unequivalence is 376 Hz by using *ionic*-**b** and remarkably increases to 496 Hz in the presence of the analogous cation having the 1-(1-naphthyl)ethyl moiety (*ionic*-**c**) (Figure 3) and to 440 Hz for CDA *ionic*-**d**, where the mixed amine derivative is employed. Also for the diastereoisomeric mixtures arising from the complexation of the allene **2**, producing two signals for each complexed enantiomer,

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Table 1. ^{195}Pt NMR (64.3 MHz, C_6D_6, 25 °C) Unequivalences (Hz) Measured by Using *ionic*-b−d as CDAs, Given as Differences between the Chemical Shifts of the More ($\Delta\delta_1$) and Less ($\Delta\delta_2$) Abundant Diastereoisomers in the Complexes Formed with Compounds 1−9

	ionic-**b**		*ionic*-**c**		*ionic*-**d**	
substrate	$\Delta\delta_1$	$\Delta\delta_2$	$\Delta\delta_1$	$\Delta\delta_2$	$\Delta\delta_1$	$\Delta\delta_2$
1	376[a]		496		440	
2	420[a]	372[a]	515	473	437	391
3	118[a]	148[a]	145	189	109	147
4	134	284	243	343	182	361
5	99	270	187	240	71	148
6	0	0	373	473	224	355
7	120[a]	196[a]	132	292	84	182
8	141	48	180	93	116	0
9	114[a]	0[a]	153	0	0	0

[a] Data reported in ref 6.

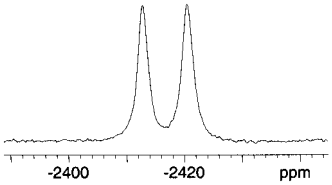

Figure 3. ^{195}Pt NMR spectrum (64.3 MHz, C_6D_6, 25 °C, Na_2PtCl_6 as external standard) of the diastereoisomeric mixtures formed from *rac*-**1** and *ionic*-**c**.

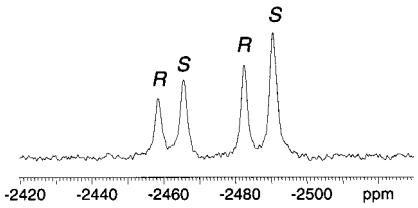

Figure 4. ^{195}Pt NMR spectrum (64.3 MHz, C_6D_6, 25 °C, Na_2PtCl_6 as external standard) of the diastereoisomeric mixtures formed from (*S*)-**2** (ee 18%) and *ionic*-**c**.

the unequivalences measured are markedly superior by using *ionic*-**c** ($\Delta\delta_1$ 515 Hz and $\Delta\delta_2$ 473 Hz) (Figure 4) than they are for *ionic*-**b** ($\Delta\delta_1$ 420 Hz and $\Delta\delta_2$ 372 Hz) or *ionic*-**d** ($\Delta\delta_1$ 437 Hz and $\Delta\delta_2$ 391 Hz). In the complexation of open-chain vinyl ethers **3**−**5**, the superior performances of CDA *ionic*-**c** with respect to *ionic*-**b** and *ionic*-**d** are evidenced once again at least for the $\Delta\delta_1$ value. In the case of cyclic allyl ether **6** only by using *ionic*-**c** and *ionic*-**d** enantiodiscrimination is observed. The complex *ionic*-**c** is also the more efficient CDA for the analyses of simple olefins **7**−**8**. For the chiral olefin **9**, having the chiral carbon atom in beta position to the double bond, unequivalences are measured only for the more abundant diastereoisomers produced by *ionic*-**c** and *ionic*-**b**, but this fact does not prevent us from determining the enantiomeric composition as this can be also based on the comparison between the areas of the signals originated by two corresponding species (the more or less abundant diastereoisomers). This is exact as a consequence of the fact that the same diastereoselectivity for the complexation of the two enantiomers of each substrate is observed.

By extending the analysis to the corresponding transcovalent complexes *trans*-**b**−**d**, we can observe that only in the case of trisubstituted allene **2** the complex *trans*-**b** has efficiency comparable to that of the corresponding ionic complex *ionic*-**b**.[6] For all other unsaturated substrates, *trans*-**b** did not allow to measure significant unequivalences. In the use of *trans*-**c** as CDA, the ^{195}Pt NMR spectra of the diastereoisomeric mixtures reveal the presence of a great number of complexed species (see the Supporting Information, Figure S3, as an example), which can be explained taking into account that also complexed ethylene is not freely rotating in the CDA and, hence, in the complexation of nonsymmetrical unsaturated chiral compounds, simultaneous presence of different rotamers must be expected for each diastereoisomer. The situation is more complicated in the use of CDA *trans*-**d**, which, due to the chirality of nitrogen, is present as a mixture of two diastereoisomers one having the ethylene in free rotation and the other slowly rotating. Therefore, *trans*-**b** has a limited enantiodiscriminating capability and *trans*-**c** and *trans*-**d** cannot be employed at all as CDAs.

The covalent complex *trans*-**e** containing the primary amine (*S*)-1-(1-naphthyl)ethylamine does not discriminate the enantiomers of allene **2** and the corresponding ionic complex *ionic*-**e** only produces very small unequivalences (Supporting Information, Figure S4).

Stereochemical Analysis of CDAs. As already discussed, the stereochemistry of the asymmetrical amine **d** as well as of its hydrochloride salt **d′** has been determined by NOE measurements. The intrinsic equivalence of corresponding nuclei of the two chiral units of **b′** unabled us to define its conformation. In **c′**, a highly diagnostic NOE between the methine protons and the naphthalene proton H_7 was detected, indicating that the C−H bond of one 1-(1-naphthyl)ethyl group points at the H_7 aromatic proton of the other chiral residue (Figure 1). Thus, the two methines must be cis and internal to the structure of the amine, and, being (*S*,*S*), the absolute configuration of the two chiral carbon atoms, the two naphthalene rings must be trans as well as the methyl groups. Hence, the conformation of **c′** is similar to that of **d′**, and it can be reasonably extended to **b′** (Figure 1).

In the ionic complexes *ionic*-**b**−**d**, the ammonium cations show the same NOEs patterns detected in the free state and the ethylene produces an A4 resonance system in the ^{1}H NMR spectra, indicating that it is freely rotating around the coordination axis. This last one produces NOEs (Supporting Information, Figure S5) only on the methyl and aromatic protons of the amine (mainly H_2 and H_3 in the case of *ionic*-**c** and both H_2−H_3 and phenyl protons for *ionic*-**d**), and no dipolar interaction is detected with the methine protons. Therefore, in the hypothesis that the ammonium cation interacts, via formation of an hydrogen bond, with the chlorine atom trans to ethylene, the two chiral units lie on opposite sides with respect to the coordination plane with the aromatic ring of one unit and the methyl group of the other one pointing at the metal and hence at the ethylene as in Figure 5. In the complex *ionic*-**d**, containing the mixed secondary ammonium cation **d′**, the NOEs produced by the ethylene on both naphthalene and phenyl protons and on the methyl groups indicate that the CDA is present in solution as a mixture, fast exchanging on NMR time scale, of the two possible structures represented in Figure 5.

In the formation of trans-covalent complexes *trans*-**b** and *trans*-**c**, corresponding nuclei of the two chiral residues become unequivalent as a consequence of the complexation of the nitrogen. As obtained from NOE

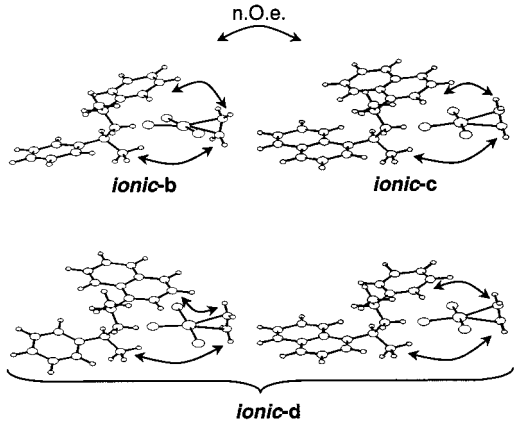

Figure 5. Representation of the ionic complexes *ionic*-**b**−**d**.

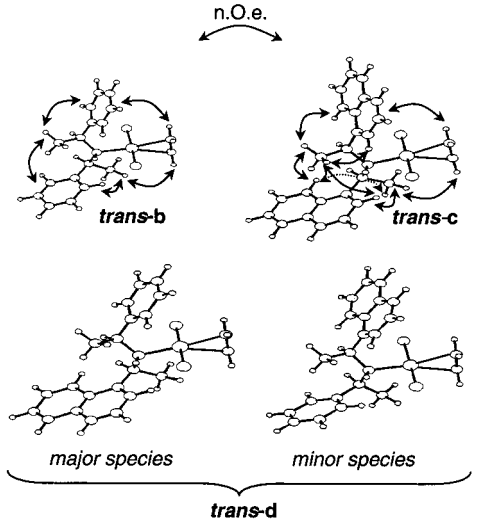

Figure 6. Representation of the trans-covalent complexes *trans*-**b**−**d**.

measurements (Supporting Information, Figure S6), the complexed amines of *trans*-**b** and *trans*-**c** have a conformation different with respect to that observed for the corresponding ammonium salts in the ionic complexes: the aromatic moieties are nearly perpendicular and one methyl group is between them, whereas the other one is external to the structure of the amine and only close to the aromatic ring of its own residue (Figure 6). The ethylene produces NOEs only on this last methyl group (that one external to the structure of the amine) and on the aromatic ring of the other chiral residue. In the case of the complex *trans*-**b**, the resonance of the coordinated ethylene holds the A4 pattern found for the ionic complexes (Figure 2a), i.e., it is freely rotating, whereas in *trans*-**c**, the rotation of the olefin is not free (AA′BB′ system in Figure 2b) as a consequence of the spatial proximity to the naphthalene ring. In *trans*-**d**, the simultaneous presence of the signals corresponding to the two diastereoisomers in a 80:20 ratio did not allow us to define their stereochemical features, but it is reasonable to suppose that the major diastereoisomer, the one having the ethylene freely rotating, has the phenyl ring bent at the ethylene as in Figure 6, and the minor species, where the rotation of ethylene is slow, has the naphthalene ring in spatial proximity of it.

In the complexes containing the primary amine (*ionic*-**e** and *trans*-**e**) only a NOE between the ethylene protons and the methyl group of the amine has been detected to indicate that the aromatic group is far away from the coordinated olefin.

Conclusions

The efficiency of the new ionic platinum(II) complexes, containing secondary amines, is strongly dependent on the nature of aromatic group present in the amine, the highest unequivalences for the complex containing the more hindered (1*S*,1′*S*)-bis[1-(1-naphthyl)ethyl]amine being measured. In fact, this last one allows us to detect unequivalences in the ^{195}Pt NMR spectra of the diastereoisomeric mixtures arising from the complexation to the metal of trisubstituted allenes, simple olefins having the stereogenic centers α or β to the double bond, vinyl ethers, and allyl ethers. Therefore, it represents one of the most versatile organometallic CDAs for the analyses of chiral unsaturated compounds. This is an important result, taking into account that, overall in the case of simple olefins, no alternative methods are available.

By contrast, the corresponding trans-covalent CDAs containing secondary amines have remarkable limitations: their applicability is limited as only symmetrical secondary amines having reduced steric hindrance can be employed. In fact, the diastereoisomeric mixtures obtained from trans-**c** produce very complicated ^{195}Pt NMR spectra due to the presence of several slow-exchanging rotamers for each complexed species. The trans-covalent CDA containing (1*S*,1′*S*)-*N*-[1′-(1-naphthyl)ethyl]-1-phenylethylamine also adds the problem of being present in solution as a diastereoisomeric mixture due to the stereogenicity of the nitrogen.

The results obtained explain the enhanced efficiency of ionic complexes containing secondary amines with respect to those containing primary amines: in the former ones the unsaturated ligand simultaneously interacts with the alkyl and aromatic substituents of the amine lying on opposite sides of the coordination plane, in the latter ones the complexed olefin is only affected by the amine on one side of the coordination plane. In *ionic*-**c**, which is the more efficient CDA, the interaction with the complexed olefin involves the naphthalene ring of the amine instead of a phenyl as in *ionic*-**b**.

Experimental Section

General Methods. All spectra were recorded using a spectrometer operating at 300, 75, and 64.3 MHz for ^{1}H, ^{13}C and ^{195}Pt, respectively and the temperature was controlled to ±0.1 °C. All ^{1}H and ^{13}C NMR chemical shifts are referred to TMS as external standard. ^{195}Pt NMR spectra were recorded in $CDCl_3$ or C_6D_6 and all ^{195}Pt NMR chemical shifts are referred to Na_2PtCl_6 as external standard. Standard pulse sequences have been employed for ^{195}Pt NMR measurements by using a spectral width of 50 000 Hz and an acquisition time of 0.3 s. No relaxation delays have been inserted between pulses. The 2D NMR spectra were obtained by using standard sequences. The DQF-COSY (double-quantum filter correlated spectroscopy) experiments were recorded with the minimum spectral width required; 512 increments of 8 scans and 2K data points were acquired. The relaxation delay was 10 s. The data were zero-filled to 2K × 1K, and a Gaussian function was applied for processing in both dimensions. The NOESY (nuclear Overhauser and exchange spectroscopy) spectra were recorded in the phase-sensitive mode, by employing a mixing time of 0.6 s. The spectral width used was the minimum required in both ω_1 and ω_2 dimensions. The pulse delay was maintained at 10 s; 512 hypercomplex increments of 8 scans

and 2K data points each were collected. The data matrix was zero-filled at 2K × 1K and a Gaussian function was applied for processing in both dimensions. The HETCOR (heteronuclear chemical shift-correlation) spectra were acquired with a spectral width of 11 000 Hz in F_2 and 3500 Hz in F_1 in 2K data points using 32 scans of the 256 increments. The relaxation delay was 2 s. The data were zero-filled to 2K × 1K, and a Gaussian function was applied for processing in both dimensions.

The $^1H\{^1H\}$-NOE experiments were performed in the difference mode. The decoupler power used was the minimum required to saturate the spin of interest. A waiting time of 5−10 s was used to allow the system to reach the equilibrium. Each NOE experiment was repeated at least four times. All the solutions were accurately degassed by freeze−pump−thaw cycles for 1D and 2D NOE experiments.

Melting points were determined using a Kofler hot-stage apparatus.

Materials. Tetrahydrofuran (THF) was distilled from Na/K alloy. Acetophenone, 1-acetonaphthone (*S*)-1-phenylethylamine, (*S*)-1-(1-naphthyl)ethylamine, 3-methyl-1-pentene, and Zeise's salt were purchased from Aldrich. Unless noted, all the other reagents were used without purification.

1-Phenyl-3,4,4-trimethyl-1,2-pentadiene (**1**),[10] 1-phenyl-3-methyl-1,2-pentadiene (**2**),[10] and 2-vinyltetrahydropyran (**6**)[11] were prepared as described elsewhere. Literature methods were used to prepare 1,2,2-trimethylpropyl vinyl ether (**3**),[12] 2,2-dimethyl-1-phenylpropyl vinyl ether (**4**),[12] 1-phenylethyl vinyl ether (**5**),[12] 3-phenyl-1-butene (**7**),[13] and 5,5-dimethyl-4-phenyl-1-hexene (**9**).[13]

General Procedure. Chiral Secondary Amine (*S,S*)-b−d.[8] According to the literature procedure reported in ref 8, (*S*)-1-phenylethylamine and (*S*)-1-(1-naphthyl)ethylamine were converted into the corresponding imines ((*S*)-*N*-(1-phenylethylidene)-1-phenylethylamine, (*S*)-*N*-[(1-naphthyl)ethylidene]-1-phenylethylamine, and (*S*)-*N*-[(1-naphthyl)ethylidene]-1-(1-naphthyl)ethylamine) by reacting the former with acetophenone and 1-acetonaphthone and the latter with 1-acetonaphthone. The resulting isomeric mixtures of syn and anti imines was hydrogenated in the presence of 10% Pd/C and the corresponding amine **b**−**d** were recovered as diastereoisomeric mixtures ((*S*,*S*)/(*S*,*R*) 88:12, 94:6 and 90:10 for **b**, **c**, and **d** respectively, as determined by ^1H NMR analysis). The pure (*S*,*S*)-diastereisomers of amines were obtained by crystallization of their hydrocloride salt **b′**−**d′** from H_2O for **b′** and from $CHCl_3$/pentane (1:2) for **c′** and **d′**. The free amine was then regenerated by treating the corresponding salt with KOH (10%).

Hydrochloride salt of (1*S*,1′*S*)-bis(1-phenylethyl)-amine (b′): mp 192−194 °C; $[\alpha]^{22}_D = -74.9°$ (c 4.0, EtOH); ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.90 (6H, Me, d, J = 6.7 Hz), 3.84 (2H, CH, q, J = 6.7 Hz), 7.33−7.46 (6H, Ph, m), 7.52 (4H, Ph, d, J = 7.9 Hz), 10.48 (2H, NH_2^+, bs); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 21.5 (Me), 57.2 (chiral CH), 128.2, 129.0, 129.2 (phenyl CH); 136.3 (quaternary C). Anal. Calcd for $C_{16}H_{20}NCl$: C, 73.41; H, 7.70; N, 5.35. Found: C, 73.68; H, 8.53; N, 5.20.

Hydrochloride salt of (1*S*,1′*S*)-bis[1-(1-naphthyl)ethyl]-amine (c′): mp 231−233 °C; $[\alpha]^{22}_D = +317.19°$ (*c* 0.89, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 2.09 (6H, Me, d, J = 6.8 Hz), 4.96 (2H, CH, q, J = 6.8 Hz), 6.33 (2H, H_8, bs), 6.56 (2H, H_7, dd, J = 8.1, 6.8 Hz), 7.06 (2H, H_6, dd, J = 8.1, 6.8 Hz), 7.61 (2H, H_5, d, J = 8.1 Hz), 7.73 (2H, H_3, dd, J = 7.9, 6.8 Hz), 7.82 (2H, H_4, d, J = 7.9 Hz), 8.70 (2H, H_2, bs), 10.96 (2H, NH_2^+, bs); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 21.7 (Me), 51.0 (chiral CH), 120.4 (C_8), 125.3 (C_6), 125.5 (C_2), 125.8 (C_3 and C_7), 128.3 (C_5), 129.0 (C_4), 130.3, 132.7, 133.5 (quatenary C). Anal. Calcd for $C_{24}H_{24}NCl$: C, 79.65; H, 6.68; N, 3.87. Found: C, 79.92; H, 6.61; N, 3.76.

Hydrochloride salt of (1*S*,1′*S*)-*N*-[1′-(1-naphthyl)ethyl]-1-phenylethylamine (d′): mp 258−260 °C; $[\alpha]^{22}_D = +99.2°$ (*c* 1.00, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.99 (3H, Me′, d, J = 6.8 Hz), 2.00 (3H, Me, d, J = 6.8 Hz), 4.03 (1H, CH′, m), 4.83 (1H, CH, m), 6.99 (1H, H_8, bs), 7.17−7.34 (5H, Ph, m), 7.25 (1H, H_7, dd, J = 8.1, 6.9 Hz), 7.44 (1H, H_6, dd, J = 8.1, 6.9 Hz), 7.69 (1H, H_3, dd, J = 8.0, 6.9 Hz), 7.86 (1H, H_4, d, J = 8.0 Hz), 7.88 (1H, H_5, d, J = 8.1 Hz), 8.59 (1H, H_2, bs), 10.80 (2H, NH_2^+, m); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 21.1 and 21.9 (Me′ and Me); 51.4 (chiral CH), 57.2 (chiral CH′); 121.6 (C_8); 125.5 (C_2); 125.9 (C_6); 126.1 (C_3); 126.4 (C_7); 128.3, 128.9, 129.0 (phenyl CH); 128.9 (C_4); 129.0 (C_5); 130.2, 132.7, 133.7, 136.0 (quaternary C). Anal. Calcd for $C_{20}H_{22}NCl$: C, 77.03; H, 7.11; N, 4.49. Found: C, 77.28; H, 7.05; N, 4.35.

General Procedure. *trans*-Dichloro(b−e)(ethylene)-platinum(II) Complexes (*trans*-b−e). To a solution of Zeise's salt $[PtCl_3(C_2H_4)]^-K^+$ (1.58 mmol) in H_2O/CH_3OH (2:1, 20 mL) was added, at 0 °C, a methanol solution of the appropriate amine (1.58 mmol). *Trans*-**b**−**e** were filtered off and recovered as pale yellow solids.

***trans*-Dichloro(b)(ethylene)platinum(II) (*trans*-b):** mp 166−168 °C; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.33 (3H, Me′, d, J = 7.1 Hz), 2.03 (3H, Me, d, J = 7.1 Hz), 4.25 (4H, C_2H_4, s), 4.54 and 4.57 (2H, CH, m), 5.29 (1H, NH, bt), 7.27−7.49 (10H, Ph, m);^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 22.1 (Me′), 24.3 (Me), 61.5, 62.5 (chiral CH′ and CH), 71.4 (C_2H_4), 127.0, 127.1, 128.1, 128.5, 129.2, 129.4 (phenyl CH), 140.0, 142.2 (quaternary C); ^{195}Pt NMR (64.3 MHz, C_6D_6, 25 °C) δ −2916.5. Anal. Calcd for $C_{18}H_{23}NCl_2Pt$: C, 41.63; H, 4.46; N, 2.70. Found: C, 42.06; H, 4.61; N, 2.52.

***trans*-Dichloro(c)(ethylene)platinum(II) (*trans*-c):** mp 218−220 °C; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.24 (3H, Me′, d, J = 6.4 Hz), 2.23 (3H, Me, d, J = 6.4 Hz), 4.04 (4H, C_2H_4, m), 5.59 (2H, CH and CH′, m), 5.93 (1H, NH, bs), 7.48 (2H, $H_{6'}$ and $H_{7'}$, m), 7.52 (1H, $H_{3'}$, dd, J = 8.2, 7.4 Hz), 7.58 (1H, H_6, dd, J = 8.2, 7.2 Hz), 7.61 (1H, H_3, dd, J = 8.2, 7.4 Hz), 7.68 (1H, H_7, dd, J = 8.2, 7.2 Hz), 7.74 (1H, $H_{2'}$, d, J = 7.4 Hz), 7.84 (1H, $H_{4'}$, d, J = 8.2 Hz), 7.86 (1H, $H_{5'}$, d, J = 8.2 Hz), 7.87 (1H, H_2, d, J = 7.4 Hz), 7.89 (1H, H_4, d, J = 8.2 Hz), 7.95 (1H, H_5, d, J = 8.2 Hz), 8.08 (1H, $H_{8'}$, d, J = 8.2 Hz), 8.23 (1H, H_8, d, J = 8.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 23.2 (Me′), 25.1 (Me), 56.4, 57.6 (chiral CH and CH′), 70.9 (C_2H_4), 121.8 (C_8), 123.1 (C_2), 123.8 ($C_{8'}$), 124.9 ($C_{3'}$), 125.4 (C_6), 125.8 ($C_{6'}$ and $C_{7'}$), 126.0 (C_3), 126.3 ($C_{2'}$), 127.2 (C_7), 128.8 ($C_{5'}$ and $C_{4'}$), 129.0 (C_4), 129.4 (C_5), 130.3, 133.8, 134.2, 137.4, 139.4, 141.2 (quaternary C); ^{195}Pt NMR (64.3 MHz, C_6D_6, 25 °C) δ −2916.5. Anal. Calcd for $C_{26}H_{27}NCl_2Pt$: C, 50.41; H, 4.39; N, 2.26. Found: C, 50.66; H, 4.46; N, 2.11.

***trans*-Dichloro(d)(ethylene)platinum(II) (*trans*-d):** mp 204−206 °C; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) (* denotes the minor species) δ 1.23 (3H, Me′, d, J = 6.8 Hz), 1.35 (3H, Me′*, d, J = 6.8 Hz), 2.12 (3H, Me*, d, J = 6.8 Hz), 2.17 (3H, Me, d, J = 6.8 Hz), 4.01 (4H, C_2H_4*, m), 4.28 (4H, C_2H_4, s), 4.64 (1H, CH* and CH′, m), 5.51 (1H, CH and CH′*, m), 5.64 (1H, NH* and NH, m), 7.05−8.30 (12H, Np*, Np and Ph*, Ph, m); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 21.8, 23.8, 24.5, 24.9 (Me, Me′, Me* and Me′*); 55.5, 62.8 (CH, CH′, CH* and CH′*); 70.7 (C_2H_4*); 71.3 (C_2H_4); 121.7, 122.7, 123.3, 123.7, 124.8, 125.4, 125.7, 125.8, 126.0, 126.2, 126.8, 127.0, 127.2, 127.3, 127.6, 128.2, 128.5, 128.8, 128.9, 129.3, 129.4, 130.6, 131.1, 133.9, 134.1, 137.6, 138.9, 139.9 (aromatic CH and quaternary C); ^{195}Pt NMR (64.3 MHz, C_6D_6, 25 °C) δ −2909.6, −2916.6. Anal. Calcd for $C_{22}H_{25}NCl_2Pt$: C, 46.40; H, 4.43; N, 2.46. Found: C, 46.61; H, 4.54; N, 2.36.

***trans*-Dichloro(e)(ethylene)platinum(II) (*trans*-e):** mp 113−114 °C; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 2.01 (3H, Me, d, J = 6.8 Hz), 4.30 (2H, NH_2, bs), 4.70 (4H, C_2H_4, m), 5.55 (1H, CH, q, J = 6.8 Hz), 7.47 (1H, H_3, dd, J = 8.0, 7.8 Hz), 7.52 (1H, H_6, dd, J = 8.2, 7.2 Hz), 7.54 (1H, H_2, d, J = 7.8 Hz), 7.61 (1H, H_7, dd, J = 8.5, 7.2 Hz), 7.84 (1H, H_4, d, J = 8.0 Hz), 7.89 (1H, H_5, d, J = 8.2 Hz), 8.29 (1H, H_8, d, J = 8.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 21.7 (Me); 50.7 (CH); 75.1 (C_2H_4); 122.2, 122.5, 125.3, 126.3, 127.4, 129.2, 129.4 (naphthyl CH); 130.3, 130.7, 134.0 (quaternary C); ^{195}Pt NMR (64.3 MHz,

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C_6D_6, 25 °C) δ −3068.7. Anal. Calcd for $C_{14}H_{17}NCl_2Pt$: C, 36.14; H, 3.68; N, 3.01. Found: C, 36.49; H, 3.58; N, 2.92.

General Procedure. Ionic $[PtCl_3(C_2H_4)]^-$(b′−e′)$^+$ Complexes (*ionic*-b−e). To a suspension of Zeise's salt $[PtCl_3(C_2H_4)]^-K^+$ (1.58 mmol) in $CHCl_3$ was added **b′**−**e′** (1.58 mmol). As a consequence of the rapid exchange of the two cations, a white fine powder of KCl was formed and filtered off. *ionic*-**b**−**e** were recovered as yellow solids by removal of the solvent in vacuo.

$[PtCl_3(C_2H_4)]^-$(b′)$^+$ (*ionic*-b): mp 145−148 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.83 (6H, Me, d, J = 7.0 Hz), 3.94 (2H, CH, q, J = 7.0 Hz), 4.61 (4H, C_2H_4, s), 7.33−7.48 (10H, Ph, m), 8.66 (2H, NH_2, bs); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 21.7 (Me), 57.8 (chiral CH), 69.5 (C_2H_4), 127.7, 129.6, 129.7 (phenyl CH), 135.2 (quaternary C); ^{195}Pt NMR (64.3 MHz, C_6D_6, 25 °C) δ −2825.4. Anal. Calcd for $C_{18}H_{24}NCl_3Pt$: C, 38.90; H, 4.35; N, 2.52. Found: C, 39.08; H, 4.42; N, 2.19.

$[PtCl_3(C_2H_4)]^-$(c′)$^+$ (*ionic*-c): mp 162−164 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.99 (6H, Me, d, J = 6.9 Hz), 4.70 (4H, C_2H_4, s), 4.94 (2H, CH, q, J = 6.9 Hz), 6.68 (2H, H_8, bs), 6.82 (2H, H_7, dd, J = 8.2, 6.8 Hz), 7.26 (2H, H_6, dd, J = 8.2, 6.8 Hz), 7.63 (2H, H_3, dd, J = 8.2, 6.8 Hz), 7.75 (2H, H_5, d, J = 8.2 Hz), 7.88 (2H, H_4, d, J = 8.2 Hz), 7.99 (2H, H_2, bs), 8.71 (2H, NH_2^+, bs); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 22.2 (Me), 52.7 (chiral CH), 69.7 (C_2H_4), 120.8 (C_8), 124.4 (C_2), 125.8 (C_3), 126.1 (C_6), 126.7 (C_7), 128.8 (C_5), 130.0 (C_4), 130.2, 131.3, 133.7 (quaternary C); ^{195}Pt NMR (64.3 MHz, C_6D_6, 25 °C) δ − 2827.4. Anal. Calcd for $C_{26}H_{28}NCl_3Pt$: C, 47.61; H, 4.30; N, 2.14. Found: C, 47.73; H, 4.35; N, 2.01.

$[PtCl_3(C_2H_4)]^-$(d′)$^+$ (*ionic*-d): mp 158−159 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.88 (3H, Me′, d, J = 6.8 Hz), 1.94 (3H, Me, d, J = 6.8 Hz), 3.98 (1H, CH′, m), 4.66 (4H, C_2H_4, s), 4.89 (1H, CH, m), 7.13 (2H, $H_{2'}$, d, J = 7.5 Hz), 7.33 (2H, $H_{3'}$, dd, J = 7.5, 7.5 Hz), 7.34 (1H, H_8, d, J = 8.2 Hz), 7.38 (1H, $H_{4'}$, t, J = 7.5 Hz), 7.42 (1H, H_7, dd, J = 8.2, 7.0 Hz), 7.54 (1H, H_6, dd, J = 8.2, 7.0 Hz), 7.66 (1H, H_3, dd, J = 8.0, 7.6 Hz), 7.92 (1H, H_5, d, J = 8.2 Hz), 7.94 (1H, H_4, d, J = 8.0 Hz), 7.97 (1H, H_2, d, J = 7.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 21.6 (Me′), 22.4 (Me), 52.7 (chiral CH), 58.3 (chiral CH′), 69.5 (C_2H_4), 121.4 (C_8), 124.5 (C_2), 126.0 (C_3), 126.4 (C_6), 127.0 (C_7), 127.8 ($C_{2'}$), 129.2 ($C_{4'}$), 129.4 ($C_{3'}$), 129.8 (C_5), 129.9 (C_4), 131.4, 133.0, 133.8, 134.6 (quaternary C); ^{195}Pt NMR (64.3 MHz, C_6D_6, 25 °C) δ −2825.6. Anal. Calcd for $C_{22}H_{26}NCl_3Pt$: C, 43.61; H, 4.33; N, 2.31. Found: C, 43.72; H, 4.38; N, 2.25.

$[PtCl_3(C_2H_4)]^-$(e′)$^+$ (*ionic*-e): mp 183−185 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.90 (3H, Me, d, J = 6.8 Hz), 4.30 (4H, C_2H_4, m), 5.60 (1H, CH, m), 7.41 (3H, NH_3^+, bs), 7.49 (1H, H_6, dd, J = 8.2, 6.9 Hz), 7.52 (1H, H_3, dd, J = 8.2, 7.2 Hz), 7.58 (1H, H_7, dd, J = 8.5, 6.9 Hz), 7.77 (1H, H_2, d, J = 7.2 Hz), 7.84 (1H, H_4, d, J = 8.2 Hz), 7.86 (1H, H_5, d, J = 8.2 Hz), 8.07 (1H, H_8, d, J = 8.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 21.0 (Me), 48.3 (chiral CH), 70.2 (C_2H_4), 122.2, 123.8, 125.6, 126.4, 127.5, 129.2, 129.8 (naphthyl CH), 129.9, 132.8, 133.9 (quaternary C); ^{195}Pt NMR (64.3 MHz, C_6D_6, 25 °C) δ −2842.5. Anal. Calcd for $C_{14}H_{18}NCl_3Pt$: C, 33.51; H, 3.62; N, 2.79. Found: C, 33.66; H, 3.57; N, 2.61.

General Procedure Involved in the Use of the CDAs for the Enantiodiscrimination Measurements. The chiral substrate (**1**−**9**) was added (substrate/CDA 0.8:1) to a solution containing 50−100 mg of CDA in 0.5 mL of C_6D_6 and the ^{195}Pt NMR spectra of the reaction mixtures were analyzed. The ^{195}Pt resonances of the small excess of *trans*-**b**−**e** (from −2909.6 to −3068.7 ppm) and *ionic*-**b**−**e** (from-2825.4 to −2842.5 ppm) are at low frequencies with respect to the absorptions due to complexes containing the substrate **1**−**9**.

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Supporting Information Available: ^{1}H{^{1}H}-NOE difference spectra of **d′** in $CDCl_3$. ^{1}H NMR spectra of ionic complexes. ^{195}Pt NMR spectra of the diastereoisomeric mixtures obtained for **2** by using CDAs *trans*-**c**, *trans*-**e** and *ionic*-**e**. ^{1}H{^{1}H}-NOE difference spectra corresponding to the saturation of the ethylene protons of ionic complexes. ^{1}H{^{1}H}-NOE difference spectra of *trans*-**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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