trans-[PtCl$_2$(Am)(C$_2$H$_4$)] and [PtCl$_3$(C$_2$H$_4$)]$^-$[AmH]$^+$, Containing Binaphthyl Secondary Amines − Efficient Chiral Derivatizing Agents for the Enantiodiscrimination of Chiral Olefins by ^{195}Pt NMR Spectroscopy

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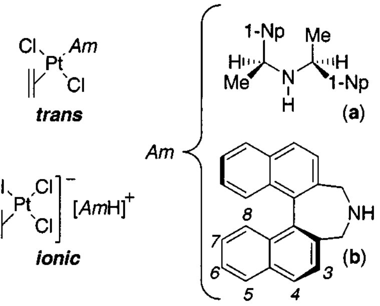
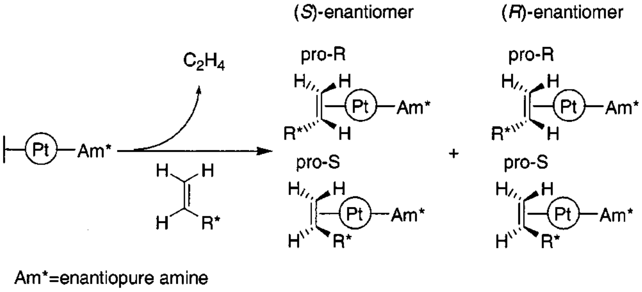
The complexes [PtCl$_3$(C$_2$H$_4$)]$^-$[AmH]$^+$ and *trans*-[PtCl$_2$(Am)(C$_2$H$_4$)], containing the binaphthyl secondary amine (*S*)-3,5-dihydro-4*H*-dinaphth[2,1-*c*:1′,2′-*e*]azepine, are efficient and versatile CDAs for the enantiodicrimination of simple olefins by ^{195}Pt NMR analysis of their diastereoisomeric derivatives.

Introduction

NMR methods for determining the enantiomeric composition of chiral compounds involve the detection of the resonances of their diastereoisomeric derivatives,[1,2] obtained by use of suitable chiral auxiliaries of one of the three classes: chiral derivatizing agents (CDAs),[1−4] chiral solvating agents (CSAs),[1,2,5,6] and chiral lanthanide shift reagents (CLSRs).[1,2,7−9] However, their applications to the analyses of apolar compounds are quite limited. A significant contribution in this field has arisen from the development of organometallic CDAs,[10−16] the use of which can involve the coordination of π-moieties to the metal center as a derivatization process, thus making the analysis of unsaturated or aromatic compounds possible. We have recently introduced[17,18] the new and promising organometallic CDAs *trans*-[PtCl$_2$(Am)(C$_2$H$_4$)] (*trans*) and [PtCl$_3$(C$_2$H$_4$)]$^-$[AmH]$^+$ (*ionic*) (Scheme 1), containing chiral secondary amines, for the enantiomeric composition determination of several classes of unsaturated compounds. These were prepared by very simple experimental procedures from Zeise's salt,[17,18] and their use as CDAs is based on the exchange of coordinated ethylene by the enantiomers of the chiral unsaturated compounds (Scheme 2). The corresponding diastereoisomeric mixtures were analyzed by ^{195}Pt NMR spectroscopy. In view of the great versatility and efficiency of the CDA *ionic*-**a**,[18] which contains the symmetrical amine (1*S*,1′*S*)-bis[1-(1-naphthyl)ethyl]amine (Scheme 1), we have now prepared the complexes *trans*-**b** and *ionic*-**b**, employing the binaphthylic secondary amine (*S*)-3,5-dihydro-4*H*-dinaphth[2,1-*c*:1′,2′-*e*]azepine (**b**) (Scheme 1). This amine is also symmetrical and possesses two naphthalene moieties, but offers different steric hindrance than amine **a** in the vicinity of the nitrogen atom. The enantiodiscriminating capabilities of the new CDAs were evaluated by analyzing the ^{195}Pt NMR spectra of diastereoisomeric mixtures produced by complexation of the chiral unsaturated compounds shown in Scheme 3.



Scheme 1



Scheme 2

Results and Discussion

(*S*)-3,5-Dihydro-4*H*-dinaphth[2,1-*c*:1′,2′-*e*]azepine (**b**) (Scheme 1) was prepared by following the literature procedure.[19,20]

The complexes *ionic*-**b** and *trans*-**b** were prepared starting from Zeise's salt,[17,18] using the amine **b** in its hydrochloride

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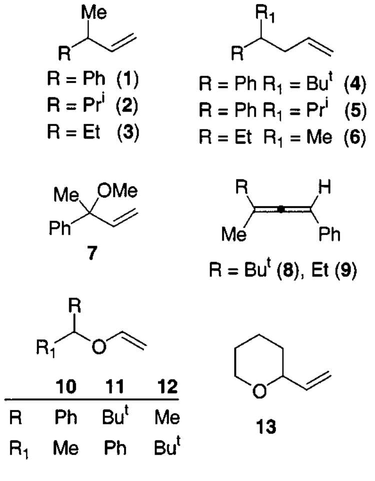
salt and free base forms, respectively. Both were characterized by NMR spectroscopy. The ^{1}H NMR spectral features of the CDA *ionic*-**b** are very similar to those of the ionic complexes previously reported.[18] In fact, only one set of resonances is produced by corresponding protons in the two naphthalene and methylene groups, as in the free hydrochloride salt, with the NH_2^+ protons not coupled to platinum. The ethylene protons produce a single resonance, as in an A4 system, with platinum-195 satellites. In the covalent complex *trans*-**b** the two units of the amine also produce one set of signals, but the amine proton NH shows satellites due to coupling to platinum-195 and the ethylene protons are again equivalent, as in *ionic*-**b**. It is to be noted, though, that the spectral features of *trans*-**b** are very different from those of *trans*-**a**, in which complexation to the metal results in the nonequivalence of the two naphthalene rings and the ethylene slowly rotates about the coordination axis (AA′BB′ system).[18]

In order to assess the enantiodiscriminating capabilities of the two new complexes *ionic*-**b** and *trans*-**b**, we used ^{195}Pt NMR spectroscopy to analyze the diastereoisomeric mixtures produced by the exchange of the ethylene of the CDAs (Scheme 2) by the unsaturated compounds of Scheme 3, which include simple olefins, allenes, and unsaturated ethers. The complexation of each enantiomer of the substrate may proceed at the two prochiral faces of the double bond (the less-substituted one in the case of trisubstituted allenes), thus producing up to two diastereoisomers, which are usually present in different amounts depending on the diastereoselectivity of the complexation. As each diastereoisomer can produce a single ^{195}Pt NMR resonance, the enantiomeric composition of the unsaturated compound involved in the exchange can be determined simply by comparing the areas (or the sum of the areas) of the signals produced by each enantiomer. Two values of nonequivalence must be defined; these are given as the difference between the chemical shifts (Hz) of the major ($\Delta\delta_1$) and minor ($\Delta\delta_2$) diastereoisomers produced by each complexed enantiomer (Table 1).



Scheme 3

Table 1. ^{195}Pt NMR (64.3 MHz, 25 °C) nonequivalences (Hz) measured using *ionic*-**a**−**b** and *trans*-**b** 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**−**13**

	ionic-**a**[a]		*trans*-**b**[b]		*ionic*-**b**[a]	
Compound	$\Delta\delta_1$	$\Delta\delta_2$	$\Delta\delta_1$	$\Delta\delta_2$	$\Delta\delta_1$	$\Delta\delta_2$
1	132[c]	292[c]	707	328	192	45
2	141	55	1241	379	764	454
3	156	76	401	351	112	289
4	153[c]	0[c]	172	0	188	404
5	0	0	296	0	98	332
6	0	0	0	0	190	0
7	0	351	1176	1100	0	0
8	496[c]		97		0	
9	515[c]	473[c]	165	0	378	385
10	187[c]	240[c]	n.d.[d]	n.d.	153	562
11	243[c]	343[c]	n.d.	n.d.	220	0
12	145[c]	189[c]	n.d.	n.d.	0	258
13	373[c]	473[c]	n.d.	n.d.	0	0

[a] C_6D_6 solvent. − [b] $CDCl_3$ solvent. − [c] data reported in reference 18. − [d] n.d. = not determined.

In the enantiodiscrimination of simple olefins, the new complexes *trans*-**b** and *ionic*-**b**, both containing the binaphthylic amine, show remarkable efficiency, superior to that of the previously reported[18] complex *ionic*-**a**, which contains (1*S*,1′*S*)-bis[1-(1-naphthyl)ethyl]amine (**a**). In fact, these two complexes allowed us to enantiodiscriminate olefins with either α or β chiral centers with respect to the complexation site (i.e., the double bond). In particular, the covalent complex *trans*-**b** was the most efficient for the α-olefins **1**−**3**, whereas *ionic*-**b** showed a superior performance in the analysis of the β-olefins **4**−**6** (Table 1). As an example, the complexation of racemic 3-phenyl-1-butene (**1**) produced four diastereoisomers, each giving a single resonance: at $\delta = -3022.0$, -3033.0, -3037.9 and -3043.0, respectively. Among these, the two resonances at $\delta = -3022.0$ and -3043.0 were due, respectively, to the major and minor diastereoisomers originating from complexation of the *R* enantiomer, and those at $\delta = -3033.0$ and -3037.9 to the corresponding species generated by the complexed *S* enantiomer (Figure 1). For the major diastereoisomers, therefore, the nonequivalence was 11 ppm (707 Hz) and for the minor ones 5.1 ppm (328 Hz) (Table 1). The ionic complex *ionic*-**b**, also possessing the binaphthylamine moiety, also displayed a good enantiodiscriminating capability, producing nonequivalence values of 192 Hz and 45 Hz. On complexation of the same olefin **1** in the complex *ionic*-**a**,[18] the values measured were 132 Hz and 292 Hz, respectively (Figure 2). For the other two chiral olefins **2** and **3**, both possessing the double bond α to the chiral center, but bearing only alkyl groups, the nonequivalences measured using *trans*-**b** or *ionic*-**b** were markedly greater than with *ionic*-**a** (Table 1). In the complexation of olefins possessing the double bond β with respect to the chiral center, *ionic*-**b** was the more efficient CDA (Figure 3 refers to compound **4**), even allowing us to enantiodiscriminate the olefin **6**, in which both groups bound to the chiral carbon atom are alkyl (methyl and ethyl) and display very similar steric hindrances. In this last case, a nonequivalence was measured only for the two major diastereoisomers (190 Hz), but this fact did not prevent us from evaluating the enantiomeric composition of enriched samples, as the complexation of the two enantiomers occurred with the same diastereoselectivity. Another interesting case is the complexation of the open-chain allyl ether **7**, for which nonequivalences greater than 1000 Hz (Table 1) were obtained when *trans*-**b** was used and values of about 400 Hz when *ionic*-**a** was used (Figure 4). Surprisingly, however, no nonequivalence was measured when using *ionic*-**b**. However, *ionic*-**a** is the most versatile,[18] as it allowed us to enantiodiscriminate allyl ethers (**7**,**13**), vinyl ethers (**10**−**12**), and trisubstituted allenes (**8**−**9**); *ionic*-**b** enantiodiscriminated only vinyl ethers, producing nonequivalences comparable to those found using *ionic*-**a** as the CDA.

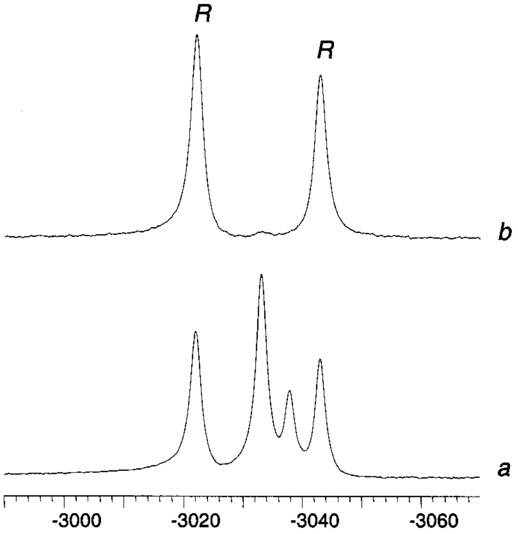


Figure 1. ^{195}Pt NMR (64.3 MHz, $CDCl_3$, 25 °C, Na_2PtCl_6 as external standard) spectra of the diastereoisomeric mixtures formed from *trans*-**b** and: (a) (*RS*)-**1**, (b) (*R*)-**1**

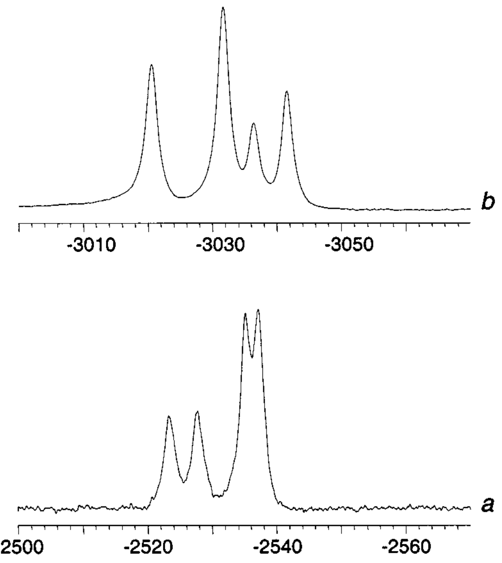


Figure 2. ^{195}Pt NMR (64.3 MHz, 25 °C, Na_2PtCl_6 as external standard) spectra of the diastereoisomeric mixtures formed from **1** and: (a) *ionic*-**a** (C_6D_6), (b) *trans*-**b** ($CDCl_3$)

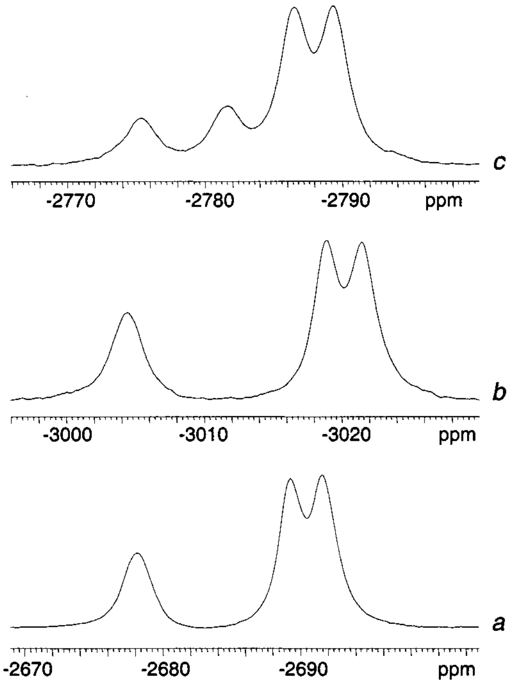


Figure 3. ^{195}Pt NMR (64.3 MHz, 25 °C, Na_2PtCl_6 as external standard) spectra of the diastereoisomeric mixtures formed from **4** and: (a) *ionic*-**a** (C_6D_6), (b) *trans*-**b** ($CDCl_3$), (c) *ionic*-**b** (C_6D_6)

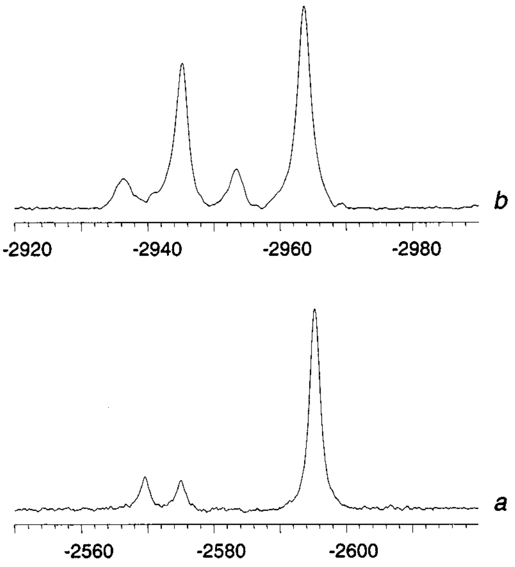


Figure 4. ^{195}Pt NMR (64.3 MHz, 25 °C, Na_2PtCl_6 as external standard) spectra of the diastereoisomeric mixtures formed from **7** and: (a) *ionic*-**a** (C_6D_6), (b) *trans*-**b** ($CDCl_3$)

The covalent complex *trans*-**b** discriminated allenes (**8**,**9**) and the open-chain allyl ether **7**, but could not be used for the analysis of vinyl ethers or cyclic allyl ethers, as the ^{195}Pt NMR spectra contained more signals than expected, probably due to hindered rotation of the complexed substrates about the coordination axis, resulting in the presence of rotational isomers, as in the previously discussed case of *trans*-**a**.[18]

Conclusion

Of the platinum(II) complexes proposed by us,[14−18] the new *trans*-**b** and *ionic*-**b**, containing (*S*)-3,5-dihydro-4*H*-dinaphth[2,1-*c*:1′,2′-*e*]azepine moieties, are the most efficient for the enantiodiscrimination of simple olefins, as they produce remarkable differentiation in the ^{195}Pt NMR spectra of the diastereoisomeric derivatives of samples with their chiral centers either α or β to the double bond. For substrates of these kinds, the measured nonequivalences are markedly superior to those obtained using the previously reported ionic complex *ionic*-**a**, containing (1*S*,1′*S*)-bis[1-(1-naphthyl)ethyl]amine (**a**), although this latter remains the most versatile CDA so far proposed. Taking into account that the complexed olefins can be quantitatively recovered simply by treating the diastereoisomeric mixtures with ethylene under pressure, this result constitutes a significant improvement in the field of the analysis of simple olefins, for which very few alternative direct NMR methods for determining the enantiomeric composition are available.

Experimental Section

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 referenced 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 referenced to Na_2PtCl_6 as external standard. Standard pulse sequences were employed for the ^{195}Pt NMR measurements, using a spectral width of 50000−100000 Hz and an acquisition time of 0.3 s. No relaxation delays were 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 2 K data points were acquired. The relaxation delay was 10 s. The data were zero-filled to 2 K × 1 K 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, employing a mixing time of 0.6 s. The spectral width used was the minimum required in both dimensions. The pulse delay was maintained at 10 s; 512 hypercomplex increments of 8 scans and 2 K data points each were collected. The data matrix was zero-filled to 2 K × 1 K and a Gaussian function was applied for processing in both dimensions.

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

Zeise's salt and 3-methyl-1-pentene (**3**) were purchased from Aldrich. Literature methods were used to prepare 3-phenyl-1-butene (**1**),[21] 3,4-dimethyl-1-pentene (**2**),[21] 5,5-dimethyl-4-phenyl-1-hexene (**4**),[21] 5-methyl-4-phenyl-1-hexene (**5**),[21] 4-methyl-1-hexene (**6**),[21] 1-phenyl-3,4,4-trimethyl-1,2-pentadiene (**8**),[22] 3-methyl-1-phenyl-1,2-pentadiene (**9**),[22] 1-phenylethyl vinyl ether (**10**),[23] 2,2-dimethyl-1-phenylpropyl vinyl ether (**11**),[23] 1,2,2-trimethylpropyl vinyl ether (**12**),[23] 2-vinyltetrahydropyran (**13**),[24] and 3-methoxy-3-phenyl-1-butene (**7**).[25]

(1*S*,1′*S*)-Bis[1-(1-naphthyl)ethyl]amine (**a**)[17,18] and its complex *ionic*-**a** were prepared as described elsewhere.[17,18] (*S*)-3,5-Dihydro-4*H*-dinaphth[2,1-*c*:1′,2′-*e*]azepine (**b**) was prepared by following the literature procedure (Supporting Information).[19,20]

***trans*-Dichloro(b)(ethylene)platinum(II) (*trans*-b):** A methanol solution of the amine **b** (1.58 mmol) was added at 0 °C 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). Compound *trans*-**b** was filtered off and recovered as a pale yellow solid in quantitative yield: m.p. 159−160 °C. − ^{1}H NMR (300 MHz, [D$_6$]acetone, 25 °C): δ = 2.97 (br. s, 1 H, NH), 4.08 (d, J = 12.9 Hz, 2 H, *H*CHN), 4.40 (d, J = 12.9 Hz, 2 H, HC*H*N), 4.56 (s, J_{Pt} = 60 Hz, 4 H, C_2H_4), 7.32 (ddd, J = 8.3, J = 6.5 and J = 1.2 Hz, 2 H, H_7 and $H_{7'}$), 7.38 (br. d, J = 8.3 Hz, 2 H, H_8 and $H_{8'}$), 7.54 (ddd, J = 8.3, J = 6.5 and J = 1.2 Hz, 2 H, H_6 and $H_{6'}$), 7.89 (d, J = 8.3 Hz, 2 H, H_3 and $H_{3'}$), 8.07 (br. d, J = 8.3 Hz, 2 H, H_5 and $H_{5'}$), 8.12 (d, J = 8.3 Hz, 2 H, H_4 and $H_{4'}$). − ^{13}C NMR (75 MHz, [D$_6$]acetone, 25 °C): δ = 51.6 (CH_2); 73.5 (C_2H_4); 126.3, 126.4, 127.3, 128.8, 128.9, 129.1 (CH); 131.4, 134.1, 135.7 (quaternary C). − ^{195}Pt NMR (64.3 MHz, [D$_6$]acetone, 25 °C): δ = −2815.4. − $C_{24}H_{21}Cl_2NPt$ (589.43): calcd. C 48.91, H 3.59, N 2.38; found C 48.85, H 3.61, N 2.42.

(*ionic*)·$[PtCl_3(C_2H_4)]^-(b')^+$ complex (*ionic*-b): The hydrochloride salt of the amine **b** (1.58 mmol) was added to a suspension of Zeise's salt $[PtCl_3(C_2H_4)]^-K^+$ (1.58 mmol) in $CHCl_3$. Because of rapid exchange of the two cations, a fine, white powder of KCl was formed and filtered off. The compound *ionic*-**b** was recovered as a yellow solid in quantitative yield by removal of the solvent in vacuo: m.p. 163−165 °C. − ^{1}H NMR (300 MHz, $CDCl_3$, 25° C) δ = 3.86 (dt, J = 13.1 and J = 7.6 Hz, 2 H, *H*CHN), 4.48 (s, J_{Pt} = 62 Hz, 4 H, C_2H_4), 4.69 (d, J = 13.1 Hz, 2 H, HC*H*N), 7.30 (ddd, J = 8.2, J = 6.9 and J = 1.4 Hz, 2 H, H_7 and $H_{7'}$), 7.40 (br. d, J = 8.2 Hz, 2 H, H_8 and $H_{8'}$), 7.53 (ddd, J = 8.2, J = 6.9 and J = 1.3 Hz, 2 H, H_6 and $H_{6'}$), 7.88 (d, J = 8.4 Hz, 2 H, H_3 and $H_{3'}$), 7.98 (br. d, J = 8.2 Hz, 2 H, H_5 and $H_{5'}$), 8.05 (d, J = 8.4 Hz, 2 H, H_4 and $H_{4'}$), 8.39 (br. s, 2 H, NH_2^+). − ^{13}C NMR (75 MHz, $CDCl_3$, 25° C) δ = 47.1 (CH_2); 69.9 (C_2H_4); 126.6, 126.9, 127.4, 128.1, 128.6, 129.9 (CH); 131.2, 134.2, 135.7 (quaternary C). − ^{195}Pt NMR (64.3 MHz, $CDCl_3$, 25 °C): δ = −2847.9. − $C_{24}H_{22}Cl_3NPt$ (625.89): calcd. C 46.06, H 3.54, N 2.24; found C 45.98, H 3.60, N 2.28.

General Procedure Involved in the Use of the CDAs for Enantiodiscrimination Measurements: The chiral substrate (**1**−**13**) was added to a solution containing the CDA (50−100 mg; substrate/CDA = 0.8:1) in C_6D_6 or $CDCl_3$ (0.5 mL) and the ^{195}Pt NMR spectra of the diastereoisomeric products were analyzed. The ^{195}Pt resonances of the small excess of *trans*-**b** and *ionic*-**a/b** are at lower frequencies than the signals due to complexes containing the substrate **1**−**13**.

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