

# Effect of the Coordination to M(II) Metal Centers (M = Zn, Cd, Pt) on the Quadratic Hyperpolarizability of Various Substituted 5-X-1,10-phenanthrolines (X = Donor Group) and of *trans*-4-(Dimethylamino)-4'-stilbazole

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Coordination to a Zn(II) center of chelating  $\pi$ -delocalized nitrogen donor ligands such as 5-X-1,10-phenanthrolines (X = OMe, NMe<sub>2</sub>, *trans*-CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>, *trans,trans*-(CH=CH)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>) produces a significant enhancement of their quadratic hyperpolarizability measured either by the EFISH technique ( $\beta_{1.34}$ ) or by absorption and emission solvatochromic investigations ( $\beta_{CT}$ ) working with an incident wavelength of 1.34  $\mu$ m. However, the enhancement factor by metal coordination of the quadratic hyperpolarizability of planar 5-X-1,10-phenanthrolines is lower than that of the nonplanar and flexible ligand 4-(*p*-(dibutylamino)styryl)-4'-methyl-2,2'-bipyridine because this latter ligand becomes planar and rigid by coordination. Coordination of 5-(*trans*-CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>)-1,10-phenanthroline to the softer Cd(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub> does not produce an enhancement of the quadratic hyperpolarizability. This is due to a significant decrease of  $\Delta\mu_{eg}$  (difference of the dipole moment in the excited and ground states of the intraligand charge transfer (ILCT)) upon coordination to the Cd(II) center. Strangely enough, the second-order NLO response of Zn(II) and Pt(II) complexes carrying two 4-*trans*-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub> stilbazole ligands in a tetrahedral or planar coordination indicates a significant increase, upon coordination, of the quadratic hyperpolarizability  $\beta_{CT}$ , along the ILCT transition of the ligand, but an irrelevant increase of  $\beta_{1.34}$ , which is the vectorial component of the tensor  $\beta$  along the molecular dipole moment axis, although in the free ligand both  $\beta_{CT}$  and  $\beta_{1.34}$  are comparable. The lack of coincidence of the molecular dipole moment axis with the direction of the ILCT transition of the ligand, a major origin of the second-order NLO response, could explain why  $\beta_{CT}$  and  $\beta_{1.34}$  values are not comparable. In fact, a detailed solvatochromic analysis shows that the increase of  $\beta_{CT}$  upon coordination to Zn(II) or Pt(II) of the single stilbazole ligand is not significant, in agreement with EFISH measurements and the irrelevant red shift of the ILCT transition.

## Introduction

In the past few years, organometallic and coordination complexes have emerged as interesting molecular materials for second-order nonlinear optical (NLO) applica-

tions, because they offer a great diversity of tunable electronic properties by virtue of the metal center.<sup>1,2</sup> In particular with pyridines,<sup>3,4</sup> stilbazoles,<sup>3-5</sup> or bipyridines<sup>2,6</sup> bearing an electron-donor substituent,  $\beta_{vec}$ , the vectorial projection of the quadratic hyperpolarizability

tensor along the ground-state molecular dipole moment ( $\mu$ ) direction, measured by the solution-phase dc electric-field-induced second-harmonic (EFISH) generation method,<sup>7</sup> increases upon coordination to a metal center. As confirmed by a solvatochromic investigation,<sup>8,9</sup> this enhancement is mainly due to a red shift of the intraligand charge transfer (ILCT) transition. With a simple ligand such as 4-(dimethylamino)pyridine, the enhancement is as high as about  $10^2$  times<sup>3</sup> and is modulated by the different donor–acceptor properties of the metal center. Coordination of 4-(dimethylamino)pyridine to relatively soft acceptor centers such as “*cis*-M(CO)<sub>2</sub>Cl” (M = Rh(I) 4d<sup>8</sup>, Ir(I) 5d<sup>8</sup>)<sup>3</sup> and “*fac*-Os(CO)<sub>3</sub>Cl<sub>2</sub>” (Os(II) 5d<sup>6</sup>)<sup>3</sup> produces an increase of  $\beta_{\text{vec}}$  about 10 times higher than coordination to the less accepting and softer center “Cr<sup>0</sup>(CO)<sub>5</sub>” (3d<sup>6</sup>).<sup>4</sup> Strangely enough, a similar increase of  $\beta_{\text{vec}}$  has been reported to occur by coordination to both the relatively soft acid “*cis*-Rh(CO)<sub>2</sub>Cl”<sup>3</sup> and the hard Lewis acid BF<sub>3</sub>.<sup>10</sup> With more  $\pi$ -delocalized para-substituted pyridines such as stilbazoles, the increase of  $\beta_{\text{vec}}$  upon coordination not only is less relevant (enhancement of about 1.5–2 times with respect to the free ligand) but decreases with an increase in the length of the  $\pi$ -delocalized bridge between the donor group and the pyridine ring.<sup>3,4</sup> The remarkable increase of  $\beta_{\text{vec}}$  of the flexible chelating ligand 4-(*p*-(dibutylamino)styryl)-4'-methyl-2,2'-bipyridine upon coordination to the Zn(II) Lewis acids<sup>6</sup> (enhancement with respect to the free ligand of about 10 times) prompted us to investigate the effect on  $\beta_{\text{vec}}$  of coordination of the  $\eta^1$  pseudolinear stilbazole 4-*trans*-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub> and of the rigid chelating ligands 5-X-1,10-phenanthrolines (X being a donor group such as OMe, NMe<sub>2</sub>, *trans*-CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>, and *trans,trans*-(CH=CH)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>) to M(II) ions of increasing hardness (from Pt(II) to Cd(II) to Zn(II)). The choice of position 5 of the 1,10-phenanthroline ring was based on a preliminary MNDO-CPHF theoretical investigation (see Table 1 in the Experimental Section) of the identification of the best position (2, 3, 4, or 5) of the substituent “*trans*-CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>” (Table 1). Comparable values of both dipole moment  $\mu$  and static quadratic hyperpolarizability  $\beta_0$  were obtained when the substituent was located at positions 4 and 5, while substitution at position 3 afforded a slightly higher

value of  $\beta_0$  but a smaller value of  $\mu$ , therefore giving comparable  $\mu\beta_0$  values. Only in position 2 were values of both  $\mu$  and  $\beta_0$  smaller. Therefore, due to the easier synthesis of the ligands, we investigated the second-order NLO properties of 1,10-phenanthrolines substituted at position 5 and their Zn(II) and, in one case, Cd(II) complexes.

## Experimental Section

**General Comments.** ZnCl<sub>2</sub>, Zn(CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>·2H<sub>2</sub>O, M(CH<sub>3</sub>-CO)<sub>2</sub>·2H<sub>2</sub>O (M = Zn, Cd), *cis*-[PtCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>], 4-*trans*-NC<sub>5</sub>H<sub>4</sub>-CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>, 1,10-phenanthroline, 5-methyl-1,10-phenanthroline, and 4-(dimethylamino)cinnamaldehyde were purchased from Sigma-Aldrich and were used without further purification. Some 5-X-1,10-phenanthrolines (X = OMe (**1**), NMe<sub>2</sub> (**2**); see Scheme 1) were prepared according to a reported synthesis,<sup>11</sup> whereas other 5-X-1,10-phenanthrolines (X = *trans*-CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub> (**3**), *trans,trans*-(CH=CH)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub> (**4**)) and all the M(II) (M = Zn, Cd, Pt) complexes were prepared as described below. All solvents were dried over molecular sieves (4 Å) prior to use. Products were characterized by <sup>1</sup>H NMR (Bruker AC-200 and a Bruker Avance DRX 300 spectrometers) and UV–visible (Jasco V-570 spectrophotometer) spectroscopy and by elemental analysis and in few cases also by infrared spectroscopy (Nicolet MX-1FT and a Bruker Vector 22 spectrometers) and mass spectrometry (Varian VG-9090 spectrometer). Dipole moments,  $\mu$ , were measured in CHCl<sub>3</sub> by using a WTW-DM01 dipole meter (dielectric constant) coupled with a Pulfrich Zeiss PR2 refractometer (refractive index) and calculated by using the Guggenheim method.<sup>12</sup> Elemental analyses were carried out at the Dipartimento di Chimica Inorganica, Metallorganica e Analitica of the Università di Milano.

**Determination of the Second-Order NLO Responses.** EFISH measurements<sup>7</sup> of  $\beta_{\text{vec}}$ , the vectorial component of the quadratic hyperpolarizability tensor  $\beta$  along the molecular dipole moment axis, were carried out at the École Normale Supérieure de Cachan in CHCl<sub>3</sub> solutions of different concentrations (10<sup>-3</sup>–10<sup>-4</sup> M) working at a fundamental incident wavelength of 1.34  $\mu\text{m}$  and, in a few cases, of 1.06  $\mu\text{m}$ , using a Q-switched, mode-locked Nd:YAG laser with pulse duration of 15 or 90 ns at a 10 Hz repetition rate. All experimental EFISH  $\beta_2$  values are defined according to the “phenomenological” convention.<sup>13</sup>

The computational evaluation of dipole moments and of the quadratic hyperpolarizability (vectorial projection of the quadratic hyperpolarizability tensor along the dipole moment vector, which corresponds to EFISH  $\beta_2$  values) of both 5-X-1,10-phenanthrolines and some of their Zn(II) complexes was carried out using the MNDO<sup>14</sup> semiempirical method and the coupled perturbed Hartree–Fock (CPHF) approach,<sup>15</sup> as previously described for various para-substituted pyridines.<sup>3</sup> We also evaluated the best position (2, 3, 4, or 5) for the substituent *trans*-CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub> on the 1,10-phenanthroline system in order to optimize both the ground-state dipole moment  $\mu$  and the static quadratic hyperpolarizability ( $\beta_0$  or  $\beta_{0,\text{TOT}}$ ; see Table 1).

The quadratic hyperpolarizability along the charge-transfer direction,  $\beta_{\text{CT}}$ , of Zn(II), Pt(II), or Cd(II) complexes of 4-*trans*-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub> and 5-X-1,10-phenanthrolines (X = NMe<sub>2</sub>, *trans*-(CH=CH)<sub>n</sub>C<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>, where *n* = 1, 2) and the free ligand 5-(*trans*-CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>)-1,10-phenan-

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**Table 1. Investigation, by the MNDO-CPHF Semiempirical Method, of the Best Position for the Substituent "trans-CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>" on the 1,10-Phenanthroline (Phen) Ring in Order To Optimize both the Values of Dipole Moment  $\mu$  and of  $\beta_0^b$  Obtained from EFISH Measurements**

molecule	$\mu$ , D	$\beta_{0,TOT}^a$ , $10^{-30}$ cm <sup>5</sup> esu <sup>-1</sup>	$\beta_0^b$ , $10^{-30}$ cm <sup>5</sup> esu <sup>-1</sup>	$\mu\beta_0$ , $10^{-30}$ D cm <sup>5</sup> esu <sup>-1</sup>
5-(trans-CH=CHC <sub>6</sub> H <sub>4</sub> -4'-NMe <sub>2</sub> )-Phen	4.92	6.64	6.37	31.3
4-(trans-CH=CHC <sub>6</sub> H <sub>4</sub> -4'-NMe <sub>2</sub> )-Phen	4.96	6.98	6.56	32.5
3-(trans-CH=CHC <sub>6</sub> H <sub>4</sub> -4'-NMe <sub>2</sub> )-Phen	3.67	14.16	9.20	33.8
2-(trans-CH=CHC <sub>6</sub> H <sub>4</sub> -4'-NMe <sub>2</sub> )-Phen	1.33	14.42	2.35	3.12

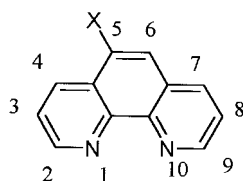
<sup>a</sup>  $\beta_{0,TOT}$  is the total intrinsic quadratic hyperpolarizability at zero frequency (see ref 3). <sup>b</sup>  $\beta_0$  is the vectorial projection of the quadratic hyperpolarizability tensor ( $\beta_{vec}$  of eq 2) at zero frequency.

throleine was obtained by solvatochromic measurements, using both absorption and emission spectra in various solvents (cyclohexane, carbon tetrachloride, toluene, chloroform, ethyl acetate, dichloromethane, 1,2-dichloroethane, acetone, acetonitrile), following the methodology described in the case of trans-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub> and 5-NMe<sub>2</sub>-1,10-phenanthroline.<sup>8</sup> The quadratic hyperpolarizability tensor  $\beta_{CT}$  along the charge-transfer axis of the major charge-transfer absorption involved in the NLO response is calculated according to the Oudar two-level equation:<sup>16</sup>

$$\beta_{CT} = \frac{3}{2f^2 c^2} \frac{\nu_a 2r_{eg}^2 \Delta\mu_{eg}}{(\nu_a^2 - \nu_L^2)(\nu_a^2 - 4\nu_L^2)} \quad (1)$$

where  $r_{eg}$  is the transition dipole moment related to the integrated intensity  $f$  of the absorption band,  $\nu_a$  is the frequency of the charge-transfer absorption band,  $\nu_L$  is the frequency of the incident radiation, and  $\Delta\mu_{eg}$  is the variation of the dipole moment upon excitation.

**Synthesis of 5-X-1,10-Phenanthrolines.** For the numbering used in the attribution of the <sup>1</sup>H NMR signals, see the following structure:



**5-{2-Hydroxy-2-[4-(dimethylamino)phenyl]ethyl}-1,10-phenanthroline (5).** A 3 mL portion of 2 M lithium diisopropylamide (LDA) in THF was added dropwise under N<sub>2</sub> at 0 °C to a solution of 0.5 g (2.6 mmol) of 5-methyl-1,10-phenanthroline in 5 mL of anhydrous THF. The mixture was stirred at this temperature for 75 min, and then a solution of 0.8 g (5.2 mmol) of *p*-(dimethylamino)benzaldehyde in 5 mL of THF was added with a syringe. The mixture was left at 0 °C for 75 min and then cooled to room temperature and left overnight. The excess LDA was destroyed with MeOH, the solvent was removed under reduced pressure, the residue was dissolved in 50 mL of CH<sub>2</sub>Cl<sub>2</sub>, and this solution was washed with a small amount of H<sub>2</sub>O. The organic layer was separated, washed with 10 mL of brine, dried over Na<sub>2</sub>CO<sub>3</sub>, and evaporated, affording a residue which was purified by column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH/NH<sub>4</sub>OH = 95/4.5/0.5) to give 0.46 g of an orange solid, crystallized from methanol to afford 0.27 g (30%) of pure **5** as a yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 9.14 (dd, 1H,  $J = 1.6$  Hz,  $J = 4.3$  Hz, H<sub>2</sub>), 9.12 (dd, 1H,  $J = 1.7$  Hz,  $J = 4.3$  Hz, H<sub>9</sub>), 8.44 (dd, 1H,  $J = 1.6$  Hz,  $J = 8.4$  Hz, H<sub>4</sub>), 8.12 (dd, 1H,  $J = 1.7$  Hz,  $J = 8.1$  Hz, H<sub>7</sub>), 7.62 (s, 1H, H<sub>6</sub>), 7.60 (dd, 1H,  $J = 4.3$  Hz,  $J = 8.0$  Hz, H<sub>3</sub>), 7.57 (dd, 1H,  $J = 4.4$  Hz,  $J = 7.7$  Hz, H<sub>8</sub>), 7.26 (d, 2H,  $J = 8.7$  Hz, C<sub>6</sub>H<sub>4</sub> meta), 6.70 (d, 2H,  $J = 8.7$  Hz, C<sub>6</sub>H<sub>4</sub> ortho), 5.04 (t, 1H,  $J = 7.0$  Hz,  $J = 5.9$  Hz, CHOH), 3.52 (m, 2H, CH<sub>2</sub>OH,

2.93 (s, 6H, CH<sub>3</sub>), 2.20 (br s, 1H, D<sub>2</sub>O exchange); MS-FAB<sup>+</sup>:  $m/e$  344 (M + 1)<sup>+</sup>, calcd for C<sub>22</sub>H<sub>21</sub>N<sub>3</sub>O  $m/e$  343. Anal. Calcd (found): C, 76.94 (76.62); H, 6.16 (6.02); N, 12.24 (12.40).

**5-[4-(Dimethylamino)- $\alpha$ -styryl]-1,10-phenanthroline (3).**

A 0.27 g portion of **5** (0.79 mmol) in 8 mL of aqueous 10% H<sub>2</sub>SO<sub>4</sub> was maintained at reflux under magnetic stirring for 1 h. The mixture was cooled to room temperature, made alkaline with aqueous 20% NaOH, and extracted with CH<sub>2</sub>Cl<sub>2</sub> (2  $\times$  60 mL). The organic phase was washed with 50 mL of brine, dried over Na<sub>2</sub>CO<sub>3</sub>, and evaporated to dryness in vacuo. The residue was purified by column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH/NH<sub>4</sub>OH = 90/9.8/0.2) to give 0.3 g of a dark orange solid, crystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O to afford 0.18 g (72%) of pure **3** as an orange solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 9.20 (dd, 1H,  $J = 1.6$  Hz,  $J = 4.3$  Hz, H<sub>2</sub>), 9.12 (dd, 1H,  $J = 1.7$  Hz,  $J = 4.3$  Hz, H<sub>9</sub>), 8.62 (dd, 1H,  $J = 1.7$  Hz,  $J = 8.4$  Hz, H<sub>4</sub>), 8.22 (dd, 1H,  $J = 1.7$  Hz,  $J = 8.1$  Hz, H<sub>7</sub>), 7.94 (s, 1H, H<sub>6</sub>), 7.66 (dd, 1H,  $J = 4.3$  Hz,  $J = 8.4$  Hz, H<sub>3</sub>), 7.60 (dd, 1H,  $J = 4.3$  Hz,  $J = 8.4$  Hz, H<sub>8</sub>), 7.56 (d, 2H,  $J = 16.1$  Hz, H<sub>11</sub>), 7.52 (d, 2H,  $J = 8.9$  Hz, C<sub>6</sub>H<sub>4</sub> meta), 7.20 (d, 1H,  $J = 15.8$  Hz, H<sub>12</sub>), 6.76 (d, 2H,  $J = 8.8$  Hz, C<sub>6</sub>H<sub>4</sub> ortho), 3.02 (s, 6H, CH<sub>3</sub>). MS-FAB<sup>+</sup>:  $m/e$  326 (M + 1)<sup>+</sup>, calcd for C<sub>22</sub>H<sub>19</sub>N<sub>3</sub>  $m/e$  325. Anal. Calcd (found): C, 81.20 (80.90); H, 5.88 (6.02); N, 12.91 (12.70).

**5-{2-Hydroxy-2-[4-(dimethylamino)phenyl]-3-butenyl}-1,10-phenanthroline (6).** A 3 mL portion of 2 M lithium diisopropylamide (LDA) in THF was added dropwise under N<sub>2</sub> at 0 °C to a solution of 0.5 g (2.6 mmol) of 5-methyl-1,10-phenanthroline in 5 mL of anhydrous THF. The resulting mixture was stirred at this temperature for 75 min, and then a solution of 0.91 g (5.2 mmol) of *p*-(dimethylamino)benzaldehyde in 5 mL of THF was added via syringe. The mixture was left at 0 °C for 75 min and then cooled to room temperature and reacted overnight. The excess LDA was destroyed with MeOH, and the solvent was removed under reduced pressure. The resulting residue was dissolved in 50 mL of CH<sub>2</sub>Cl<sub>2</sub> and washed with a small amount of H<sub>2</sub>O. The organic layer was separated, washed with 10 mL of brine, dried over Na<sub>2</sub>CO<sub>3</sub>, and evaporated, affording a residue which was purified by column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH/NH<sub>4</sub>OH = 95/4.5/0.5) to give 0.32 g of a brown solid. This product was purified by crystallization from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O to afford 0.27 g (28%) of pure **6** as a yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 9.14 (dd, 1H,  $J = 1.3$  Hz,  $J = 4.2$  Hz, H<sub>2</sub>), 9.12 (dd, 1H,  $J = 1.6$  Hz,  $J = 4.4$  Hz, H<sub>9</sub>), 8.49 (dd, 1H,  $J = 1.4$  Hz,  $J = 8.4$  Hz, H<sub>4</sub>), 8.14 (dd, 1H,  $J = 1.6$  Hz,  $J = 8.1$  Hz, H<sub>7</sub>), 7.70 (s, 1H, H<sub>6</sub>), 7.61 (dd, 1H,  $J = 4.2$  Hz,  $J = 8.3$  Hz, H<sub>3</sub>), 7.57 (dd, 1H,  $J = 4.4$  Hz,  $J = 8.1$  Hz, H<sub>8</sub>), 7.23 (d, 2H,  $J = 8.7$  Hz, C<sub>6</sub>H<sub>4</sub> meta), 6.65 (d, 2H,  $J = 8.8$  Hz, C<sub>6</sub>H<sub>4</sub> ortho), 6.54 (d, 1H,  $J = 15.9$  Hz, H<sub>14</sub>), 6.14 (dd, 1H,  $J = 6.9$  Hz,  $J = 15.8$  Hz, H<sub>13</sub>), 4.75 (q, 1H, CHOH), 3.40 (m, 2H, CH<sub>2</sub>OH), 2.90 (s, 6H, CH<sub>3</sub>), 2.10 (br. s, 1H, D<sub>2</sub>O exchange). MS-EI:  $m/e$  351 (M - H<sub>2</sub>O), calcd for C<sub>24</sub>H<sub>21</sub>N<sub>3</sub>  $m/e$  351. Anal. Calcd (found): C, 82.02 (82.23); H, 6.02 (6.05); N, 11.96 (12.01).

**5-[4-[4-(Dimethylamino)phenyl]-3-butadienyl]-1,10-phenanthroline (4).** A 0.22 g portion of **6** (0.60 mmol) in 15 mL of aqueous 10% H<sub>2</sub>SO<sub>4</sub> was maintained at reflux under magnetic stirring for 1 h. The mixture was cooled to room temperature, made alkaline with aqueous 20% NaOH, and extracted with CH<sub>2</sub>Cl<sub>2</sub> (2  $\times$  60 mL). The organic phase was

(16) (a) Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *66*, 2664. (b) Oudar, J. L. *J. Chem. Phys.* **1977**, *67*, 446. (c) Oudar, J. L.; Le Person, H. *Opt. Commun.* **1975**, *15*, 258.



washed with 50 mL of brine, dried over  $\text{Na}_2\text{CO}_3$ , and evaporated to dryness in vacuo. The residue was purified by column chromatography ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}/\text{NH}_4\text{OH} = 90/9.8/0.2$ ) to give 0.3 g of a dark solid, crystallized from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  to afford 0.19 g (72%) of pure **4** as an orange solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 9.20 (dd, 1H,  $J = 1.6$  Hz,  $J = 4.3$  Hz,  $\text{H}_2$ ), 9.12 (dd, 1H,  $J = 1.7$  Hz,  $J = 4.4$  Hz,  $\text{H}_3$ ), 8.60 (dd, 1H,  $J = 1.6$  Hz,  $J = 8.4$  Hz,  $\text{H}_4$ ), 8.22 (dd, 1H,  $J = 1.7$  Hz,  $J = 8.1$  Hz,  $\text{H}_7$ ), 7.94 (s, 1H,  $\text{H}_6$ ), 7.67 (dd, 1H,  $J = 4.3$  Hz,  $J = 8.4$  Hz,  $\text{H}_3$ ), 7.60 (dd, 1H,  $J = 4.3$  Hz,  $J = 8.1$  Hz,  $\text{H}_8$ ), 7.40 (d, 2H,  $J = 8.8$  Hz,  $\text{C}_6\text{H}_4$  meta), 7.25 (d, 1H,  $J = 15.0$  Hz,  $\text{H}_{11}$ ), 7.14 (dd, 1H,  $J = 14.9$  Hz,  $J = 15.0$  Hz,  $\text{H}_{12}$ ), 6.95 (dd, 1H,  $J = 15.3$  Hz,  $J = 15.3$  Hz,  $\text{H}_{13}$ ), 6.74 (d, 1H,  $J = 15.3$  Hz,  $\text{H}_{14}$ ), 6.71 (d, 2H,  $J = 8.8$  Hz,  $\text{C}_6\text{H}_4$  ortho), 3.00 (s, 6H,  $\text{CH}_3$ ); MS-FAB $^+$ :  $m/e$  352 ( $\text{M} + 1$ ) $^+$ , calcd for  $\text{C}_{24}\text{H}_{21}\text{N}_3$   $m/e$  351. Anal. Calcd (found): C, 82.02 (81.83); H, 6.02 (6.15); N, 11.90 (11.94).

**General Procedure for the Synthesis of  $\text{M}(\text{CH}_3\text{CO}_2)_2$  ( $\text{M} = \text{Zn}, \text{Cd}$ ) Complexes of Ligands 1–4.** In a 50 mL flask, the 5-X-1,10-phenanthroline (150 mg) was dissolved in  $\text{CH}_2\text{Cl}_2$  (15 mL) and, then, 1 equiv of the solid salt  $\text{M}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$  where  $\text{M} = \text{Zn}, \text{Cd}$  was added. The mixture was stirred at room temperature overnight and evaporated to dryness, affording, in quantitative yield, pure  $[\text{M}(\text{CH}_3\text{CO}_2)_2(5\text{-X-1,10-phenanthroline})]$ , recrystallized from dichloromethane/pentane at room temperature.

**1-Zn( $\text{CH}_3\text{CO}_2$ ) $_2$ :** yellow solid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 9.29 (dd, 1H,  $J = 1.4$  Hz,  $J = 4.7$  Hz,  $\text{H}_2$ ), 9.11 (dd, 1H,  $J = 1.4$  Hz,  $J = 4.8$  Hz,  $\text{H}_3$ ), 8.80 (dd, 1H,  $J = 1.4$  Hz,  $J = 8.4$  Hz,  $\text{H}_4$ ), 8.34 (dd, 1H,  $J = 1.4$  Hz,  $J = 8.2$  Hz,  $\text{H}_7$ ), 7.90 (dd, 1H,  $J = 4.7$  Hz,  $J = 8.4$  Hz,  $\text{H}_3$ ), 7.81 (dd, 1H,  $J = 4.7$  Hz,  $J = 8.2$  Hz,  $\text{H}_8$ ), 7.28 (s, 1H,  $\text{H}_6$ ), 3.00 (s, 6H,  $(\text{CH}_3)_2\text{N}$ ), 2.10 (s, 6H,  $\text{CH}_3\text{CO}_2$ ); MS-FAB $^+$   $m/e$  347 ( $\text{M} - \text{CH}_3\text{CO}_2$ ) $^+$ , calcd for  $\text{C}_{18}\text{H}_{19}\text{N}_3\text{O}_4\text{-Zn}$   $m/e$  406. Anal. Calcd (found): C, 53.15 (53.04); H, 4.71 (4.82); N, 10.30 (10.19).

**2-Zn( $\text{CH}_3\text{CO}_2$ ) $_2$ :** white solid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 9.30 (dd, 1H,  $J = 1.3$  Hz,  $J = 4.8$  Hz,  $\text{H}_2$ ), 9.10 (dd, 1H,  $J = 1.1$  Hz,  $J = 4.8$  Hz,  $\text{H}_3$ ), 8.88 (dd, 1H,  $J = 1.4$  Hz,  $J = 8.4$  Hz,  $\text{H}_4$ ), 8.36 (dd, 1H,  $J = 1.1$  Hz,  $J = 8.2$  Hz,  $\text{H}_7$ ), 7.91 (dd, 1H,  $J = 4.8$  Hz,  $J = 8.4$  Hz,  $\text{H}_3$ ), 7.81 (dd, 1H,  $J = 4.7$  Hz,  $J = 8.2$  Hz,  $\text{H}_8$ ), 7.09 (s, 1H,  $\text{H}_6$ ), 4.1 (s, 3H,  $\text{CH}_3\text{O}$ ), 2.05 (s, 6H,  $\text{CH}_3\text{CO}_2$ ); MS-FAB $^+$   $m/e$  333 ( $\text{M} - \text{CH}_3\text{CO}_2$ ) $^+$ , calcd for  $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_5\text{-Zn}$   $m/e$  392. Anal. Calcd (found): C, 51.86 (51.66); H, 4.09 (4.11); N, 7.11 (7.14).

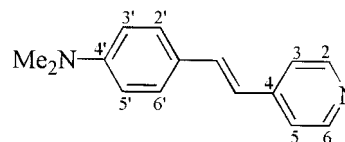
**3-Zn( $\text{CH}_3\text{CO}_2$ ) $_2$ :** red solid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 9.34 (d, 1H,  $J = 4.7$  Hz,  $\text{H}_2$ ), 9.23 (d, 1H,  $J = 4.7$  Hz,  $\text{H}_3$ ), 8.79 (dd, 1H,  $J = 1.1$  Hz,  $J = 8.5$  Hz,  $\text{H}_4$ ), 8.47 (dd, 1H,  $J = 1.3$  Hz,  $J = 8.3$  Hz,  $\text{H}_7$ ), 8.06 (s, 1H,  $\text{H}_6$ ), 7.94 (dd, 1H,  $J = 4.7$  Hz,  $J = 8.5$  Hz,  $\text{H}_3$ ), 7.87 (dd, 1H,  $J = 4.7$  Hz,  $J = 8.5$  Hz,  $\text{H}_8$ ), 7.52 (d, 2H,  $J = 8.8$  Hz, H ortho), 7.50 (d, 1H,  $J = 15.4$  Hz,  $\text{H}_{11}$ ), 7.25 (d, 1H,  $J = 15.4$  Hz,  $\text{H}_{12}$ ), 6.75 (d, 2H,  $J = 8.8$  Hz, H meta), 3.03 (s, 6H,  $(\text{CH}_3)_2\text{N}$ ), 2.05 (s, 6H,  $\text{CH}_3\text{CO}_2$ ); MS-FAB $^+$   $m/e$  450 ( $\text{M} - \text{CH}_3\text{CO}_2$ ) $^+$ , calcd for  $\text{C}_{26}\text{H}_{25}\text{N}_3\text{O}_4\text{-Zn}$   $m/e$  509. Anal. Calcd (found): C, 61.34 (61.09); H, 4.95 (5.06); N, 8.26 (8.42).

**4-Zn( $\text{CH}_3\text{CO}_2$ ) $_2$ :** red solid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 9.34 (d, 1H,  $J = 4.5$  Hz,  $\text{H}_2$ ), 9.22 (d, 1H,  $J = 4.5$  Hz,  $\text{H}_3$ ), 8.84 (d, 1H,  $J = 8.1$  Hz,  $\text{H}_4$ ), 8.47 (d, 1H,  $J = 7.3$  Hz,  $\text{H}_7$ ), 8.05 (s, 1H,  $\text{H}_6$ ), 7.95 (dd, 1H,  $J = 4.7$  Hz,  $J = 8.5$  Hz,  $\text{H}_3$ ), 7.87 (dd, 1H,  $J = 4.8$  Hz,  $J = 8.2$  Hz,  $\text{H}_8$ ), 7.40 (d, 2H,  $J = 8.8$  Hz, H ortho), 7.20–7.18 (m, 2H,  $\text{H}_{11}, \text{H}_{12}$ ), 6.94 (ddd, 1H,  $J = 15.4$  Hz,  $J = 3.2$  Hz,  $J = 2.8$  Hz,  $\text{H}_{13}$ ), 6.79 (d, 1H,  $J = 15.4$  Hz,  $\text{H}_{14}$ ), 6.71 (d, 2H,  $J = 8.8$  Hz, meta), 3.00 (s, 6H,  $(\text{CH}_3)_2\text{N}$ ), 2.05 (s, 6H,  $\text{CH}_3\text{CO}_2$ ); MS-FAB $^+$   $m/e$  474 ( $\text{M} - \text{CH}_3\text{CO}_2$ ) $^+$ , calcd for  $\text{C}_{28}\text{H}_{27}\text{N}_3\text{O}_4\text{-Zn}$   $m/e$  533. Anal. Calcd (found): C, 62.87 (62.64); H, 5.09 (5.21); N, 7.85 (7.68).

**3-Cd( $\text{CH}_3\text{CO}_2$ ) $_2$ :** red solid;  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  (ppm) 8.84 (d, 1H,  $J = 8.9$  Hz,  $\text{H}_4$ ), 8.81 (d, 1H,  $J = 4.7$  Hz,  $\text{H}_2$ ), 8.75 (d, 1H,  $J = 4.6$  Hz,  $\text{H}_3$ ), 8.43 (d, 1H,  $J = 8.0$  Hz,  $\text{H}_7$ ), 8.08 (s, 1H,  $\text{H}_6$ ), 7.78 (dd, 1H,  $J = 4.7$  Hz,  $J = 8.0$  Hz,  $\text{H}_3$ ), 7.75 (dd, 1H,  $J = 4.7$  Hz,  $J = 8.0$  Hz,  $\text{H}_8$ ), 7.54 (d, 1H,  $J = 15.9$  Hz,  $\text{H}_{11}$ ), 7.50 (d, 2H,  $J = 8.8$  Hz, H ortho), 7.28 (d, 1H,  $J = 15.8$  Hz,  $\text{H}_{12}$ ), 6.73 (d, 2H,  $J = 8.8$  Hz, H meta), 2.95 (s, 6H,  $(\text{CH}_3)_2\text{N}$ ), 1.90

(s, 6H,  $\text{CH}_3\text{CO}_2$ ); MS-FAB $^+$   $m/e$  498 ( $\text{M} - \text{CH}_3\text{CO}_2$ ) $^+$ , calcd for  $\text{C}_{26}\text{H}_{25}\text{N}_3\text{O}_4\text{-Cd}$   $m/e$  557. Anal. Calcd (found): C, 56.17 (55.72); H, 4.53 (4.65); N, 7.56 (7.64).

**General Procedure for the Synthesis of  $[\text{ZnY}_2\text{L}_2]$  Complexes ( $\text{L} = 4\text{-trans-NC}_5\text{H}_4\text{CH=CHC}_6\text{H}_4\text{-4'-NMe}_2$ ;  $\text{Y} = \text{Cl}, \text{CH}_3\text{CO}_2, \text{CF}_3\text{CO}_2$ ).** The Zn(II) salt (0.814 mmol) was kept under vacuum ( $10^{-2}$  Torr) for 3 h at  $100^\circ\text{C}$  in a two-necked flask (250 mL). Then anhydrous  $\text{CH}_2\text{Cl}_2$  (150 mL) and 4-*trans*- $\text{NC}_5\text{H}_4\text{CH=CHC}_6\text{H}_4\text{-4'-NMe}_2$  (0.364 g; 1.628 mmol) were added under  $\text{N}_2$ ; the mixture was stirred overnight in the dark (the flask was covered with aluminum foil), affording a solution evaporated to dryness to give, in quantitative yield,  $[\text{ZnY}_2(4\text{-trans-NC}_5\text{H}_4\text{CH=CHC}_6\text{H}_4\text{-4'-NMe}_2)_2]$  recrystallized from dichloromethane/pentane. For the numbering used in the attribution of the  $^1\text{H}$  NMR signals, see the following structure:



**$[\text{ZnCl}_2\text{L}_2]$ :** red solid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 8.63 (4 H,  $2\text{H}_2$  and  $2\text{H}_6$ ), 7.55 (4 H,  $2\text{H}_3$  and  $2\text{H}_5$ ), 7.49 (d, 4 H,  $2\text{H}_2'$  and  $2\text{H}_6'$ ,  $J = 8.6$  Hz), 7.41 (d, 2 H,  $2\text{CHPh}$ ,  $J_{\text{trans}} = 16.0$  Hz), 6.84 (d, 2 H,  $2\text{PyCH}$ ,  $J_{\text{trans}} = 16.0$  Hz), 6.73 (d, 4 H,  $2\text{H}_3'$  and  $2\text{H}_5'$ ,  $J = 8.6$  Hz), 3.07 (s, 12 H,  $2\text{NMe}_2$ ); MS (FAB $^+$ )  $m/e$  549 (molecular ion peak - Cl). Anal. Calcd (found): C, 61.55 (61.29); H, 5.47 (5.69); N, 9.57 (9.33).

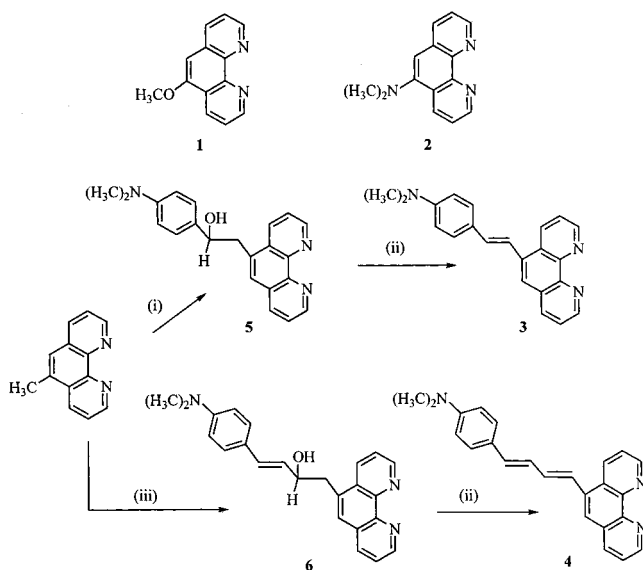
**$[\text{Zn}(\text{CH}_3\text{CO}_2)_2\text{L}_2]$ :** yellow solid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 8.64 (d, 4 H,  $2\text{H}_2$  and  $2\text{H}_6$ ,  $J = 5.7$  Hz), 7.47 (d, 4 H,  $2\text{H}_2'$  and  $2\text{H}_6'$ ,  $J = 8.7$  Hz), 7.42 (d, 4 H,  $2\text{H}_3$  and  $2\text{H}_5$ ,  $J = 5.7$  Hz), 7.31 (d, 2 H,  $2\text{CHPh}$ ,  $J_{\text{trans}} = 16.0$  Hz), 6.80 (d, 2 H,  $2\text{PyCH}$ ,  $J_{\text{trans}} = 16.0$  Hz), 6.72 (d, 4 H,  $2\text{H}_3'$  and  $2\text{H}_5'$ ,  $J = 8.7$  Hz), 3.03 (s, 12 H,  $2\text{NMe}_2$ ), 2.13 (s, 6 H,  $2\text{O}_2\text{CCH}_3$ ); IR (as KBr)  $\nu_{\text{asym}}(\text{CO}_2)$  and  $\nu_{\text{sym}}(\text{CO}_2)$  1642 and  $1430\text{ cm}^{-1}$ , respectively, in agreement with unidentate acetates.<sup>17</sup> Anal. Calcd (found): C, 64.56 (64.36); H, 6.01 (6.13); N, 8.86 (8.99).

**$[\text{Zn}(\text{CF}_3\text{CO}_2)_2\text{L}_2]$ :** yellow solid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 8.61 (d, 4 H,  $2\text{H}_2$  and  $2\text{H}_6$ ,  $J = 6.3$  Hz), 7.53 (d, 4 H,  $2\text{H}_3$  and  $2\text{H}_5$ ,  $J = 6.3$  Hz), 7.49 (d, 4 H,  $2\text{H}_2'$  and  $2\text{H}_6'$ ,  $J = 8.8$  Hz), 7.39 (d, 2 H,  $2\text{CHPh}$ ,  $J_{\text{trans}} = 16.1$  Hz), 6.82 (d, 2 H,  $2\text{PyCH}$ ,  $J_{\text{trans}} = 16.1$  Hz), 6.73 (d, 4 H,  $2\text{H}_3'$  and  $2\text{H}_5'$ ,  $J = 8.8$  Hz), 3.06 (s, 12 H,  $2\text{NMe}_2$ ); IR (as KBr)  $\nu_{\text{asym}}(\text{CO}_2)$  and  $\nu_{\text{sym}}(\text{CO}_2)$  1700 and  $1433\text{ cm}^{-1}$ , respectively, in agreement with unidentate trifluoroacetates;<sup>17</sup> MS (FAB $^+$ )  $m/e$  625 (molecular ion peak -  $\text{O}_2\text{CCF}_3$ ). Anal. Calcd (found): C, 55.14 (55.35); H, 4.32 (4.50); N, 7.56 (7.39).

**Synthesis of *cis*- $[\text{PtCl}_2\text{L}_2]$ .** In a two-necked flask (250 mL) under  $\text{N}_2$ , 4-*trans*- $\text{NC}_5\text{H}_4\text{CH=CHC}_6\text{H}_4\text{-4'-NMe}_2$  (0.160 g; 0.715 mmol) was added to a suspension of *cis*- $[\text{PtCl}_2(\text{CH}_3\text{CN})_2]$  (0.124 g; 0.357 mmol) in anhydrous  $\text{CH}_2\text{Cl}_2$  (150 mL). After it was stirred for 1 h at room temperature, the final yellow solution was evaporated to dryness to give, in quantitative yield, *cis*- $[\text{PtCl}_2(4\text{-trans-NC}_5\text{H}_4\text{CH=CHC}_6\text{H}_4\text{-4'-NMe}_2)_2]$ , recrystallized from dichloromethane/pentane, as a yellow solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 8.50 (d, 4 H,  $2\text{H}_2$  and  $2\text{H}_6$ ,  $J = 6.3$  Hz), 7.49 (8 H,  $2\text{H}_3$ ,  $2\text{H}_5$ ,  $2\text{H}_2'$  and  $2\text{H}_6'$ ), 7.39 (d, 2 H,  $2\text{CHPh}$ ,  $J_{\text{trans}} = 16.1$  Hz), 6.84 (d, 2 H,  $2\text{PyCH}$ ,  $J_{\text{trans}} = 16.1$  Hz), 6.73 (d, 4 H,  $2\text{H}_3'$  and  $2\text{H}_5'$ ,  $J = 8.6$  Hz), 3.06 (s, 12 H,  $2\text{NMe}_2$ ). IR (as polyethylene pellet):  $\nu(\text{Pt-Cl}) = 390$  and  $349\text{ cm}^{-1}$ , slightly lower than those of *cis*- $[\text{PtCl}_2(\text{CH}_3\text{CN})_2]$  (397 and  $351\text{ cm}^{-1}$ ). Anal. Calcd (found): C, 50.37 (50.19); H, 4.48 (4.60); N, 7.84 (8.01).

## Results and Discussion

### 1. Synthesis of Ligands and of Their Complexes and Determination of Some Ground-State Proper-

Scheme 1. Synthesis of Ligands **3** and **4**<sup>a</sup>

<sup>a</sup> Legend: (i) *p*-(dimethylamino)benzaldehyde, 2 M LDA in anhydrous THF, 0 °C, 2.5 h, room temperature, 16 h; (ii) 10% H<sub>2</sub>SO<sub>4</sub> in H<sub>2</sub>O, reflux (103 °C), 1 h; (iii) *p*-(dimethylamino)cinnamaldehyde, 2 M LDA in anhydrous THF, 0 °C, for 2.5 h, room temperature for 16 h.

**ties. 1.1. 5-X-1,10-phenanthrolines (5-X-Phen) and Their Complexes with Zn(II) and Cd(II).** Ligands **1** and **2** (X = OMe, NMe<sub>2</sub>, respectively; see Scheme 1) were synthesized according to the literature,<sup>11</sup> whereas ligands **3** and **4** (X = *trans*-CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>, *trans,trans*-(CH=CH)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>, respectively) were prepared as shown in Scheme 1, starting from commercially available 5-Me-1,10-phenanthroline. Complexes were prepared by reaction at room temperature of the ligands dissolved in CH<sub>2</sub>Cl<sub>2</sub> with a stoichiometric amount of ZnCl<sub>2</sub>, Zn(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>, or Cd(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub> (see Experimental Section). Both phenanthroline ligands and their complexes were characterized by UV-visible spectroscopy (Table 2), elemental analysis, <sup>1</sup>H NMR spectroscopy, and mass spectrometry (see Experimental Section). Dipole moments were determined in CHCl<sub>3</sub> by the standard Guggenheim method<sup>12</sup> (Table 2).

**1.1.1. <sup>1</sup>H NMR Spectra and Dipole Moments.** In the <sup>1</sup>H NMR spectra (see Experimental Section) of phenanthrolines coordinated to Zn(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>, the signals of hydrogens in a position  $\alpha$  to the phenanthroline nitrogen atoms are shifted to lower fields ( $\Delta\delta$  in CDCl<sub>3</sub> 0.11–0.14 ppm) due to some electron transfer to Zn(II), while the relatively small shift to lower field of the signals of the NMe<sub>2</sub> protons becomes negligible as the bridge length between the donor group and the metal increases ( $\Delta\delta$  in CDCl<sub>3</sub> 0.1, 0.01, and 0 ppm for ligands **2**–**4**, respectively). Dipole moments (Table 2) of ligands **1** and **2** are comparable and slightly lower than those of the more  $\pi$ -delocalized ligands **3** and **4**. The dipole moment enhancement occurring upon coordination to M(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub> (M = Zn, Cd) is higher for phenanthrolines **1** and **2** ( $\mu$  enhancement factor 1.9–2) than for the more  $\pi$ -delocalized **3** and **4** ( $\mu$  enhancement factor 1.6, comparable to that reported upon coordination of 4-(*trans*-CH=CHC<sub>6</sub>H<sub>4</sub>-*p*-NBu<sub>2</sub>)-4'-CH<sub>3</sub>-2,2'-bipyridine to Zn(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>).<sup>6</sup>

**1.2. Complexes of Zn(II) and Pt(II) with 4-*trans*-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>.** The complexes [ZnY<sub>2</sub>(4-*trans*-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>)<sub>2</sub>] (Y = Cl, CH<sub>3</sub>CO<sub>2</sub>, CF<sub>3</sub>CO<sub>2</sub>) and *cis*-[PtCl<sub>2</sub>(4-*trans*-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>)<sub>2</sub>] were prepared by room-temperature reaction in CH<sub>2</sub>Cl<sub>2</sub> of 4-*trans*-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub> with the stoichiometric amount of ZnY<sub>2</sub> or *cis*-[PtCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>]. They were characterized by UV-visible spectroscopy (Table 3), elemental analysis, infrared and <sup>1</sup>H NMR spectroscopy, and, in some cases, mass spectrometry (see Experimental Section). Dipole moments were determined in CHCl<sub>3</sub> by the standard Guggenheim method<sup>12</sup> (Table 3).

**1.2.1. <sup>1</sup>H NMR Spectra and Dipole Moments.** In the <sup>1</sup>H NMR spectra (see Experimental Section), coordination to Zn(II) causes a shift to lower field of the signals of the hydrogens in a position  $\alpha$  with respect to the pyridine nitrogen atom. In accord with the increased accepting character of Zn(II),  $\delta$  in CHCl<sub>3</sub> goes from 8.52 to 8.64, 8.63, and 8.61 ppm when Y = CH<sub>3</sub>CO<sub>2</sub>, Cl, CF<sub>3</sub>CO<sub>2</sub>, respectively. However, such a shift is not observed upon coordination to the softer center "*cis*-PtCl<sub>2</sub>" ( $\delta$  8.52 ppm), which behaves as "*cis*-M(CO)<sub>2</sub>Cl" (M = Rh, Ir).<sup>3</sup> The chemical shift of the NMe<sub>2</sub> protons ( $\delta$  3.03 ppm) is not too affected by coordination ( $\delta$  3.03–3.07 ppm).<sup>3</sup> The coupling constant between the *trans* olefinic hydrogens of 4-*trans*-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub> ( $J_{H-H}$  = 16.2 Hz) does not change upon coordination. Therefore, a fair comparison of the electronic properties between the free and metal-coordinated ligands is possible.<sup>3</sup> Dipole moments of Zn(II) and Pt(II) complexes are reported in Table 3, along with those of related Rh(I),<sup>3</sup> Ir(I),<sup>3</sup> and BF<sub>3</sub><sup>10</sup> complexes. The highest increase of the dipole moment of 4-*trans*-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub> occurs upon coordination to the strong Lewis acid BF<sub>3</sub> ( $\mu$  enhancement factor 3);<sup>10</sup> the molecular dipole moment of the square-planar *cis*-[PtCl<sub>2</sub>(4-*trans*-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>)<sub>2</sub>] complex is higher than that of the pseudolinear arrangement in square-planar *cis*-[M(CO)<sub>2</sub>Cl(4-*trans*-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>)] (M = Rh, Ir) complexes<sup>3</sup> and smaller than that of tetrahedral [ZnY<sub>2</sub>(4-*trans*-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>)<sub>2</sub>] (Y = Cl, CF<sub>3</sub>CO<sub>2</sub>) complexes, which increases in the order expected for the increased electron-accepting strength of the ancillary ligand Y. While in Rh(I) and Ir(I) complexes and in the adduct with BF<sub>3</sub> we have a limited orthogonal contribution to the dipole moment which roughly lies along the ligand axis,<sup>3</sup> in tetrahedral Zn(II) and Cd(II) complexes and in the square-planar Pt(II) complex the molecular dipole moment is the vectorial sum of the dipole moments of two pseudolinear arrangements; therefore, it does not lie along the ligand axis. For instance, for the Pt(II) complex (angles Cl–Pt–Cl and N–Pt–N of about 90°), if we assume a value of about 2.5 D for the dipole moment of each Pt–Cl bond<sup>18</sup> and of 3.9 D (corresponding to the value of the unperturbed free ligand)<sup>3</sup> for the dipole moment of each Pt–(4-*trans*-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>) segment, by addition of the two vectorial contributions we obtain a dipole moment of 9 D, quite close to the experimental value of 8.0 D. This would suggest that the dipole moment of the ligand is not enhanced very much by

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**Table 2. Electronic Spectra, Dipole Moments, and EFISH  $\beta_{1.34}$  Values in  $\text{CHCl}_3$  of Substituted 5-X-1,10-phenanthrolines (5-X-Phen) and Their Complexes with “ $\text{Zn}(\text{CH}_3\text{CO}_2)_2$ ” and “ $\text{Cd}(\text{CH}_3\text{CO}_2)_2$ ”**

molecule	$\lambda_{\text{max}}^{a,b}$ nm	$\mu,^a$ D	$\mu\beta_{1.34}^c 10^{-30}$ D $\text{cm}^5 \text{esu}^{-1}$	$\beta_{1.34}^a 10^{-30}$ $\text{cm}^5 \text{esu}^{-1}$	EF <sup>d</sup>
5-MeO-Phen	272	4.0	9.6	4.0 <sup>e</sup>	
[Zn(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> (5-MeO-Phen)]	284	7.6	74	13	3.2
5-NMe <sub>2</sub> -Phen	328	3.8	20	7.2	
[Zn(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> (5-NMe <sub>2</sub> -Phen)]	344	7.7	175	33	4.6
5-( <i>trans</i> -CH=CHC <sub>6</sub> H <sub>4</sub> -4'-NMe <sub>2</sub> )-Phen	371	4.9	127	41	
[Zn(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> (5-( <i>trans</i> -CH=CHC <sub>6</sub> H <sub>4</sub> -4'-NMe <sub>2</sub> )-Phen)]	419	8.0	338	77	1.9
[Cd(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> (5-( <i>trans</i> -CH=CHC <sub>6</sub> H <sub>4</sub> -4'-NMe <sub>2</sub> )-Phen)]	411	7.7	202	46	1.1
5-( <i>trans,trans</i> -(CH=CH) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -4'-NMe <sub>2</sub> )-Phen	399	4.9	215	75	
[Zn(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> (5-( <i>trans,trans</i> -(CH=CH) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -4'-NMe <sub>2</sub> )-Phen)]	432	7.7	450	112	1.5
4-( <i>trans</i> -CH=CHC <sub>6</sub> H <sub>4</sub> -4'-NBu <sub>2</sub> )-4'-CH <sub>3</sub> -2,2'-bipyridine <sup>f</sup>	388	5.1	41	14	
[Zn(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> (4-( <i>trans</i> -CH=CHC <sub>6</sub> H <sub>4</sub> -4'-NBu <sub>2</sub> )-4'-CH <sub>3</sub> -2,2'-bipyridine) <sup>f</sup> ]	447	7.9	450	116	8.3

<sup>a</sup> Experimental values in  $\text{CHCl}_3$ . <sup>b</sup>  $\lambda_{\text{max}}$  (ILCT) mainly involved in the NLO response. <sup>c</sup>  $\beta$  measured by EFISH at 1.34  $\mu\text{m}$  and converted to  $\beta_0$  with the two-level expression (eq 3).<sup>16</sup> <sup>d</sup> EF is the  $\beta_{1.34}$  enhancement factor:  $\beta_{1.34}(\text{complex})/\beta_{1.34}(\text{free phenanthroline})$ . <sup>e</sup> A similar  $\beta_{1.34}$  value ( $3.7 \times 10^{-30} \text{ cm}^5 \text{esu}^{-1}$ ) is obtained by carrying out the EFISH measurement at 1.06  $\mu\text{m}$  and converting it to  $\beta_{1.34}$  with the two-level expression (eq 3).<sup>16</sup> <sup>f</sup> Reference 6.

**Table 3. Electronic Spectra, Dipole Moments, and EFISH  $\beta_{1.34}$  Values in  $\text{CHCl}_3$  of Zn(II), Pt(II), Rh(I), Ir(I), and  $\text{BF}_3$  Complexes with 4-*trans*-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>**

molecule	$\lambda_{\text{max}}^{a,b}$ nm	$\mu,^a$ D	$\mu\beta_{1.34}^c 10^{-30}$ D $\text{cm}^5 \text{esu}^{-1}$	$\beta_{1.34}, 10^{-30} \text{ cm}^5 \text{esu}^{-1}$	EF <sup>d</sup>
4- <i>trans</i> -NC <sub>5</sub> H <sub>4</sub> CH=CHC <sub>6</sub> H <sub>4</sub> -4'-NMe <sub>2</sub> (L) <sup>e</sup>	374	3.9	215	55	
[Zn(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> L <sub>2</sub> ]	376 <sup>f</sup>	8.0	384	48	0.9
[ZnCl <sub>2</sub> L <sub>2</sub> ]	410	8.4	706	84	1.5
[Zn(CF <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> L <sub>2</sub> ]	420	10.5	1019	97	1.8
<i>cis</i> -[PtCl <sub>2</sub> L <sub>2</sub> ]	375	8.0	328	41	0.8
<i>cis</i> -[Ir(CO) <sub>2</sub> CIL] <sup>e</sup>	431	6.0	768	128	2.3
<i>cis</i> -[Ir(COT) <sub>2</sub> CIL] <sup>e,g</sup>	413	8.1	664	82	1.5
<i>cis</i> -[Rh(CO) <sub>2</sub> CIL] <sup>e</sup>	421	7.0	777	111	2.0
BF <sub>3</sub> L <sup>h</sup>	438	11.8	1522	129	2.3

<sup>a</sup> Experimental values in  $\text{CHCl}_3$ . <sup>b</sup> ILCT transition. <sup>c</sup>  $\beta$  measured by EFISH at 1.34  $\mu\text{m}$ . <sup>d</sup> EF is the  $\beta_{1.34}$  enhancement factor:  $\beta_{1.34}(\text{complex})/\beta_{1.34}(\text{free stilbazole})$ . <sup>e</sup> Data from ref 3. <sup>f</sup> For [Cd(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>L<sub>2</sub>],  $\lambda_{\text{max}}$  375 nm. <sup>g</sup> COT = cyclooctene. <sup>h</sup> Data from ref 10. Surprisingly, both  $\mu$  and EFISH  $\beta_{1.34, \mu\text{m}}$  values of the ligand 4-*trans*-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub> measured in  $\text{CHCl}_3$  ( $\mu = 10$  D;  $\beta_{1.34, \mu\text{m}} = 45 \times 10^{-30} \text{ D cm}^5 \text{esu}^{-1}$ ) are quite different from the values measured by some of us under similar conditions.<sup>3</sup>

coordination to a soft metal center such as Pt(II). The same conclusion can be reached for the tetrahedral [ZnCl<sub>2</sub>(4-*trans*-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>)<sub>2</sub>] complex; assuming that the values are the same as above for the various contributions and that the angles Cl–Zn–Cl and N–Zn–N are roughly 109°, the calculated value of the dipole moment is 7.4 D, slightly lower but not too far from the experimental value of 8.4 D. In this latter case MNDO calculations show that the electronic density distribution on the various atoms of 4-*trans*-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub> is not significantly affected by coordination to “ZnCl<sub>2</sub>” or “Zn(CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>”, in agreement with a relatively small perturbation.

**2. Charge-Transfer Bands in UV–Visible Spectra.** UV–visible spectra in  $\text{CHCl}_3$  of the complexes *cis*-[M(CO)<sub>2</sub>Cl(4-*trans*-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>)] (M = Rh, Ir), *cis*-[Ir(cyclooctene)<sub>2</sub>Cl(4-*trans*-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>)], and *fac*-[Os(CO)<sub>3</sub>Cl<sub>2</sub>(4-*trans*-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>)] have one major band ( $\log \epsilon = \text{ca. } 4.5$ ) in the region 413–435 nm, attributed to an intraligand charge transfer (ILCT) transition, red-shifted when compared to the same band ( $\lambda_{\text{max}} = 374$  nm) in the free ligand.<sup>3,9,10</sup> This transition emanates from the NMe<sub>2</sub> donor end of the stilbazole ligand and is usually sensitive to the Lewis acidity of the metal moiety, which increases the  $\pi^*$  acceptor properties of the pyridine ring, thus producing a red shift of the ILCT. Therefore,  $\Delta\lambda_{\text{max}}$  was used by some of us as a way to estimate the relative Lewis acidity of an acceptor metal center.<sup>3</sup> In agreement with this assumption, the higher

$\Delta\lambda_{\text{max}}$  (64 nm) was reported with the strong Lewis acid BF<sub>3</sub>.<sup>10</sup>

The UV–visible spectra of complexes of Zn(II) and Pt(II) with 4-*trans*-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub> (Table 3) are also characterized by such an intense ILCT transition ( $\log \epsilon = \text{ca. } 4.5$ ); however, the red shift does not follow a trend which can be easily related to the Lewis acidity. It is very small upon coordination to “Zn(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>” ( $\Delta\lambda_{\text{max}} = 2$  nm) and “PtCl<sub>2</sub>” ( $\Delta\lambda_{\text{max}} = 1$  nm), but it is significant upon coordination to “ZnCl<sub>2</sub>” ( $\Delta\lambda_{\text{max}} = 36$  nm) and particularly to “Zn(CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>” ( $\Delta\lambda_{\text{max}} = 46$  nm). Therefore, differently from pseudolinear molecules with *one* stilbazole ligand linked to a Lewis metal center,<sup>3,10</sup> the  $\Delta\lambda_{\text{max}}$  of the ILCT transition cannot be used as a direct measure of the relative Lewis acidity when *two* stilbazole ligands are linked to a metal center in a tetrahedral or square-planar arrangement. The UV–visible spectrum of free phenanthroline, when X = NMe<sub>2</sub>, shows two bands (Table 2). The first ( $\lambda_{\text{max}} = 281$  nm) can be attributed to a  $\pi \rightarrow \pi^*$  transition, by analogy with the  $\pi \rightarrow \pi^*$  transition of the unsubstituted phenanthroline ( $\lambda_{\text{max}} = 265$  nm),<sup>19</sup> whereas the second ( $\lambda_{\text{max}} = 328$  nm) can be attributed to the intraligand charge transfer (ILCT) from the NMe<sub>2</sub> group to the  $\pi^*$  system of the phenanthroline ring.<sup>8</sup> When X = 4-*trans*-(CH=CH)<sub>n</sub>C<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub> ( $n = 1, 2$ ) as in ligands **3** and **4**, this ILCT transition is shifted, as expected, to lower energy ( $\lambda_{\text{max}} = 371$  and 399 nm for  $n = 1$  and 2,

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respectively). When X = MeO, the UV-visible spectrum shows only one band at ca. 272 nm, attributed to the overlap of the  $\pi \rightarrow \pi^*$  transition and the ILCT from the MeO group to the  $\pi^*$  system of the phenanthroline ring.<sup>9</sup> The higher energy of the ILCT is reasonable because a blue shift ( $\Delta\lambda = 59$  nm) of a similar ILCT band was reported to occur, going from ((dialkylamino)styryl)-bipyridine to (alkoxystyryl)bipyridine.<sup>6</sup> Upon coordination to "Zn(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>" all these ILCT transitions are red-shifted:  $\Delta\lambda_{\max}$  is 12, 16, 33, and 48 nm for X = OMe, NMe<sub>2</sub>, 4-*trans,trans*-(CH=CH)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>, 4-*trans*-CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>, respectively. Coordination of ligand **4** (X = 4-*trans*-CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>) to "Cd(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>" also induces a significant red shift ( $\Delta\lambda_{\max} = 40$  nm) of the ILCT transition.

**3. EFISH and Theoretical Investigation of Second-Order NLO Properties.** The molecular quadratic hyperpolarizabilities ( $\beta$ ) of the ligands and their complexes (Tables 2 and 3) were measured in CHCl<sub>3</sub> by the solution-phase dc electric-field-induced second-harmonic (EFISH) generation method,<sup>7</sup> which provides information on the quadratic hyperpolarizability through the equation

$$\gamma_{\text{EFISH}} = (\mu\beta_{\text{vec}}/5kT) + \gamma_0(-2\omega; \omega, \omega, 0) \quad (2)$$

where  $\mu\beta_{\text{vec}}/5kT$  is the dipolar orientational contribution and  $\gamma_0(-2\omega; \omega, \omega, 0)$ , a third-order term at frequency  $\omega$  of the incident radiation, is the electronic contribution which is always considered negligible in these kinds of ligands and their metal complexes.<sup>2-6</sup> In the following,  $\beta_{\text{vec}}$ , which is the vectorial projection of the quadratic hyperpolarizability tensor along the dipole moment vector  $\mu$ , will be reported as EFISH  $\beta_{1,34}$  or simply  $\beta_{1,34}$  when 1.34  $\mu\text{m}$  is the fundamental incident wavelength. Its second harmonic ( $\lambda/2 = 670$  nm) occurs quite far from any significant absorption band (see Tables 2 and 3), so that dispersive enhancements of the EFISH response are minimized.<sup>20</sup> We have shown in section 2 that both the ligands and their metal complexes show one major ILCT absorption band; therefore, the zero-frequency quadratic hyperpolarizability  $\beta_0$  can be approximately calculated from experimental EFISH  $\beta_{1,34}$  using the two-level model,<sup>16</sup> which assumes that only a one-dimensional charge-transfer process to one excited state is involved in the nonlinear response. This model leads to the expression

$$\beta_0 = \beta_\lambda(1 - (2\lambda_{\max}/\lambda)^2)(1 - (\lambda_{\max}/\lambda)^2) \quad (3)$$

where  $\lambda$  is the fundamental incident wavelength and  $\lambda_{\max}$  is the value of the maximum of the absorption band of the ILCT transition (Tables 2 and 3), which, according to solvatochromic investigations,<sup>8,9</sup> is the major origin of the second-order NLO response. However, the two-level model applies quite well only to pseudolinear molecular arrangements<sup>3,9,10</sup> characterized by a charge transfer process which occurs nearly along the dipole moment axis. This arrangement does not occur in tetrahedral Zn(II) or square-planar Pt(II) complexes with two stilbazole ligands, where the dipole moment axis is in a direction quite different from the ILCT transition, located along the stilbazole ligand. Therefore,

the two-level model could not be applied safely in these latter cases.<sup>21</sup>

**3.1. Phenanthroline Ligands.** It was shown experimentally that the two-level model applies well to the ligand 4-*trans*-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub> and its pseudolinear complexes with "*cis*-M(CO)<sub>2</sub>Cl" (M = Rh(I), Ir(I)) or "*fac*-Os(CO)<sub>3</sub>Cl<sub>2</sub>".<sup>3</sup> Even if the molecular geometries are not pseudolinear, this model appears to be valid also for 5-X-1,10-phenanthrolines. For instance, the EFISH  $\beta_\lambda$  value of 5-methoxy-1,10-phenanthroline was measured both at 1.06  $\mu\text{m}$  and at 1.34  $\mu\text{m}$  incident wavelengths (Table 2) and it was found that  $\beta_{1,34}$ , calculated with the two-level expression (eq 3) from experimental EFISH  $\beta_{1,06}$ , was in good agreement with experimental EFISH  $\beta_{1,34}$  ( $3.7 \times 10^{-30}$  compared to  $4.0 \times 10^{-30}$  cm<sup>5</sup> esu<sup>-1</sup>, the difference being within experimental error). Such an agreement would suggest that, for this kind of ligand, other tensorial components of the quadratic hyperpolarizability inaccessible to EFISH measurements are probably not so relevant. In agreement with this hypothesis, values of  $\beta_{0,\text{TOT}}$  (the total static quadratic hyperpolarizability at zero frequency which takes into account all the  $\beta_i$  tensor components) and static EFISH  $\beta_0$  of the 5-X-1,10-phenanthrolines investigated (X = OMe, NMe<sub>2</sub>, *trans*-CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>, *trans,trans*-(CH=CH)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>; Table 4), calculated using the semiempirical MNDO-CPHF method,<sup>3</sup> are quite comparable. As expected, experimental EFISH  $\beta_{1,34}$  values of these ligands increase with the electron-donating strength of the X substituent and, more significantly, with an increase of the  $\pi$ -conjugated electron network linking the NMe<sub>2</sub> group to the phenanthroline ring (Table 2). This trend, occurring also with 4-X-pyridines,<sup>3</sup> is in agreement with the red shift of  $\lambda_{\max}$  of the ILCT transition (Table 2) major origin of the second-order NLO response.<sup>8,9</sup> Interestingly, while both EFISH  $\beta_{1,34}$  and  $\mu\beta_0$  of linear 4-*trans*-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub> and of rigid 5-(*trans*-CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>)-1,10-phenanthroline ligands are of the same order of magnitude, the flexible 4-(*trans*-CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NBU<sub>2</sub>)-4'-CH<sub>3</sub>-2,2'-bipyridine ligand was reported to have much lower values of EFISH  $\beta_{1,34}$  and  $\mu\beta_0$  (Tables 2 and 3).<sup>6</sup>

Dipole moments and static EFISH  $\beta_0$  and in some cases EFISH  $\beta_{1,34}$  of the various phenanthroline ligands were calculated by the theoretical MNDO-CPHF method (Table 4), which proved to be convenient to predict the experimental dipole moments and the trend of the quadratic hyperpolarizability of various 4-X-pyridines.<sup>3</sup> The calculated dipole moments of the more  $\pi$ -delocalized 5-X-1,10-phenanthrolines (X = *trans*-CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>, *trans,trans*-(CH=CH)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>) are in fair agreement with the experimental values as reported for 4-*trans*-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>.<sup>3</sup> However, when X = OMe, NMe<sub>2</sub>, the calculated values are lower than the experimental ones, as in the case of 4-(*trans*-CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NBU<sub>2</sub>)-4'-CH<sub>3</sub>-2,2'-bipyridine (Table 4).<sup>6</sup> MNDO-CPHF calculated EFISH  $\beta_0$  values of 5-X-1,10-phenanthrolines (X = NMe<sub>2</sub>, *trans*-CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>, *trans,trans*-(CH=CH)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>) and of the flexible chelating ligand 4-(*trans*-CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NBU<sub>2</sub>)-4'-CH<sub>3</sub>-2,2'-bipyridine are underestimated (Table 4) by

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**Table 4. Comparison of Experimental and Theoretical (MNDO-CPHF Semiempirical Method) Values of Dipole Moments and EFISH  $\beta_0$  Values of 4-(*trans*-CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NBU<sub>2</sub>)-4'-CH<sub>3</sub>-2,2'-bipyridine, 4-*trans*-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>, and Various 5-X-1,10-phenanthroline (5-X-Phen) Ligands and of Selected Zn(II) Complexes**

molecule	$\mu$ , D		$\beta_0$ ( $\beta_{0,TOT}$ ), <sup>a</sup> 10 <sup>-30</sup> cm <sup>5</sup> esu <sup>-1</sup>	
	exptl <sup>b</sup>	MNDO-CPHF	exptl <sup>b</sup>	MNDO-CPHF
4-( <i>trans</i> -CH=CHC <sub>6</sub> H <sub>4</sub> -4'-NBU <sub>2</sub> )-4'-CH <sub>3</sub> -2,2'-bipyridine	5.1 <sup>c</sup>	2.8	8 <sup>c</sup>	2.8 <sup>d</sup>
4- <i>trans</i> -NC <sub>5</sub> H <sub>4</sub> CH=CHC <sub>6</sub> H <sub>4</sub> -4'-NMe <sub>2</sub> <sup>e</sup>	3.9	4.6	35	10.4 (10.4)
ZnCl <sub>2</sub> (4- <i>trans</i> -NC <sub>5</sub> H <sub>4</sub> CH=CHC <sub>6</sub> H <sub>4</sub> -4'-NMe <sub>2</sub> ) <sub>2</sub>	8.4	16.7	48 <sup>f</sup>	15.0
Zn(CF <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> (4- <i>trans</i> -NC <sub>5</sub> H <sub>4</sub> CH=CHC <sub>6</sub> H <sub>4</sub> -4'-NMe <sub>2</sub> ) <sub>2</sub>	10.5	20.5	53 <sup>f</sup>	17.0
5-MeO-Phen	4.0	2.7	2.4	2.0 (2.4)
5-Me <sub>2</sub> N-Phen	3.8	2.7	5.7	0.57 (0.59)
5-( <i>trans</i> -CH=CHC <sub>6</sub> H <sub>4</sub> -4'-NMe <sub>2</sub> )-Phen <sup>g</sup>	4.9	4.9	26	6.4 <sup>h</sup> (6.6)
5-( <i>trans,trans</i> -(CH=CH) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -4'-NMe <sub>2</sub> )-Phen	4.9	5.0	44	8.7 (9.0)

<sup>a</sup>  $\beta_{0,TOT}$  is the intrinsic quadratic hyperpolarizability at zero frequency.<sup>3</sup> <sup>b</sup> Experimental value in CHCl<sub>3</sub>; the value of  $\beta_0$  was extrapolated from experimental EFISH  $\beta_{1,34}$  by the two-level model.<sup>16</sup> <sup>c</sup> Reference 6. <sup>d</sup> The calculated  $\beta_{1,34}$  value is  $3.6 \times 10^{-30}$  cm<sup>5</sup> esu<sup>-1</sup>; for 4-(*trans*-CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>)-4'-CH<sub>3</sub>-2,2'-bipyridine, calculated  $\mu$  and  $\beta_0$  values are 4.0 D and  $10.1 \times 10^{-30}$  cm<sup>5</sup> esu<sup>-1</sup>, respectively. <sup>e</sup> Reference 3. <sup>f</sup> Approximate value because the two-level model<sup>16</sup> cannot be applied safely to this tetrahedral Zn(II) complex. <sup>g</sup> By coordination to "Zn(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>", experimental and MNDO calculated dipole moments become 8 and 10.9 D, respectively. <sup>h</sup> The calculated  $\beta_{1,34}$  value is  $8.3 \times 10^{-30}$  cm<sup>5</sup> esu<sup>-1</sup>.

a factor of 0.2–0.3, as in the case of 4-X-pyridines,<sup>3</sup> when compared to EFISH  $\beta_0$  extrapolated from experimental EFISH  $\beta_{1,34}$  by the two-level approximation (eq 3). However, the general trend is that expected, confirming that the MNDO-CPHF method can be used only as a preliminary way to define the trends of the second-order NLO response of this kind of molecules.<sup>3</sup> Strangely enough the calculated EFISH  $\beta_0$  value of 5-OMe-1,10-phenanthroline is quite in agreement with that extrapolated from experimental EFISH  $\beta_{1,34}$  by the two-level approximation (eq 3).

**3.2. Complexes of Zn(II) and Cd(II) with 5-X-1,10-phenanthrolines.** The second-order NLO response of phenanthrolines with electron donor groups is dominated by the ILCT transition, with the phenanthroline  $\pi^*$  system acting as an electron acceptor, as in para-substituted pyridines.<sup>3</sup> By interaction with a Lewis acid, a red shift of  $\lambda_{max}$  of the ILCT occurs, which is related to an increase of the second-order NLO response.<sup>3,4</sup> However, although  $\Delta\lambda_{max}$  of the ILCT of 5-(*trans*-CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>)-1,10-phenanthroline is comparable upon coordination to those of "Cd(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>" or "Zn(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>", this is not reflected in the EFISH  $\beta_{1,34}$  value, which is almost unaffected by coordination to the relatively soft "Cd(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>" acid, whereas it is significantly increased by coordination to the harder "Zn(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>" acid (Table 2). The enhancement factor (EF) of EFISH  $\beta_{1,34}$  upon coordination to "Zn(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>" of 5-X-1,10-phenanthrolines is higher for the better donor group NMe<sub>2</sub> (EF = 4.6) than for OMe (EF = 3.2). It becomes less and less relevant by increasing the length of the  $\pi$ -delocalized bridge between the donor group NMe<sub>2</sub> and the phenanthroline moiety (Table 2), a trend already reported to occur with 4-X-pyridines.<sup>3</sup> When X = NMe<sub>2</sub>, the enhancement factor of EFISH  $\beta_{1,34}$  (4.6) is much lower than that (ca. 10<sup>2</sup>) of 4-NMe<sub>2</sub>-C<sub>5</sub>H<sub>4</sub>N when interacting with BF<sub>3</sub><sup>10</sup> or even with Ir(I), Rh(I), and Os(II) metal centers.<sup>3</sup> This difference can be explained by taking into account that the EFISH  $\beta_{1,34}$  value of 5-NMe<sub>2</sub>-1,10-phenanthroline is much higher (by a factor of 10<sup>2</sup>) than that of 4-NMe<sub>2</sub>-C<sub>5</sub>H<sub>4</sub>N,<sup>3</sup> as expected for the larger  $\pi$ -conjugated electron network of the phenanthroline system, which acts as a better  $\pi^*$  acceptor of the ILCT transition than the pyridine ring. Consequently, the effect of coordination on the  $\pi^*$  level of the ligand is less significant. Interestingly, the enhancement

factor of EFISH  $\beta_{1,34}$  upon coordination of 5-(*trans*-CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>)-1,10-phenanthroline to "Zn(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>" (EF = 1.9) is much smaller than that reported to occur upon coordination of 4-(*trans*-CH=CHC<sub>6</sub>H<sub>4</sub>-*p*-NBU<sub>2</sub>)-4'-CH<sub>3</sub>-2,2'-bipyridine (EF = 8.2).<sup>6</sup> This latter large effect is related to the particularly low quadratic hyperpolarizability of the flexible bipyridine ligand (Table 2). MNDO-CPHF calculations (Table 4) show that such a low value must be attributed to the nonplanarity of both the bipyridine and the NBU<sub>2</sub>C<sub>6</sub>H<sub>4</sub> moieties due to steric repulsions of the butyl groups. Upon coordination to Zn(II), the chelated bipyridine becomes rigid and more planar; therefore, the ligand increases its  $\pi^*$  acceptor properties with a parallel significant increase of its quadratic hyperpolarizability. In agreement with this suggestion, MNDO-CPHF calculations show that by substitution of butyl groups with methyl groups we have an increased planarity of the ligand and an increase of EFISH  $\beta_0$  by a factor of 3 (Table 4).

**3.3. Complexes of Zn(II) and Pt(II) with 4-*trans*-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>.** Experimental EFISH  $\beta_{1,34}$  values of complexes [ZnY<sub>2</sub>(4-*trans*-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>)<sub>2</sub>] (Y = Cl, CH<sub>3</sub>CO<sub>2</sub>, CF<sub>3</sub>CO<sub>2</sub>) and *cis*-[PtCl<sub>2</sub>(4-*trans*-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>)<sub>2</sub>] are reported in Table 3 along, for comparison, with those of the ligand<sup>3</sup> and its complexes with BF<sub>3</sub>,<sup>10</sup> "*cis*-M(CO)<sub>2</sub>Cl" (M = Rh, Ir), and "*cis*-Ir(cyclooctene)<sub>2</sub>Cl".<sup>3</sup> As suggested in section 3, the two-level model<sup>16</sup> cannot be safely applied to tetrahedral Zn(II) or square-planar Pt(II) complexes: EFISH  $\beta_{1,34}$  of [Zn(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>(4-*trans*-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>)<sub>2</sub>], calculated by the two-level equation (eq 3) from experimental EFISH  $\beta_{1,91}$ , is quite different from the experimental value ( $29 \times 10^{-30}$  compared to  $48 \times 10^{-30}$  cm<sup>5</sup> esu<sup>-1</sup>). Therefore,  $\mu\beta_0$  values are not reported in Table 3. Although usually EFISH  $\beta_{1,34}$  of 4-*trans*-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub> increases by coordination to a metal center,<sup>3,10</sup> strangely enough EFISH  $\beta_{1,34}$  is almost unaffected by coordination to the relatively soft "*cis*-PtCl<sub>2</sub>" Lewis acid whereas it increases significantly upon coordination to the harder "ZnY<sub>2</sub>" Lewis acids, the enhancement factor EF being a function of the ancillary Y ligands (for Y = Cl, EF = 1.5; for Y = CF<sub>3</sub>CO<sub>2</sub>, EF = 1.8). However, EFISH  $\beta_{1,34}$  does not increase upon coordination to the less hard "Zn(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>" Lewis acid, in agreement with an irrelevant red shift of the ILCT transition of only 2 nm (when Y = Cl,



**Table 5. Absorption ( $\lambda_a$ ) and Emission ( $\lambda_e$ ) Solvatochromic Determination of  $\beta_{CT}$  at 1.34  $\mu\text{m}$  and Comparison with EFISH  $\beta_{1.34}$** 

molecule	$\lambda_a$ ( $\lambda_e$ ), <sup>a</sup> nm	f <sup>b</sup>	$\Delta\mu_{eg}$ , <sup>c</sup> D	$\beta_{CT}$ at 1.34 $\mu\text{m}$ , <sup>d</sup> 10 <sup>-30</sup> cm <sup>5</sup> esu <sup>-1</sup>	EFISH $\beta_{1.34}$ , <sup>d</sup> 10 <sup>-30</sup> cm <sup>5</sup> esu <sup>-1</sup>
4- <i>trans</i> -NC <sub>5</sub> H <sub>4</sub> CH=CHC <sub>6</sub> H <sub>4</sub> -4'-NMe <sub>2</sub>	374 (454)	0.39	9.8	61	55 <sup>e</sup>
[Zn(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> (4- <i>trans</i> -NC <sub>5</sub> H <sub>4</sub> CH=CHC <sub>6</sub> H <sub>4</sub> -4'-NMe <sub>2</sub> ) <sub>2</sub> ]	376 (460)	1.08	13.4	230 (132) <sup>f</sup>	48
<i>cis</i> -[PtCl <sub>2</sub> (4- <i>trans</i> -NC <sub>5</sub> H <sub>4</sub> CH=CHC <sub>6</sub> H <sub>4</sub> -4'-NMe <sub>2</sub> ) <sub>2</sub> ]	375 (455)	0.82	13.5	175 (123) <sup>f</sup>	41
5-Me <sub>2</sub> N-Phen	281	0.31	1.9	3.0	7.2
	328 (464)	0.14	5.0	6.3 9.3	
[Zn(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> (5-Me <sub>2</sub> N-Phen)]	290	0.04	15.6	3.7	33
	297	0.04	6.9	1.8	
	344 (524)	0.10	21.3	26.2 31.7	
5-( <i>trans</i> -CH=CHC <sub>6</sub> H <sub>4</sub> -4'-NMe <sub>2</sub> )-Phen	381 (508)	0.23	15.1	58	41
[Zn(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> (5-( <i>trans</i> -CH=CHC <sub>6</sub> H <sub>4</sub> -4'-NMe <sub>2</sub> )-Phen)]	419 (580)	0.39	7.5	71	77
[Cd(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> (5-( <i>trans</i> -CH=CHC <sub>6</sub> H <sub>4</sub> -4'-NMe <sub>2</sub> )-Phen)]	410 (562)	0.29	6.5	43	46
[Zn(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> (5-( <i>trans</i> -(CH=CH) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -4'-NMe <sub>2</sub> )Phen)]	432 (590)	0.37	10.1	110	112

<sup>a</sup> Experimental values in CHCl<sub>3</sub>. <sup>b</sup> *f* is the transition oscillator strength, obtained from the experimental integrated absorption coefficient in CHCl<sub>3</sub>. <sup>c</sup>  $\Delta\mu_{eg}$  is the difference between excited- and ground-state molecular dipole moments, obtained from solvatochromic data. <sup>d</sup> In CHCl<sub>3</sub>. <sup>e</sup> From ref 3. <sup>f</sup> Calculated using only the projection of  $\mu_g$  along the charge-transfer direction.

CF<sub>3</sub>CO<sub>2</sub>, the red shifts are 36 and 46 nm, respectively). As expected from the lack of enhancement of EFISH  $\beta_{1.34}$ , a similar irrelevant red shift of the ILCT transition occurs by coordination to "*cis*-PtCl<sub>2</sub>" ( $\Delta\lambda_{\text{max}} = 1$  nm). The EFISH  $\beta_{1.34}$  enhancement factor due to coordination of two stilbazole ligands to the harder Zn(II) centers is generally lower than that originated by interaction of one stilbazole ligand with "M(CO)<sub>2</sub>Cl" (M = Rh, Ir)<sup>3</sup> or BF<sub>3</sub><sup>10</sup> (Table 3). Interestingly, a positive effect due to chelation can be pointed out. The  $\mu\beta_{1.34}$  value ( $1420 \times 10^{-30}$  D cm<sup>5</sup> esu<sup>-1</sup>)<sup>22</sup> of [ZnCl<sub>2</sub>(4,4'-bis(*trans*-CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NBU<sub>2</sub>)-2,2'-bipyridine)] is much higher than that of the related nonchelated complex [ZnCl<sub>2</sub>(4-*trans*-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>)<sub>2</sub>] ( $706 \times 10^{-30}$  D cm<sup>5</sup> esu<sup>-1</sup>). This could be due to the more planar arrangement of the chelated ligand.

**4. Solvatochromic Investigation of the Second-Order NLO Responses.** Solvatochromic studies are a useful way to investigate the electronic origin of the second-order NLO response of molecular species.<sup>8</sup> The quadratic hyperpolarizability  $\beta_{CT}$ , obtained by solvatochromic measurements, is usually different from EFISH  $\beta_i$ . Only when the charge-transfer transition involved in the NLO response is close in direction to the axis of the dipole moment may they be compared. For instance, for ligands such as 5-X-phenanthrolines and *trans*-4-(dimethylamino)-4'-stilbazole<sup>8</sup> and Ir(I) and Rh(I) pseudolinear complexes of *trans*-4-(dimethylamino)-4'-stilbazole<sup>9</sup> solvatochromic  $\beta_{CT}$  values at 1.34  $\mu\text{m}$  are comparable to, although slightly lower than, EFISH  $\beta_{1.34}$  values. With these limits in mind, we carried out a solvatochromic investigation of the second-order NLO response of some ligands and of their Zn(II), Pt(II), and Cd(II) complexes, studied in this work (Table 5). First we noted that for 5-Me<sub>2</sub>N-1,10-phenanthroline the major contribution to  $\beta_{CT}$  is given by the absorption band at lower energy (328 nm in the free ligand and 344 nm in its Zn(II) complex) characterized by the highest  $\Delta\mu_{eg}$  (difference between excited- and ground-state molecular dipole moments) value. This result is in agreement with the assignment of this absorption to a ILCT transition

(see section 2). The absorptions at higher energy (281 nm in the ligand and 290 and 297 nm in its Zn(II) complex) show a smaller contribution to  $\beta_{CT}$ , as expected for  $\pi \rightarrow \pi^*$  transitions of the unsaturated aromatic ring. For nonchelated systems with two ligands, such as complexes of 4-*trans*-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub> with "Zn(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>" and "*cis*-PtCl<sub>2</sub>",  $\beta_{CT}$  at 1.34  $\mu\text{m}$  is much higher than EFISH  $\beta_{1.34}$ . In these latter molecules the dipole moment is directed along the binary axis, thus bisecting the angle formed by the directions of the two equivalent ILCT charge transfers located on the two stilbazole ligands (see section 1.2.1), while in the free stilbazole ligand, which shows a far better agreement between  $\beta_{CT}$  at 1.34  $\mu\text{m}$  and EFISH  $\beta_{1.34}$ , the dipole moment axis and the ILCT direction are substantially coincident. However, when only the component of  $\mu_g$  along the charge-transfer direction is considered for both "Zn(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>" and "*cis*-PtCl<sub>2</sub>", the resulting value of  $\beta_{CT}$  becomes only slightly higher than twice that of the free ligand itself. This result would confirm an irrelevant enhancement of  $\beta_{CT}$  of the free ligand upon coordination to "Zn(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>" or "*cis*-PtCl<sub>2</sub>", as expected from the irrelevant red shift of the ILCT transition in both complexes and the comparable value of EFISH  $\beta_{1.34}$  of Zn(II) and Pt(II) complexes and of the free ligand.

For free phenanthrolines (in particular **2-4**) and their complexes with "Zn(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>" and for the complex [Cd-(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>(5-(*trans*-CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub>)-1,10-phenanthroline)] there is a very good correspondence between  $\beta_{CT}$  at 1.34  $\mu\text{m}$  and EFISH  $\beta_{1.34}$  (Table 5), in agreement with a satisfactory coincidence of the direction of the ILCT charge transfer and of the dipole moment axis, already suggested in section 3.1. A detailed analysis shows that when the donor group NMe<sub>2</sub> is not directly linked to the phenanthroline ring (ligands **3** and **4**) the appreciable increase of  $\beta_{CT}$  upon coordination to "Zn-(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>" is due to a high oscillator strength and to the low energy of the ILCT transition rather than to an increase of  $\Delta\mu_{eg}$ , which in contrast decreases from 15.1 to 7.5 D upon coordination (Table 5), while when the donor group NMe<sub>2</sub> is directly linked to the phenanthroline ring (ligand **2**), the relevant enhancement of  $\beta_{CT}$  is mainly due to a large increase of  $\Delta\mu_{eg}$  (from 5.0

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to 21.3 D). In the Cd(II) complex the lack of increase of EFISH  $\beta_{1,34}$  on coordination, despite the red shift of  $\lambda_{\max}$  of the ILCT transition, is explained by a small decrease of the energy of this latter transition and by the relatively small increase of its oscillator strength, which do not compensate the unexpected high decrease of  $\Delta\mu_{\text{eg}}$  (from 21.3 to 6.5 D), therefore producing in total an irrelevant enhancement of  $\beta_{\text{CT}}$  upon coordination (Table 5).

### Conclusion

In this work we added further evidence that coordination to relatively hard tetrahedral Zn(II) centers produces, as already reported by Le Bozec et al. for chelating bipyridine ligands,<sup>2,6</sup> a significant enhancement of  $\beta_{\text{CT}}$  or EFISH  $\beta_{1,34}$  of chelating  $\pi$ -delocalized nitrogen donor ligands such as 5-X-1,10-phenanthrolines bearing a NMe<sub>2</sub> group linked to position 5 via a  $\pi$ -delocalized network (ligands **2–4**). As for  $\eta^1$  donor pyridines<sup>3</sup> this effect is more significant when the NMe<sub>2</sub> group is directly linked to the ring bound to the acceptor center. However, this is not a general trend: for instance, such an enhancement does not occur when the phenanthroline ligand **3** is coordinated to a softer center such as Cd(II), although a red shift of the ILCT transition of the free ligand, which is the origin of the second-order NLO response, occurs. The enhancement factor upon coordination of the quadratic hyperpolarizability of chelating ligands is lower for planar phenanthrolines than for nonplanar and flexible bipyridines.<sup>6</sup> We have attributed this significant difference to the planarity and rigidity induced by coordination of bipyridines, thus producing a better  $\pi^*$  acceptor system for the ILCT transition and therefore its significant shift to lower energies.

The behavior is different when two stilbazole ligands with a NMe<sub>2</sub> group in a para position are coordinated to tetrahedral “Zn(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>” or square-planar “cis-PtCl<sub>2</sub>” acceptor centers. In this case we could not observe the expected significant increase of EFISH  $\beta_{1,34}$ ; even when the ancillary CH<sub>3</sub>CO<sub>2</sub><sup>-</sup> ligand is substituted by more electronegative ancillary ligands such as Cl<sup>-</sup> or CF<sub>3</sub>CO<sub>2</sub><sup>-</sup>. With these latter ligands the increase of EFISH  $\beta_{1,34}$  is much less significant than that occurring in structurally related Zn(II) complexes with chelated bipyridines.<sup>6</sup> Obviously chelation seems to be a structural requirement to increase the second-order NLO response. These unexpected results were interpreted by a solvatochromic investigation. The lack of increase of EFISH  $\beta_{1,34}$  or  $\beta_{\text{CT}}$  of phenanthroline **3** upon coordination to “Cd(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>” is due to a very large decrease of  $\Delta\mu_{\text{eg}}$ , which is not compensated by a relatively small red shift, and the increase of the oscillator strength of the ILCT transition, while in the related Zn(II) complex a less relevant decrease of  $\Delta\mu_{\text{eg}}$  is compensated by a more significant red shift and by a high oscillator strength of the ILCT transition.

$\beta_{\text{CT}}$  at 1.34  $\mu\text{m}$  and EFISH  $\beta_{1,34}$  of tetrahedral “Zn-(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>” and square-planar “cis-PtCl<sub>2</sub>” complexes with two stilbazole ligands with a NMe<sub>2</sub> group in the para position are significantly different because the dipole moment axis is not coincident with the direction of the ILCT transition of the ligand. It follows that the two-level model<sup>16</sup> cannot be safely applied to EFISH  $\beta_{1,34}$  values of these complexes in order to evaluate their static quadratic hyperpolarizability. However, the solvatochromic analysis of the second-order NLO response along the single ligand direction has confirmed the lack of a significant increase upon coordination to Zn(II) or Pt(II) of the quadratic hyperpolarizability of the single stilbazole ligands, as suggested by EFISH measurements and by the irrelevant red shift of the ILCT transition. This is an unexpected result, because usually there is a significant increase of EFISH  $\beta_{1,34}$  of this kind of ligand upon coordination to hard or soft metal centers.<sup>3,4,10</sup> In comparison with the high increase of EFISH  $\beta_{1,34}$  of related chelated bipyridines in a planar arrangement, this is probably due to the nonplanar arrangement of the two stilbazole ligands, as confirmed by the identification of the best geometry by MNDO calculations. Therefore, the combined use of EFISH and solvatochromic measurements is an excellent way to analyze the electronic and steric origin of the second-order NLO response of these kinds of complexes.

Finally, the very stable Zn(II) complex with phenanthroline **4** has a  $\mu\beta_0$  value of  $450 \times 10^{-30}$  D cm<sup>5</sup> esu<sup>-1</sup>, comparable to that of some organic materials such as Disperse Red One ( $\mu\beta_0 = 500 \times 10^{-30}$  D cm<sup>5</sup> esu<sup>-1</sup>) currently used in electrooptic polymers.<sup>23</sup> This  $\mu\beta_0$  value is of the same order of magnitude found in the complex of 4-*trans*-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NMe<sub>2</sub> with BF<sub>3</sub>,<sup>10</sup> which, however, is rather unstable, or with some expensive Rh(I), Ir(I), and Os(II) metal carbonyl centers.<sup>3</sup>

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