

# Effect of the Coordination to the “Os<sub>3</sub>(CO)<sub>11</sub>” Cluster Core on the Quadratic Hyperpolarizability of *trans*-4-(4'-X-styryl)pyridines (X = NMe<sub>2</sub>, *t*-Bu, CF<sub>3</sub>) and *trans,trans*-4-(4'-NMe<sub>2</sub>-phenyl-1,3-butadienyl)pyridine

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Coordination to the “Os<sub>3</sub>(CO)<sub>11</sub>” cluster core of substituted styrylpyridines such as *trans*-4-(4'-NMe<sub>2</sub>-styryl)pyridine (**L**<sub>1</sub>), *trans*-4-(4'-*t*-Bu-styryl)pyridine (**L**<sub>2</sub>), *trans*-4-(4'-CF<sub>3</sub>-styryl)pyridine (**L**<sub>3</sub>), or *trans,trans*-4-(4'-NMe<sub>2</sub>-phenyl-1,3-butadienyl)pyridine (**L**<sub>4</sub>) produces an enhancement of their quadratic hyperpolarizability,  $\beta_{\text{EFISH}}$ , measured by the solution-phase dc electric-field-induced second harmonic (EFISH) generation method. This effect is due either to a red-shift of the intraligand charge-transfer (ILCT) transition upon coordination (when the substituent in *para* position is a strong electron donor) or to a metal-to-ligand charge-transfer (MLCT) transition (when the substituent is a strong electron acceptor). In the latter case the quadratic hyperpolarizability has a negative sign, due to the negative value of  $\Delta\mu_{\text{eg}}$ . Therefore the “Os<sub>3</sub>(CO)<sub>11</sub>” cluster core displays an ambivalent acceptor or donor role. Some of the complexes investigated in this study show significant values (between  $500 \times 10^{-48}$  and  $900 \times 10^{-48}$  esu) of the product  $\mu\beta_0$ .

## Introduction

In recent years organometallic and coordination compounds emerged as potential new systems for nonlinear optical (NLO) applications.<sup>1–7</sup> The possibility of tuning the electronic properties of the organometallic fragment, by acting on the metal center, its electronic configuration, its oxidation state, and ligand environment, offers new potential for higher second-order NLO responses. Previous works showed that coordination of *para*-substituted pyridines and stilbazoles to metal carbonyl moieties such as “M(CO)<sub>5</sub>” (M = Cr(0), W(0)),<sup>8–10</sup> “*cis*-M(CO)<sub>2</sub>Cl” (M = Rh(I), Ir(I)),<sup>11</sup> and “*fac*-Os(CO)<sub>3</sub>Cl<sub>2</sub>”<sup>11</sup> produces a significant increase of  $\beta_\lambda$ , the projection of  $\beta_{\text{VEC}}$ , the vectorial part 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 working at incident wavelength  $\lambda$ .<sup>12–14</sup>

As a general trend, very soft metal centers such as “M(CO)<sub>5</sub>” (M = Cr(0), W(0))<sup>8–10</sup> and less soft centers such as Rh(I), Ir(I), or Os(II)<sup>11</sup> carbonyl species display, in the excitation process origin of the second-order NLO response, an ambivalent acceptor or donor role toward *para*-substituted pyridines or stilbazoles, according to the electron donor or acceptor character of the *para* substituent. For instance, when the substituent is a strong donor group such as NMe<sub>2</sub>, an intraligand ILCT transition at higher energy contributes to the increase of  $\beta_\lambda$ , while when the substituent is a strong acceptor group, a metal-to-ligand MLCT transition dominates the second-order NLO response, still resulting in an increase of the absolute value of  $\beta_\lambda$  but producing a negative sign of the latter.

It was thus interesting to investigate how this general trend applies to potentially electron-rich polynuclear metallic fragments such as “soft” metal carbonyl clusters. Therefore we investigated the effect of coordination of *para*-substituted stilbazoles to a metal carbonyl cluster core such as “Os<sub>3</sub>(CO)<sub>11</sub>”.

To our knowledge there is no experimental report about second-order NLO properties of molecular metal clusters. Some attempts to study third-order NLO properties of metal carbonyl clusters such as Ru<sub>3</sub>(CO)<sub>12</sub>,

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**Table 1. Absorption ( $\lambda_{\text{abs}}$ ) and Emission ( $\lambda_{\text{em}}$ ) Spectra, Dipole Moments, and EFISH  $\beta_{1.907}$  in  $\text{CHCl}_3$  of Ligands  $\text{L}_1$ ,  $\text{L}_2$ ,  $\text{L}_3$ ,  $\text{L}_4$  and Their Complexes with " $\text{Os}_3(\text{CO})_{11}$ "**

molecule	$\lambda_{\text{abs}}$ , nm <sup>a</sup>	$\lambda_{\text{em}}$ , nm <sup>a</sup>	$\mu$ , D <sup>a</sup>	$\mu\beta_{1.907}$ , 10 <sup>-48</sup> esu <sup>b</sup>	$\mu\beta_{1.907}$ EF <sup>c</sup>	$\beta_{1.907}$ , 10 <sup>-30</sup> esu <sup>b</sup>	$\beta_0$ , 10 <sup>-30</sup> esu <sup>d</sup>
<b>1</b>	431	546	9.0	585	4.3	65	49
<b>L<sub>1</sub></b>	374	455	3.9	136		35	28
<b>2</b>	338 (sh), 376	420	5.1	100	1.5	20	16
<b>L<sub>2</sub></b>	362	445	3.3	67		20	16
<b>3</b>	312, 385 (sh)	367	8.2	-639	8.9 <sup>e</sup>	-78	-62
<b>L<sub>3</sub></b>	303	353	2.0 <sup>f</sup>	72		36	32
<b>4</b>	451	604	8.8	866	2.8	98	72
<b>L<sub>4</sub></b>	396	516	4.5	310		69	55

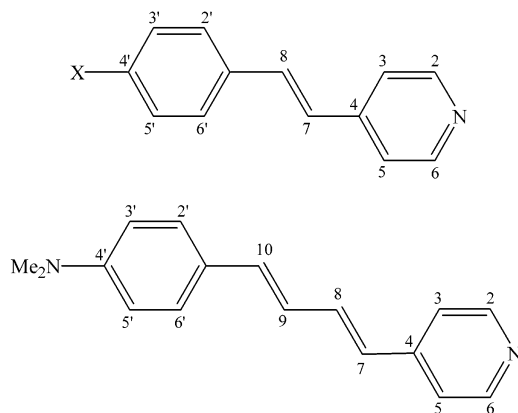
<sup>a</sup> Experimental values in  $\text{CHCl}_3$ . <sup>b</sup> Measured by EFISH at 1.907  $\mu\text{m}$ . <sup>c</sup>  $\mu\beta$  EF is the enhancement factor =  $\mu\beta_{1.907}$  complex/ $\mu\beta_{1.907}$  corresponding free ligand. <sup>d</sup> Obtained by eq 3. <sup>e</sup> Taking into account only the absolute values. <sup>f</sup> Theoretical value obtained by the MNDO method.<sup>34</sup>

$\text{Rh}_4(\text{CO})_{12}$ , and  $\text{Ir}_4(\text{CO})_{12}$  failed due to their photoinstability upon laser excitation, which induces facile M–M bond cleavage of the clusters and subsequent fragmentation.<sup>15</sup>

### Experimental Section

**General Comments.**  $\text{Os}_3(\text{CO})_{12}$  and *trans*-4-(4'-NMe<sub>2</sub>-styryl)pyridine (**L<sub>1</sub>**) were purchased from Strem and Sigma-Aldrich, respectively, and were used without further purification; *trans,trans*-4-(4'-NMe<sub>2</sub>-phenyl-1,3-butadienyl)pyridine (**L<sub>4</sub>**) was prepared according to a synthesis reported in the literature,<sup>11</sup> whereas *trans*-4-(4'-*t*-Bu-styryl)pyridine (**L<sub>2</sub>**), *trans*-4-(4'-trifluoromethyl-styryl)pyridine (**L<sub>3</sub>**), and all the osmium complexes were prepared as described below. All solvents were dried over molecular sieves (4 Å) or distilled prior to use and reactions performed under nitrogen atmosphere. Products were characterized by <sup>1</sup>H and <sup>13</sup>C NMR (Bruker AC-200 and Bruker Avance DRX 300 spectrometers), UV–visible (Jasco V-530 spectrophotometer), IR (Jasco FTIR-420 spectrometer) spectroscopies, mass spectrometry (Varian VG-9090 spectrometer), and elemental analysis (carried out in our Department). Dipole moments were measured in  $\text{CHCl}_3$  by using a WTW-DM01 dipolmeter (dielectric constant) coupled with a Pulfrich Zeiss PR2 refractometer (refractive index) and calculated by using the Guggenheim method.<sup>16–18</sup>

For the numbering used in the attribution of the NMR signals, see the following structures:



### Determination of the Second-Order NLO Response.

**(i) EFISH Measurements.** The molecular quadratic hyperpolarizabilities of complexes and free ligands (Tables 1–3) were measured by the solution-phase dc electric-field-induced second-harmonic (EFISH) generation method,<sup>12–14</sup> which can

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**Table 2. Solvatochromic Determination of  $\beta_{\text{CT}}$  of Complexes 1 and 3 at 1.907  $\mu\text{m}$  and Comparison with EFISH  $\beta_{1.907}$** 

molecule	$\lambda_{\text{abs}}$ , nm <sup>a</sup>	$f^b$	$a, c$ 10 <sup>-8</sup> cm	$\Delta\mu_{\text{eg}}$ , D <sup>d</sup>	$\beta_{\text{CT}}$ , 10 <sup>-30</sup> esu <sup>a</sup>	$\beta_{1.907}$ , 10 <sup>-30</sup> esu <sup>a</sup>
<b>1</b>	431	0.73	8.1	4.7	69	65
<b>3</b>	312	0.98	8.1	17.6	115 } 103	-78
	385 (sh)	0.12	8.1	-7.16		

<sup>a</sup> Experimental values in  $\text{CHCl}_3$ . <sup>b</sup>  $f$  is the transition oscillator strength. <sup>c</sup>  $a$  is the cavity radius estimated by molecular weight approximation. <sup>d</sup>  $\Delta\mu_{\text{eg}}$  is the difference between excited- and ground-state molecular dipole moments.

**Table 3. Comparison of  $\beta_0$  Values of Various Ligands and Their Carbonyl Complexes**

molecule	$\mu$ (D) <sup>a</sup>	$\beta_0$ , 10 <sup>-30</sup> esu	$\mu\beta_0, b$ 10 <sup>-48</sup> esu
<b>1</b>	9.0	49	441
$[\text{Ir}(\text{CO})_2\text{ClL}_1]^c$	6.0	67	402 <sup>d</sup>
$[\text{Rh}(\text{CO})_2\text{ClL}_1]^c$	7.0	61	427 <sup>d</sup>
$[\text{Os}(\text{CO})_3\text{Cl}_2\text{L}_1]^c$	7.4	43	318 <sup>d</sup>
$[\text{W}(\text{CO})_5\text{L}_1]^e$	14.9	19	283 <sup>f</sup>
<b>L<sub>1</sub></b> <sup>c</sup>	3.9	35	137 <sup>d</sup>
<b>2</b>	5.1	6	31
<b>L<sub>2</sub></b>	3.3	16	54
<b>3</b>	8.2	-68	-558
<b>L<sub>3</sub></b>	2.0 <sup>g</sup>	31	62
<b>4</b>	8.8	72	633
$[\text{Ir}(\text{CO})_2\text{ClL}_4]^c$	8.8	66	580 <sup>d</sup>
$[\text{Rh}(\text{CO})_2\text{ClL}_4]^c$	6.7	66	442 <sup>d</sup>
$[\text{Os}(\text{CO})_3\text{Cl}_2\text{L}_4]^c$	8.0	55	440 <sup>d</sup>
<b>L<sub>4</sub></b> <sup>c</sup>	4.5	47	211 <sup>d</sup>

<sup>a</sup> Experimental values in  $\text{CHCl}_3$ . <sup>b</sup> Measured by EFISH at 1.907  $\mu\text{m}$  and converted to  $\beta_0$  with the two-level expression (eq 3) unless otherwise stated. <sup>c</sup> Reference 11. <sup>d</sup> Measured by EFISH at 1.34  $\mu\text{m}$  and converted to  $\beta_0$  with the two-level expression (eq 3; ref 11). <sup>e</sup> Reference 10. <sup>f</sup>  $\beta$  measured by EFISH at 1.064  $\mu\text{m}$  and converted to  $\beta_0$  with the two-level expression (eq 3; ref 10). <sup>g</sup> Theoretical value obtained by the MNDO method (ref 40).

provide direct information on the intrinsic molecular NLO properties through eq 1:

$$\gamma_{\text{EFISH}} = (\mu\beta/5kT) + \gamma(-2\omega; \omega, \omega, 0) \quad (1)$$

where  $\mu\beta/5kT$  is the dipolar orientational contribution and  $\gamma(-2\omega; \omega, \omega, 0)$ , a third-order term at frequency  $\omega$  of the incident light, is the electronic contribution to  $\gamma_{\text{EFISH}}$ , which is negligible for the kind of molecules here investigated.<sup>10,11,19</sup> In the following the projection of  $\beta_{\text{VEC}}$ , the vectorial part of the quadratic hyperpolarizability tensor, along the dipole moment ( $\mu$ ) direction, will be reported as EFISH  $\beta_\lambda$ , where  $\lambda$  is the fundamental wavelength of the incident photon in the EFISH experiment.

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EFISH measurements<sup>12–14</sup> were carried out in our Department in CHCl<sub>3</sub> solutions of different concentrations working at a nonresonant incident wavelength of 1.907 μm, using a Q-switched, mode-locked Nd<sup>3+</sup>:YAG laser manufactured by Atalaser equipped with a Raman shifter, while the apparatus for the EFISH measurements was a prototype made by SOPRA (France).

**(ii) Solvatochromic Measurements.** The second-order NLO response of complexes **1** and **3** was investigated also by solvatochromic measurements, using absorption (JASCO V-570 spectrophotometer) spectra in various solvents (acetone, acetonitrile, carbon tetrachloride, chloroform, 1,2-dichloroethane, dichloromethane, diethyl ether, ethyl acetate, hexane, tetrahydrofuran, toluene) following a methodology described in the literature and calculating the radius *a* of the cavity produced by the solute by means of the molecular weights, the molecules being pseudospherical.<sup>20,21</sup> The quadratic hyperpolarizability tensor β<sub>CT</sub> along the charge-transfer direction involved in the NLO response was calculated according to the Oudar two-level equation:<sup>22–24</sup>

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

where *r<sub>eg</sub>* is the transition dipole moment related to the integrated intensity *f* of the absorption band, *ν<sub>a</sub>* is the frequency of the charge-transfer absorption band, *ν<sub>L</sub>* is the frequency of the incident radiation, and Δ*μ<sub>eg</sub>* is the variation of the dipole moment upon excitation.

**Synthesis of [Os<sub>3</sub>(CO)<sub>11</sub>(CH<sub>3</sub>CN)].** The complex [Os<sub>3</sub>(CO)<sub>11</sub>-(CH<sub>3</sub>CN)] was prepared by a modified literature method.<sup>25,26</sup> [Os<sub>3</sub>(CO)<sub>12</sub>] (514 mg, 0.567 mmol) was dissolved in distilled acetonitrile (750 mL) in a three-necked flask under nitrogen at reflux temperature for 1 h. The solution was cooled at 60 °C and added with a solution of freshly sublimed dry trimethylamine oxide (44 mg, 0.591 mmol) in acetonitrile (200 mL) over a period of 4 h using a pressure-equalized dropping funnel. The resulting solution was stirred for 16 h, filtered through silica gel, and evaporated to dryness. The residue crystallizes at 0 °C from acetonitrile (20 mL) to give a yellow precipitate of pure [Os<sub>3</sub>(CO)<sub>11</sub>(CH<sub>3</sub>CN)] (436 mg, 0.473 mmol, yield 84%): <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>, 25 °C) δ (ppm) 2.73 (s, 3 H, CH<sub>3</sub>CN); *ν*<sub>CO</sub> (in CH<sub>2</sub>Cl<sub>2</sub>) 2106 (w), 2052 (vs), 2040 (vs), 2017 (m, sh), 2007 (s), 1980 (m, br) cm<sup>-1</sup>; Anal. Calcd (found) C 16.98 (17.10), H 0.33 (0.43), N 1.52 (1.56).

**Preparation of *trans*-4-(4'-*tert*-Butylstyryl)pyridine (L<sub>2</sub>).** This new ligand (L<sub>2</sub>) was prepared following a synthetic method reported in the literature<sup>27</sup> by reduction with iron and acetic acid of *trans*-4-(4'-*tert*-butylstyryl)pyridine-1-oxide, obtained by condensation of 4-methylpyridine-1-oxide with 4-*tert*-butylbenzaldehyde in the presence of potassium hydroxide and dry pyridine.

**(a) Synthesis of *trans*-4-(4'-*tert*-Butylstyryl)pyridine-1-oxide.** A round-bottomed flask was charged with 4-methylpyridine-1-oxide (1.17 g; 10.7 mmol) and dry pyridine (8 mL). To this solution were added 4-*tert*-butylbenzaldehyde (2.43 g; 15 mmol) and solid potassium hydroxide (0.60 g). When the addition was complete, the reaction mixture was heated at reflux for 3 h. After cooling at room temperature, distilled water (150 mL) was added and the resulting mixture was stirred for 20 min, then neutralized with a few drops of concentrated sulfuric acid and extracted with dichloromethane (3 × 30 mL). The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to afford a brown solid, which was recrystallized

with ethanol (5 mL), yielding the product as a white solid (1.15 g; 42%): <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>, 25 °C) δ (ppm) 8.15 (AA'BB', 2 H, H<sub>2</sub> and H<sub>6</sub>, *J* = 7.1 Hz), 7.45 (AA'BB', 2 H, H<sub>2'</sub> and H<sub>6'</sub>, *J* = 8.6 Hz), 7.40 (AA'BB', 2 H, H<sub>3'</sub> and H<sub>5'</sub>, *J* = 8.6 Hz), 7.35 (AA'BB', 2H, H<sub>3</sub> and H<sub>5</sub>, *J* = 7.1 Hz), 7.15 (d, 1 H, H<sub>7</sub>, *J*<sub>trans</sub> = 16.3 Hz), 6.92 (d, 1 H, H<sub>8</sub>, *J*<sub>trans</sub> = 16.3 Hz), 1.32 (s, 9 H, CH<sub>3</sub>).

**(b) Reduction of *trans*-4-(4'-*tert*-Butylstyryl)pyridine-1-oxide.** *trans*-4-(4'-*tert*-butylstyryl)pyridine-1-oxide (1.01 g; 4 mmol) obtained as previously described was dissolved in glacial acetic acid (20 mL) and heated at 90 °C under magnetic stirring, adding in 20 min small portions of iron (1.44 g; 26 mmol in total). The resulting brown mixture was heated at 90 °C for 30 min. After cooling at room temperature, ice and a 30% aqueous solution of sodium hydroxide were added until the pH became strongly basic and a brown solid precipitated. The solid was suspended in pyridine (20 mL) and heated at reflux temperature for 30 min. The resulting mixture was filtrated at 80 °C over Celite in order to eliminate impurities and unreacted iron, and the yellow filtrate was evaporated to dryness to give *trans*-4-(4'-*t*-butylstyryl)pyridine (L<sub>2</sub>) (0.722 g; 76%) as a pale yellow solid, which was used without further purification: <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>, 25 °C) δ (ppm) 8.55 (AA'BB', 2 H, H<sub>2</sub> and H<sub>6</sub>, *J* = 6.1 Hz), 7.48 (AA'BB', 2 H, H<sub>2'</sub> and H<sub>6'</sub>, *J* = 8.5 Hz), 7.40 (AA'BB', 2 H, H<sub>3'</sub> and H<sub>5'</sub>, *J* = 8.5 Hz), 7.35 (AA'BB', 2 H, H<sub>3</sub> and H<sub>5</sub>, *J* = 6.1 Hz), 7.28 (d, 1 H, H<sub>7</sub>, *J*<sub>trans</sub> = 16.5 Hz), 6.97 (d, 1 H, H<sub>8</sub>, *J*<sub>trans</sub> = 16.3 Hz), 1.33 (s, 9 H, CH<sub>3</sub>); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>, 25 °C) δ (ppm) 152.2 (C<sub>4</sub>), 150.2 (C<sub>2</sub>, C<sub>6</sub>), 144.9 (C<sub>4'</sub>), 133.4 (C<sub>9</sub>), 133.0 (C<sub>3</sub>, C<sub>5</sub>), 126.9 (C<sub>2'</sub>, C<sub>6'</sub>), 125.9 (C<sub>3'</sub> and C<sub>5'</sub>), 125.3 (C<sub>8</sub>), 120.9 (C<sub>7</sub>), 31.8 (C-(CH<sub>3</sub>)<sub>3</sub>), 31.3 (CH<sub>3</sub>); Anal. Calcd (found) C 86.03 (86.38), H 8.07 (8.19), N 5.90 (6.01); MS-EI *m/e* 237, calcd for C<sub>17</sub>H<sub>19</sub>N *m/e* 237.

**Preparation of *trans*-4-(4'-Trifluoromethylstyryl)pyridine (L<sub>3</sub>).** This new compound (L<sub>3</sub>) was prepared following a synthetic method reported in the literature<sup>27</sup> by dehydration with acetic anhydride of 4-[2-hydroxy-2(α,α,α-trifluoro-*p*-tolyl)ethyl]pyridine, obtained by condensation of 4-methylpyridine with α,α,α-trifluoro-*p*-tolualdehyde in the presence of lithium diisopropylamide (LDA).

**(a) Synthesis of 4-[2-Hydroxy-2(α,α,α-trifluoro-*p*-tolyl)ethyl]pyridine.** A flame-dried round-bottomed flask equipped with a thermometer and a rubber septum was charged under nitrogen atmosphere with 4-methylpyridine (0.632 g; 6.78 mmol) and dry tetrahydrofuran (6 mL). This solution was cooled at -78 °C and slowly added with a tetrahydrofuran (12 mL) solution of lithium diisopropylamide (LDA), prepared by reacting at 0 °C diisopropylamine (1.15 mL, 8.134 mmol, freshly distilled from KOH) and butyllithium (5.5 mL, 1.6 M, 8.8 mmol). When the addition was complete, the reaction mixture was stirred for 1 h at -10 °C, to allow carbanion formation. To the resulting brown reaction mixture was added dropwise a solution of α,α,α-trifluoro-*p*-tolualdehyde (1.18 g; 6.81 mmol) in tetrahydrofuran (15 mL) via syringe at -10 °C. The cooling bath was then removed, and the reaction mixture, warmed at room temperature, was magnetically stirred for a further 22 h. The mixture was quenched with NH<sub>4</sub>Cl-saturated aqueous solution (30 mL), and the two phases were separated: the aqueous phase was extracted with diethyl ether (2 × 10 mL), which was added to the organic phase. The latter was washed with water (2 × 10 mL), dried over MgSO<sub>4</sub>, and evaporated to afford a yellow-orange thick residue, which was dehydrated as described below: <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>, 25 °C) δ (ppm) 8.23 (AA'BB', 2 H, H<sub>2</sub> and H<sub>6</sub>, *J* = 6.0 Hz), 7.56 (AA'BB', 2 H, H<sub>3</sub> and H<sub>5</sub>, *J* = 8.2 Hz), 7.41 (AA'BB', 2 H, H<sub>2'</sub> and H<sub>6'</sub>, *J* = 8.2 Hz), 7.06 (AA'BB', 2H, H<sub>3</sub> and H<sub>5</sub>, *J* = 6.0 Hz), 4.95 (t, 1 H, H<sub>7</sub>, *J* = 6.2 Hz), 2.96 (d, 2 H, H<sub>8</sub> and H<sub>8'</sub>, *J* = 6.2 Hz), 1.81 (br s, 1 H, OH; it disappears by addition of D<sub>2</sub>O).

**(b) Dehydration of 4-[2-Hydroxy-2(α,α,α-trifluoro-*p*-tolyl)ethyl]pyridine.** The crude 4-[2-hydroxy-2(α,α,α-tri-

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fluoro-*p*-tolyl)ethyl]pyridine, obtained as described in the previous step, was dissolved in freshly distilled acetic anhydride (25 mL) and heated at reflux temperature under magnetic stirring for 4 h. The solution was evaporated to give a brown oil, which was dissolved in dichloromethane (80 mL) and then neutralized with 10% aqueous NaOH (50 mL). The organic phase was washed with water (2 × 25 mL), dried over MgSO<sub>4</sub>, and evaporated to dryness to afford a brown solid residue. Purification by column chromatography over silica gel, using ethyl acetate as eluent, gave *trans*-4-(4'-trifluoromethylstyryl)pyridine (**L**<sub>3</sub>) as a beige solid (1.136 g; 67%): <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>, 25 °C) δ (ppm) 8.63 (AA'BB', 2 H, H<sub>2</sub> and H<sub>6</sub>, *J* = 6.0 Hz), 7.65 (AA'BB', 4 H, H<sub>2'</sub>, H<sub>3'</sub>, H<sub>5'</sub> and H<sub>6'</sub>), 7.40 (AA'BB', 2 H, H<sub>3</sub> and H<sub>5</sub>, *J* = 6.0 Hz), 7.33 (d, 1H, H<sub>7</sub>, *J*<sub>trans</sub> = 16.4 Hz), 7.12 (d, 1 H, H<sub>8</sub>, *J*<sub>trans</sub> = 16.4 Hz); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>, 25 °C) δ (ppm) 150.7 (s, C<sub>2</sub> and C<sub>6</sub>), 144.2 (s, C<sub>4</sub>), 139.9 (q, C<sub>1'</sub>, *J* = 1.4 Hz), 131.8 (s, C<sub>7</sub>), 130.7 (q, C<sub>4'</sub>, *J* = 32.6 Hz), 128.9 (s, C<sub>8</sub>), 127.5 (s, C<sub>2'</sub> and C<sub>6'</sub>), 126.1 (q, C<sub>3'</sub> and C<sub>5'</sub>, *J* = 3.8 Hz), 124.4 (q, C<sub>9</sub>, *J* = 272 Hz), 121.4 (s, C<sub>3</sub> and C<sub>5</sub>); <sup>19</sup>F NMR (282.4 MHz, CDCl<sub>3</sub>, 25 °C) δ (ppm) 63.6 (s); Anal. Calcd (found) C 67.47 (67.27), H 4.04 (4.12), N 5.62 (5.52); MS-EI *m/e* 249, calcd for C<sub>14</sub>H<sub>10</sub>NF<sub>3</sub> *m/e* 249.

**General Procedure for the Preparation of [Os<sub>3</sub>(CO)<sub>11</sub>L] (L = L<sub>1</sub>, L<sub>2</sub>, L<sub>3</sub>, and L<sub>4</sub>) Complexes.** In a two-necked flask [Os<sub>3</sub>(CO)<sub>11</sub>(CH<sub>3</sub>CN)] (0.194 g; 0.211 mmol) was dissolved at room temperature in deoxygenated dichloromethane (120 mL) under nitrogen and added with a solution of the desired ligand (0.217 mmol, 1 equivalent) in dichloromethane (50 mL). The reaction was monitored by infrared spectroscopy and when complete, about 3 h later, was evaporated to dryness. The residue was washed with pentane (5 mL), affording [Os<sub>3</sub>(CO)<sub>11</sub>L] complexes of acceptable purity, which were stored in the dark under nitrogen.

**[Os<sub>3</sub>(CO)<sub>11</sub>L<sub>1</sub>] (1):** yellow solid, yield 87%; <sup>1</sup>H NMR (300.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C) δ (ppm) 8.60 (AA'BB', 2 H, H<sub>2</sub> and H<sub>6</sub>, *J* = 6.2 Hz), 7.48 (AA'BB', 2 H, H<sub>2'</sub> and H<sub>6'</sub>, *J* = 8.6 Hz), 7.36 (d, 1 H, H<sub>8</sub>, *J* = 16.1 Hz), 7.22 (AA'BB', 2 H, H<sub>3</sub> and H<sub>5</sub>, *J* = 6.2 Hz), 6.81 (d, 1 H, H<sub>7</sub>, *J* = 16.1 Hz), 6.74 (AA'BB', 2 H, H<sub>3'</sub> and H<sub>5'</sub>, *J* = 8.6 Hz), 3.06 (s, 6 H, NMe<sub>2</sub>); ν<sub>CO</sub> (in CH<sub>2</sub>Cl<sub>2</sub>) 2103 (w), 2051 (s), 2034 (vs), 2007 (s), 1974 (m, br) cm<sup>-1</sup>; Anal. Calcd (found) C 28.31 (28.06), H 1.46 (1.59), N 2.54 (2.72); MS-FAB<sup>+</sup> *m/e* 1104 (M + 1)<sup>+</sup>, calcd for C<sub>26</sub>H<sub>16</sub>O<sub>11</sub>N<sub>2</sub>Os<sub>3</sub> *m/e* 1103.

**[Os<sub>3</sub>(CO)<sub>11</sub>L<sub>2</sub>] (2):** yellow solid, yield 82%; <sup>1</sup>H NMR (300.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C) δ (ppm) 8.70 (AA'BB', 2 H, H<sub>2</sub> and H<sub>6</sub>, *J* = 6.6 Hz), 7.54 (AA'BB', 2 H, H<sub>2'</sub> and H<sub>6'</sub>, *J* = 8.4 Hz), 7.48 (AA'BB', 2 H, H<sub>3'</sub> and H<sub>5'</sub>, *J* = 8.4 Hz), 7.42 (d, 1 H, H<sub>8</sub>, *J* = 16.2 Hz), 7.30 (AA'BB', 2 H, H<sub>3</sub> and H<sub>5</sub>, *J* = 6.6 Hz), 7.03 (d, 1 H, H<sub>7</sub>, *J* = 16.2 Hz), 1.37 (s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>); ν<sub>CO</sub> (in CH<sub>2</sub>Cl<sub>2</sub>) 2104 (w), 2051 (vs), 2034 (vs), 2008 (vs), 1976 (m, br) cm<sup>-1</sup>; Anal. Calcd (found) C 30.13 (30.15), H 1.72 (1.86), N 1.26 (1.25); MS-FAB<sup>+</sup> *m/e* 1117 (M + 1)<sup>+</sup>, calcd for C<sub>28</sub>H<sub>19</sub>O<sub>11</sub>NOs<sub>3</sub> *m/e* 1116.

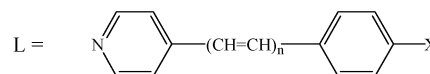
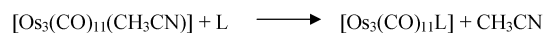
**[Os<sub>3</sub>(CO)<sub>11</sub>L<sub>3</sub>] (3):** yellow solid, yield 70%; <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>, 25 °C) δ (ppm) 8.73 (AA'BB', 2 H, H<sub>2</sub> and H<sub>6</sub>, *J* = 6.3 Hz), 7.68 (AA'BB', 4 H, H<sub>2'</sub>, H<sub>3'</sub>, H<sub>5'</sub>, and H<sub>6'</sub>), 7.39 (d, 1 H, H<sub>7</sub>, *J*<sub>trans</sub> = 16.3 Hz), 7.29 (AA'BB', 2 H, H<sub>3</sub> and H<sub>5</sub>, *J* = 6.3 Hz), 7.09 (d, 1 H, H<sub>8</sub>, *J*<sub>trans</sub> = 16.3 Hz); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>, 25 °C) δ (ppm) 159.7 (s, C<sub>2</sub> and C<sub>6</sub>), 146.1 (s, C<sub>4</sub>), 138.8 (s, C<sub>1'</sub>), 135.6 (s, C<sub>7</sub>), 131.7 (q, C<sub>4'</sub>, *J* = 32.7 Hz), 128.0 (s, C<sub>2'</sub> and C<sub>6'</sub>), 126.4 (q, C<sub>3'</sub> and C<sub>5'</sub>, *J* = 3.8 Hz), 126.3 (s, C<sub>8</sub>), 124.2 (q, C<sub>9</sub>, *J* = 272 Hz), 123.6 (s, C<sub>3</sub> and C<sub>5</sub>); <sup>19</sup>F NMR (282.4 MHz, CDCl<sub>3</sub>, 25 °C) δ (ppm) 63.7 (s); ν<sub>CO</sub> (in CH<sub>2</sub>Cl<sub>2</sub>) 2105 (w), 2052 (s), 2035 (s), 2007 (s), 1978 (m, br) cm<sup>-1</sup>; Anal. Calcd (found) C 26.62 (26.36), H 0.89 (1.04), N 1.24 (1.15); MS-FAB<sup>+</sup> *m/e* 1129 (M + 1)<sup>+</sup>, calcd for C<sub>25</sub>H<sub>10</sub>O<sub>11</sub>F<sub>3</sub>NOs<sub>3</sub> *m/e* 1128.

**[Os<sub>3</sub>(CO)<sub>11</sub>L<sub>4</sub>] (4):** orange solid, yield 86%; <sup>1</sup>H NMR (300.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C) δ (ppm) 8.60 (AA'BB', 2 H, H<sub>2</sub> and H<sub>6</sub>, *J* = 6.7 Hz), 7.40 (AA'BB', 2 H, H<sub>2'</sub> and H<sub>6'</sub>, *J* = 8.8 Hz), 7.25 (m, 1 H, H<sub>8</sub>), 7.17 (AA'BB', 2 H, H<sub>3</sub> and H<sub>5</sub>, *J* = 6.6 Hz), 6.84 (m, 2 H, H<sub>9</sub> and H<sub>10</sub>), 6.72 (AA'BB', 2 H, H<sub>3'</sub> and H<sub>5'</sub>, *J* = 8.8 Hz), 6.47 (d, 1 H, H<sub>7</sub>, *J* = 15.9 Hz), 3.03 (s, 6 H, NMe<sub>2</sub>); <sup>13</sup>C

NMR (75.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C) δ (ppm) 159.2 (s, C<sub>2</sub> and C<sub>6</sub>), 151.4 (s, C<sub>4</sub>), 147.6 (s, C<sub>4'</sub>), 139.9 (s, C<sub>10</sub>), 138.9 (s, C<sub>8</sub>), 128.9 (s, C<sub>2'</sub> and C<sub>6'</sub>), 124.5 (s, C<sub>1'</sub>), 124.3 (s, C<sub>7</sub>), 123.2 (s, C<sub>3</sub> and C<sub>5</sub>), 122.8 (s, C<sub>9</sub>), 112.4 (s, C<sub>3'</sub> and C<sub>5'</sub>), 40.4 (s, N(CH<sub>3</sub>)<sub>2</sub>); ν<sub>CO</sub> (in CH<sub>2</sub>Cl<sub>2</sub>) 2104 (w), 2051 (vs), 2034 (vs), 2007 (s), 1974 (m, br) cm<sup>-1</sup>; Anal. Calcd (found) C 29.78 (29.92), H 1.60 (1.79), N 2.48 (2.54); MS-FAB<sup>+</sup> *m/e* 1130 (M + 1)<sup>+</sup>, calcd for C<sub>28</sub>H<sub>18</sub>O<sub>11</sub>N<sub>2</sub>Os<sub>3</sub> *m/e* 1129.

## Results and Discussion

**Synthesis of [Os<sub>3</sub>(CO)<sub>11</sub>L] Complexes.** The synthesis of the [Os<sub>3</sub>(CO)<sub>11</sub>L] complexes was accomplished by exchanging the coordinated acetonitrile of [Os<sub>3</sub>(CO)<sub>11</sub>(CH<sub>3</sub>CN)] with the stilbazole ligand according to the reaction:



**L**<sub>1</sub> (X = NMe<sub>2</sub> and n = 1) gives *trans*-compound 1

**L**<sub>2</sub> (X = *t*-Bu and n = 1) gives *trans*-compound 2

**L**<sub>3</sub> (X = CF<sub>3</sub> and n = 1) gives *trans*-compound 3

**L**<sub>4</sub> (X = NMe<sub>2</sub> and n = 2) gives *trans,trans*-compound 4

All the compounds have been characterized by elemental analysis, IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies, and mass spectrometry.

**Infrared, NMR, and UV-Visible Spectra.** Infrared spectra of complexes [Os<sub>3</sub>(CO)<sub>11</sub>L] (L = L<sub>1</sub>, L<sub>2</sub>, L<sub>3</sub>, and L<sub>4</sub>) show a pattern of the carbonyl stretching frequencies typical of species such as [Os<sub>3</sub>(CO)<sub>11</sub>Py],<sup>25,29</sup> [Os<sub>3</sub>(CO)<sub>11</sub>(CH<sub>3</sub>CN)],<sup>25,30</sup> and [Os<sub>3</sub>(CO)<sub>11</sub>(η<sup>1</sup>-C<sub>7</sub>H<sub>6</sub>N<sub>2</sub>)],<sup>31</sup> thus confirming that they consist of a triangular cluster of three osmium atoms without any bridging ligand, the organic ligand being coordinated to an osmium atom of the cluster through the nitrogen atom with occupation of an axial coordination site.<sup>30,31</sup>

In the <sup>1</sup>H NMR spectra of the [Os<sub>3</sub>(CO)<sub>11</sub>L] (L = L<sub>1</sub>, L<sub>2</sub>, L<sub>3</sub>, and L<sub>4</sub>) complexes the signals of hydrogens in α position to the pyridine nitrogen atom are slightly shifted to lower fields with respect to the free ligand (Δδ about 0.05–0.10 ppm) due to some electron transfer to "Os<sub>3</sub>(CO)<sub>11</sub>", while the coupling constant between the *trans* olefinic hydrogens (*J*<sub>H-H</sub> = 16.1–16.2 Hz) does not change upon coordination. The shift to lower field is lower when compared to that reported for coordination of L<sub>1</sub> or L<sub>4</sub> to "fac-Os(CO)<sub>3</sub>Cl<sub>2</sub>" (Δδ about 0.30 ppm)<sup>11</sup> but comparable to that reported for coordination of L<sub>1</sub> to "hard" Zn(II) centers such as [ZnCl<sub>2</sub>(L<sub>1</sub>)<sub>2</sub>], [Zn(CH<sub>3</sub>-CO<sub>2</sub>)<sub>2</sub>(L<sub>1</sub>)<sub>2</sub>], and [Zn(CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>(L<sub>1</sub>)<sub>2</sub>] (Δδ about 0.10 ppm)<sup>32</sup> or to "soft" metal carbonyl centers such as "cis-M(CO)<sub>2</sub>Cl" (M = Rh(I), Ir(I)) (Δδ about 0.05 ppm),<sup>11</sup> while for coordination to the softer center "W(CO)<sub>5</sub>" this shift is not observed at all.<sup>10</sup>

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UV-visible spectra of **L**<sub>1</sub> and **L**<sub>4</sub> and of their metal complexes **1** and **4** (Table 1) show one major charge-transfer band in the region 370–400 nm, attributed to the intramolecular charge-transfer transition (ILCT)  $n \rightarrow \pi^*$  from the NMe<sub>2</sub> donor group to the pyridine ring,<sup>10</sup> red-shifted upon complexation<sup>10,11,33</sup> ( $\Delta\lambda_{\max} = 55\text{--}57$  nm or  $\Delta E = 0.38$  and  $0.44$  eV for **4** and **1**, respectively). Since this red-shift can be used as a way to estimate the relative acceptor strength of the metal center,<sup>11</sup> the size of the shift would suggest an acceptor strength of the "Os<sub>3</sub>(CO)<sub>11</sub>" core comparable to that of "fac-Os(CO)<sub>3</sub>Cl<sub>2</sub>"<sup>11</sup> ( $\Delta\lambda_{\max} = 60$  and  $61$  nm or  $\Delta E = 0.41$  and  $0.46$  eV for **L**<sub>4</sub> and **L**<sub>1</sub>, respectively) and "cis-Ir(CO)<sub>2</sub>Cl" ( $\Delta\lambda_{\max} = 53$  and  $57$  nm or  $\Delta E = 0.37$  and  $0.44$  eV for **L**<sub>4</sub> and **L**<sub>1</sub>, respectively).<sup>11</sup> The absorption spectrum of **L**<sub>2</sub> is dominated by an intense band at 362 nm, which we can attribute to a  $\pi \rightarrow \pi^*$  ligand transition, which upon coordination is only slightly red-shifted with respect to the free ligand ( $\Delta\lambda_{\max} = 14$  nm or  $\Delta E = 0.13$  eV). Such a slight shift is expected for a  $\pi \rightarrow \pi^*$  internal transition of **L**<sub>2</sub>, because the effect of the perturbation of the  $\pi^*$  levels by nitrogen coordination is less relevant upon the high-energy  $\pi \rightarrow \pi^*$  transition than upon the  $n \rightarrow \pi^*$  transition at lower energy. The absorption spectrum of complex **3** displays a strong band at 312 nm attributed to a slightly red-shifted  $\pi \rightarrow \pi^*$  internal transition of the ligand **L**<sub>3</sub> ( $\Delta\lambda_{\max} = 9$  nm or  $\Delta E = 0.12$  eV), together with a shoulder at about 385 nm, which we tentatively attributed to a metal-to-ligand charge-transfer transition (MLCT) from the "Os<sub>3</sub>(CO)<sub>11</sub>" core to the  $\pi^*$  levels of the ligand **L**<sub>3</sub> bearing an electron-acceptor group in the *para* position.<sup>10,11</sup> This latter attribution is supported by the negative  $\Delta\mu_{\text{eg}}$  value (variation of the dipole moment between the ground and the excited state) of this transition, as we will see later when discussing the results of the EFISH and solvatochromic investigation, respectively.<sup>10,11</sup>

**Dipole Moments.** Dipole moments were measured in chloroform solution by the Guggenheim method<sup>16–18</sup> and are reported in Table 1.

Dipole moments of ligands **L**<sub>1</sub>, **L**<sub>2</sub>, and **L**<sub>4</sub> are comparable. It has not been possible to obtain an experimental measurement with the Guggenheim method for **L**<sub>3</sub> probably due to dipole–dipole aggregation; therefore its value was theoretically determined using the semiempirical MNDO (modified intermediate neglect of differential overlap) method.<sup>34</sup> This method has been previously used to evaluate the dipole moment of **L**<sub>1</sub> and **L**<sub>4</sub> and proved to give values quite in agreement with the experimental determinations,<sup>11</sup> thus supporting its application also in a quite similar ligand such as **L**<sub>3</sub>.

The dipole moment enhancement ( $\mu_{\text{EF}} = \mu_{\text{complex}}/\mu_{\text{corresponding free ligand}}$ ) occurring upon coordination to "Os<sub>3</sub>(CO)<sub>11</sub>" is significant. It is higher for **L**<sub>1</sub> and **L**<sub>4</sub> ( $\mu_{\text{EF}} = 2.3$  and  $1.9$ , respectively), while it is smaller for **L**<sub>2</sub> ( $\mu_{\text{EF}} = 1.5$ ). The increase for **L**<sub>1</sub> is slightly higher than that reported<sup>11</sup> for 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>" moieties, while for **L**<sub>4</sub> the increase is quite similar (Table 3).

The small increase of the dipole moment of **L**<sub>2</sub> upon coordination is an additional evidence of a rather small effect on the  $\pi$  electronic density of this ligand. Conversely the effect on **L**<sub>3</sub> seems to be very large and probably with an inversion of sign of the dipole. In fact in ligands **L**<sub>1</sub>, **L**<sub>2</sub>, and **L**<sub>4</sub> we have a positive charge on the nitrogen atom of the electron donor *para* substituents and negative charge on the nitrogen atom of the pyridine ring. This charge distribution is maintained and increased upon coordination. On the contrary, in ligand **L**<sub>3</sub> we have a small negative charge on the trifluoromethyl group and consequently a small positive charge on the nitrogen atom of the pyridine ring. Upon coordination, there is a flow of electron density toward the acceptor "Os<sub>3</sub>(CO)<sub>11</sub>" core, which should invert this polarity.

**EFISH and Solvatochromic Investigation of Second-Order NLO Properties.** The EFISH technique<sup>12–14</sup> was used to study the effect of coordination to the "Os<sub>3</sub>(CO)<sub>11</sub>" core on the quadratic hyperpolarizability of ligands **L**<sub>1</sub>, **L**<sub>2</sub>, **L**<sub>3</sub>, and **L**<sub>4</sub>. Measurements (Table 1) were carried out in chloroform working at 1.907  $\mu\text{m}$  incident wavelength. Ligands with a donor group in the *para* position (**L**<sub>1</sub> and **L**<sub>4</sub>) display an increase of the product  $\mu\beta_{1.907}$  by coordination with an enhancement factor ( $\mu\beta_{\text{EF}} = \mu\beta_{1.907,\text{complex}}/\mu\beta_{1.907,\text{ligand}}$ ) of 4.3 for complex **1** and 2.8 for complex **4** (Table 1), as expected for a metal fragment showing acceptor properties. Complex **2** displays a value of the product  $\mu\beta_{1.907}$  slightly higher than that of the free ligand, with an enhancement factor of 1.5 (Table 1); this increase is due to the higher dipole moment as shown by the coincidence of the EFISH  $\beta_{1.907}$  values of the complex and the free ligand (Table 1). In this specific case, it seems that coordination to the "Os<sub>3</sub>(CO)<sub>11</sub>" cluster core of a ligand with a poor electron donor like the *tert*-butyl group in *para* position does not produce a relevant effect on its NLO response. Complex **3**, with ligand **L**<sub>3</sub> carrying an electron acceptor group in *para* position, has a negative sign of the quadratic hyperpolarizability, suggesting that the "Os<sub>3</sub>(CO)<sub>11</sub>" core with this specific ligand behaves as an electron donor in the excitation process by a MLCT transition<sup>10</sup> (Table 1). Remarkably, this complex has the biggest enhancement factor by coordination of the absolute value of  $\mu\beta_{1.907}$  (enhancement factor = 8.9). However it must be emphasized that in the latter case we have a large increase of the dipole moment absolute value. Thus the effect on the absolute value of the quadratic hyperpolarizability is not so relevant (Table 1).

In conclusion the "Os<sub>3</sub>(CO)<sub>11</sub>" polynuclear metallic fragment behaves not too differently when compared with the monomeric organometallic moieties: the effect on the quadratic hyperpolarizability is related to the acceptor or donor behavior of the metallic system in the electronic excitation process. The latter is modulated by the donor or acceptor properties of the group in the *para* position of the stilbazole ligand.<sup>10,11</sup>

The enhancement factor of the quadratic hyperpolarizability upon coordination to "Os<sub>3</sub>(CO)<sub>11</sub>" decreases by increasing the length of the  $\pi$ -delocalized bridge between the donor group NMe<sub>2</sub> and the pyridine ring (as it occurs going from **L**<sub>1</sub> to **L**<sub>4</sub>). This specific trend confirms what was found in previous works.<sup>10,11</sup>

It is worth pointing out that all the clusters proved to be stable upon laser excitation as confirmed by

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infrared and  $^1\text{H}$  NMR spectroscopies before and after EFISH measurements.

To confirm the electronic origin of the second-order response, we have carried out an investigation of the solvatochromic behavior of the ILCT transition of the absorption electronic spectra, which proved to give a reliable estimate of the quadratic hyperpolarizability  $\beta_{\text{CT}}$  along the major charge-transfer axis.  $\beta_{\text{CT}}$  and EFISH  $\beta_{1.907}$  may be compared when the charge-transfer transition controlling the NLO response is close in direction to the axis of the dipole moment as probably occurs in complexes **1**, **3**, and **4**. The solvatochromic investigation has shown for complex **1** a good agreement between EFISH  $\beta_{1.907}$  and  $\beta_{\text{CT}}$  values (Table 2), confirming the intraligand character of the charge-transfer transition controlling the second-order NLO response. In complex **3** the overlapping of the strong band at 312 nm (due to a  $\pi \rightarrow \pi^*$  internal transition of the ligand  $\text{L}_3$ ), with the shoulder at about 385 nm, attributed to a MLCT transition, strongly affected the reliability of the absolute value of the  $\beta_{\text{CT}}$  obtained from the solvatochromic investigation and calculated according to refs 20 and 21. As expected for a  $\pi \rightarrow \pi^*$  transition, the band at 312 nm had a slightly positive solvatochromic behavior, leading to positive values for both  $\beta_{\text{CT}}$  and  $\Delta\mu_{\text{eg}}$  (Table 2), while the band producing a shoulder at 385 nm showed a negative solvatochromic behavior with negative  $\beta_{\text{CT}}$  and  $\Delta\mu_{\text{eg}}$  values, confirming its metal-to-ligand charge-transfer character. However the exact contribution of this band to the overall  $\beta_{\text{CT}}$  value was probably strongly underestimated because even by means of deconvolution it was very difficult to determine exactly its maximum. Therefore in the case of complex **3** the overall  $\beta_{\text{CT}}$  value has a positive sign not comparable with the EFISH  $\beta_{1.907}$  value (Table 2).

We applied then the two-level model<sup>22–24</sup> to calculate the zero-frequency static quadratic hyperpolarizability  $\beta_0$  from EFISH  $\beta_{1.907}$  using the following expression, which is a different way, but easier to handle for our purpose, of writing eq 2:

$$\beta_0 = \beta_{1.907}(1 - (2\lambda_{\text{max}}/\lambda)^2)(1 - (\lambda_{\text{max}}/\lambda)^2) \quad (3)$$

where  $\lambda$  is the fundamental wavelength of the incident photon (1.907  $\mu\text{m}$ ) and  $\lambda_{\text{max}}$  is the maximum absorption value of the major charge-transfer transition (ILCT or MLCT) mainly responsible for the NLO response (Table 2). Although the two-level approach has significant implicit approximations, it can be reasonably adopted to extrapolate  $\beta_0$  values, with an acceptable error in the estimate of  $\beta_0$  that is usually within the range of experimental error ( $\pm 10\%$ ).<sup>11</sup> The static quadratic hyperpolarizability  $\beta_0$  is not frequency dependent, so it can be used to compare  $\beta_\lambda$  values obtained working with incident radiation of different wavelength, at least from a semiquantitative point of view.<sup>35</sup> With this limitation in mind,  $\beta_0$  values of complexes with a stilbazole bearing an electron donor group such as  $\text{NMe}_2$  ( $\text{L}_1$ ,  $\text{L}_4$ ) suggest unexpectedly that the “ $\text{Os}_3(\text{CO})_{11}$ ” core displays acceptor properties more close to Os(II) in [*fac*- $\text{Os}(\text{CO})_3\text{Cl}_2\text{L}_1$ ]<sup>11</sup> than to W(0) in [ $\text{W}(\text{CO})_5\text{L}_1$ ]<sup>9,10</sup> (Table 3). In particular, in agreement with significant acceptor properties, in the case of ligand  $\text{L}_4$  with an increased  $\pi$  conjugation the “ $\text{Os}_3(\text{CO})_{11}$ ” core induces a higher  $\beta_0$  value if compared

to “*cis*- $\text{M}(\text{CO})_2\text{Cl}$ ” ( $\text{M} = \text{Rh}(\text{I}), \text{Ir}(\text{I})$ )<sup>11</sup> and “*fac*- $\text{Os}(\text{CO})_3\text{Cl}_2$ ”<sup>11</sup> (Table 3). There are no second-order NLO measurements of W(0), Rh(I), Ir(I), Ru(II), and Os(II) carbonyl complexes bearing  $\text{L}_3$  as a ligand, but a comparison of  $\beta_{1.907}$  values in chloroform of **3** and of a complex with a similar kind of ligand [ $\text{W}(\text{CO})_5(\text{trans-4-(4'-NO}_2\text{-styryl)pyridine})$ ]<sup>9</sup> (respectively  $-78$  and  $-20 \times 10^{-30}$  esu) shows that despite its significant acceptor properties the potentially electron-rich “ $\text{Os}_3(\text{CO})_{11}$ ” cluster core behaves also as a fairly good donor by an excitation process from the cluster system to the  $\pi^*$  level of ligand  $\text{L}_3$ .

## Conclusion

Our study, which is, as far as we know, the first investigating the second-order NLO properties of an organic push–pull ligand coordinated to a carbonyl cluster fragment, has indicated that a zerovalent trimeric cluster core such as “ $\text{Os}_3(\text{CO})_{11}$ ” shows a significant dual “acceptor–donor” behavior with respect to the perturbation of the second-order NLO response of the ligand. This behavior is more relevant to that reported for monomeric metal carbonyl moieties such as “ $\text{M}(\text{CO})_5$ ” ( $\text{M} = \text{W}(0)$ ),<sup>8–10</sup> “*cis*- $\text{M}(\text{CO})_2\text{Cl}$ ” ( $\text{M} = \text{Rh}(\text{I}), \text{Ir}(\text{I})$ ),<sup>11</sup> and “*fac*- $\text{Os}(\text{CO})_3\text{Cl}_2$ ”.<sup>11</sup> In particular, while a significant electron transfer by excitation to the  $\pi^*$  system of a stilbazole ligand carrying in *para* position an electron-withdrawing substituent such as  $\text{CF}_3$  ( $\text{L}_3$ ) is expected, in consideration of a significant polarizability of the electron density of a trimeric cluster core with metals in the zero oxidation state, the significant  $\sigma$  acceptor properties, comparable to that of a Os(II) metal carbonyl center when the stilbazole carries an electron donor group such as  $\text{NMe}_2$  ( $\text{L}_1$  and  $\text{L}_4$ ) are quite unexpected.

It seems that the “ $\text{Os}_3(\text{CO})_{11}$ ” cluster core behaves as a localized monomeric metal center, but it induces the highest perturbation of the second-order NLO response of stilbazoles carrying either strong electron donor or electron-withdrawing groups.

Remarkably all the osmium carbonyl clusters here investigated are quite stable and do not decompose upon laser excitation to give M–M bond cleavage (as previously observed for  $\text{Ru}_3(\text{CO})_{12}$ ,  $\text{Rh}_4(\text{CO})_{12}$ , and  $\text{Ir}_4(\text{CO})_{12}$ );<sup>15</sup> in addition, some complexes here described have  $\mu\beta_0$  values comparable to those of Disperse Red 1 (*trans*-4,4'- $\text{O}_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{NEt}(\text{CH}_2\text{CH}_2\text{OH})$ ),  $\mu\beta_0 = 500 \times 10^{-48}$  esu), which is currently used in electrooptic polymers.<sup>36</sup>

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