# **Inorganic Chemistry**

# pH-Switchability and Second-Order Nonlinear Optical Properties of Monocyclopentadienylruthenium(II)/iron(II) Tetrazoles/Tetrazolates: Synthesis, Characterization, and Time-Dependent Density Functional Theory Calculations

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**Supporting Information** 

**A B S T R A C T**: T e t r a z o l e / t e t r a z o l a t e monocyclopentadienyliron(II) and ruthenium(II) compounds of general formulas  $[(\eta^5-C_5H_5)M(dppe)(N_4(H)CC_6H_4NO_2)]$ - $[PF_6]/[(\eta^5-C_5H_5)M(dppe)(N_4CC_6H_4NO_2)]$  were investigated for their pH-switching second-order nonlinear optical (SONLO) properties. Compounds  $[(\eta^5-C_5H_5)M(dppe)-(N_4CC_6H_4NO_2)]$  (M = Fe, Ru) and compound  $[(\eta^5-C_5H_5)Ru(dppe)(N_4(H)CC_6H_4NO_2)][PF_6]$  were fully characterized by  $(^{1}H_{-}, ^{13}C_{-}, ^{31}P_{-})$  NMR, cyclic voltammetry, and elemental analysis, and compounds  $[(\eta^5-C_5H_5)Fe(dppe)-(N_4CC_6H_4NO_2)]$  and  $[(\eta^5-C_5H_5)Ru(dppe)(N_4(H)-C_6H_4NO_2)]$  and  $[(\eta^5-C_5H_5)Ru(dppe)(N_4(H)-C_6H_4NO_2)]$ 



 $(N_4CC_6H_4NO_2)$  and  $[(\eta^5-C_5H_5)Ru(dppe)(N_4(H)-CC_6H_4NO_2)]$  and  $[(\eta^5-C_5H_5)Ru(dppe)(N_4(H)-CC_6H_4NO_2)]$  were further characterized by single-crystal X-ray diffraction; the synthesis of  $[(\eta^5-C_5H_5)Fe(dppe)(N_4(H)-CC_6H_4NO_2)]$  [PF<sub>6</sub>] was unsuccessful. Time-dependent density functional theory calculations were performed using PBE0 and CAM-B3LYP functionals to evaluate the first hyperpolarizability ( $\beta_{tot}$ ) of the tetrazole/tetrazolate complexes and for a detailed analysis of the experimental data. Both functionals predict (i) high first hyperpolarizabilities for the tetrazolate complexes  $[(\eta^5-C_5H_5)Ru(dppe)(N_4CC_6H_4NO_2)]$ , with  $\beta_{tot}[Ru] \approx 1.2\beta_{tot}[Fe]$ , and (ii) a 3-fold reduction in  $\beta_{tot}[Ru]$  upon protonation, in complex  $[(\eta^5-C_5H_5)Ru(dppe)(N_4(H)CC_6H_4NO_2)]^+$ , forecasting  $[(\eta^5-C_5H_5)Ru(dppe)(N_4CC_6H_4NO_2)]/[(\eta^5-C_5H_5)Ru(dppe)-(N_4(H)CC_6H_4NO_2)]^+$  complexes as on/off, pH-switchable SONLO forms.

# ■ INTRODUCTION

Compounds with enhanced second-order nonlinear optical (SONLO) properties have been extensively investigated over the last quarter-century due to the large panel of possible technological applications, such as building blocks for optical communications, optical data processing and storage, or electro-optical devices.<sup>1</sup> Among those, there has been a growing interest in molecular species with switchable SONLO properties, since the possibility to modulate the NLO behavior of molecular materials using an external stimulus increases their potential for application in optoelectronic and photonic technologies.<sup>2</sup> The quadratic hyperpolarizability ( $\beta$ ) of chromophores can be manipulated by reversibly modifying specific parts of the active molecules. Since most SONLO chromophores are of the donor(D)- $\pi$  system-acceptor(A) type, alterations are categorized in three types, (i) reducing the donor ability of D by oxidation or protonation, (ii) reducing the acceptor behavior of A by reduction or deprotonation, or,

(iii) structural or chemical modification of the bridging group, breaking the conjugation between D and  $A^{2a}$  Thus, SONLO switches can be achieved through an external stimulus such as a pH variation, a redox process, or by interaction with electromagnetic radiation.

In this trend, coordination complexes offer significant advantages over organic NLO chromophores due to NLO active charge-transfer transitions between the metal and the ligands, and the opportunity for fine-tuning their electronic properties by modification of the metal center, its oxidation state and coordination sphere.<sup>3</sup> Group 8 organometallic complexes were first highlighted in the NLO context by Green et al., which unveiled good second harmonic generation (SHG) efficiencies for ferrocenyl derivatives.<sup>4</sup> Although interesting results have been achieved with ferrocene systems,<sup>5</sup>

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group 8 half-sandwich complexes have later boosted the SONLO response of organometallic complexes due to the possibility of d(metal)- $\pi$ (chromophore) orbital conjugation. Systematic studies performed on iron and ruthenium complexes of general formulas  $[(\eta^5-C_5H_5)M(PP)$  (chromophore)] (PP = mono- or bidentate phosphanes), with different types of chromophores (e.g., phenyl, thienyl) bound to the metal center through nitrile or acetylide linkages revealed  $[(\eta^5-C_5H_5)M(PP)]^+$  organometallic moieties as efficient donors for SONLO purposes, consistently leading to higher  $\beta$  values than the best organic donor groups (e.g., NR<sub>2</sub>).<sup>6</sup>

Considerable efforts have been made in designing and preparing metallic complexes with effective pH-, redox-, or photoswitchable SONLO responses, in solution and in the solid state,<sup>2,7</sup> and the fragments  $[(\eta^5-C_5Me_5)Fe(dppe)]^+$  and  $[(\eta^5-C_5H_5)Ru(dppe)]^+$  were previously studied for their redox-switchable properties. In this family the monometallic complex  $[(\eta^5-C_5Me_5)Fe(dppe)(4-C \equiv C-C_6H_4-NO_2)]$  revealed a remarkable switchability,<sup>8</sup> and more recently,  $[(\eta^5-C_5H_5)M(dppe)(L)]^+$  complexes (M = Fe, Ru; L= 5-(3-(thiophen-2-yl)benzo[c]thiophen-1-yl)-thiophene-2-carbonitrile) were investigated by time-dependent density functional theory (TD-DFT) calculations, with calculated  $\beta_{tot}$  values for one-electron oxidized species increasing up to 8.3 times (M = Ru) in relation to the nonoxidized complexes.<sup>9</sup>

Remarkably, ruthenium<sup>10</sup> and iron<sup>10d,11</sup> compounds of general formulas  $[(\eta^5-C_5H_5)M(PP)(L)][X]$  (PP = mono- or bidentate phosphanes; L = N-donor ligand; X = counterion) have also been recognized also as good anticancer agents. Some of us have developed tetrazole-carbohydrate ligands and the respective ruthenium glycoconjugates,<sup>10c</sup> given the interest in 5-substituted-1*H*-tetrazoles (RCN<sub>4</sub>H) as metabolism-resistant isosteric replacements for carboxylic acids (RCO<sub>2</sub>H).<sup>12</sup> Owing to their multiple N-donor atoms and various coordination modes, tetrazoles and derivatives have also the potential as functional ligands in coordination chemistry and crystal engineering,<sup>13</sup> and in this context, zinc(II)-tetrazole metal–organic frameworks previously exhibited SHG up to 5 times the urea standard.<sup>14</sup>

Given the above referred studies on the SONLO and anticancer properties of  $[(\eta^5 \cdot C_5 H_5)M(PP)(L)]$  complexes (M = Fe, Ru), and the interesting electronic and structural properties of tetrazoles,<sup>15</sup> we ended up wondering, (i) how efficient would the tetrazolate heteroring (RCN<sub>4</sub><sup>-</sup>) be as metalchromophore linker in neutral complexes of the type  $[(\eta^5 \cdot C_5 H_5)M(PP)(N_4C-chromophore-A)]$ , and moreover, (ii) whether the tetrazolate/tetrazole complex pair would have the right properties for a SONLO pH-switch, due to conjugation loss in the protonated tetrazole complexes. Ruthenium-alkynyl complexes of general formulas *trans*-[Ru-(dppe)<sub>2</sub>Cl(C=C-C<sub>6</sub>H<sub>4</sub>-R)] and the corresponding vinylidene forms *trans*-[Ru(dppe)<sub>2</sub>Cl(C=CHC<sub>6</sub>H<sub>4</sub>-R)]PF<sub>6</sub>, were studied in this context,<sup>16</sup> and variations up to 5-fold in  $\beta$  and  $\beta_0$  were observed for alkynyl/vinylidene complex pairs.

In this context, we planned the development of new tetrazolate complexes of general formula  $[(\eta^{5}-C_{5}H_{5})M(dppe)-(4-N_{4}C-C_{6}H_{4}-NO_{2})]$  (M = Fe, Ru; dppe = 1,2-bis-(diphenylphosphino)ethane), conjugating the strong  $[(\eta^{5}-C_{5}H_{5})M(dppe)]^{+}$  donor and  $-NO_{2}$  acceptor moieties, and of the respective tetrazole complexes as hexafluorophosphate salts. Here we describe their synthesis, spectroscopic (<sup>1</sup>H-, <sup>13</sup>C-, <sup>31</sup>P NMR), electrochemical and structural characterization of compounds  $[(\eta^{5}-C_{5}H_{5})Fe(dppe)(4-N_{4}C-C_{6}H_{4}-NO_{2})]$  and

 $[(\eta^5-C_5H_5)Ru(dppe)(4-N_4(H)C-C_6H_4-NO_2)][PF_6]$  by single-crystal X-ray diffraction. TD-DFT calculations were performed to evaluate the SONLO response of the tetrazole/ tetrazolate complexes, and the theoretical results are discussed together with experimental data in view of their SONLO potential as molecular switches.

# RESULTS AND DISCUSSION

Synthetic Studies. Scheme 1 presents the synthetic route for the target organometallic compounds. The ligand 5-(4-

Scheme 1. Synthesis of the Tetrazole Ligand T-H and the Organometallic Complexes  $RuT^+$ ,  $FeT^0$ , and  $RuT^{0ct}$ 



<sup>*a*</sup>(a) HONH<sub>2</sub>·HCl, pyridine, r.t.; Ac<sub>2</sub>O. NaN<sub>3</sub>, NH<sub>4</sub>Cl, DMF, 90 °C. (b) TIPF<sub>6</sub> (or NH<sub>4</sub>PF<sub>6</sub>), CH<sub>2</sub>Cl<sub>2</sub>, r.t. (c) TIOEt, THF, r.t.

nitrophenyl)-1*H*-tetrazole (**T-H**, Scheme 1a) was obtained in good yield from 4-nitrobenzaldehyde by generation of the oxime with hydroxylamine hydrochloride, in situ dehydration with acetic anhydride, and final (3 + 2) azide cycloaddition of the resulting nitrile.<sup>10c</sup>

With **T-H** in hand, we planned the synthesis of both tetrazolate neutral complexes  $FeT^0/RuT^0$  and tetrazole  $PF_6^-$  salts  $FeT^+/RuT^+$  (Scheme 1b,c). Neutral tetrazolate complexes  $FeT^0/RuT^0$  were synthesized by in situ generation of thallium(I) tetrazolate with thallium(I) ethoxide and subsequent reaction with the parent neutral complexes [CpM-(dppe)X] (Cp  $\equiv (\eta^5 \cdot C_5 H_5)$ ; M = Fe, X = I; M = Ru, X = Cl), and isolated in good yields of 78 and 89%, respectively (Scheme 1c).

The synthesis of complexes  $FeT^+/RuT^+$  was first attempted by halide abstraction of the parent neutral complexes [CpM(dppe)X] (M = Fe, X = I; M = Ru, X = Cl) with thallium(I) hexafluorophosphate in the presence of a slight excess of T-H (Scheme 1b). While RuT<sup>+</sup> was obtained in good yield following this synthetic methodology, we were not able to isolate its iron analogue FeT<sup>+</sup>. Aware of a possible thallium(I)induced oxidation of the electron-rich iron(II) center, we attempted the synthesis of FeT<sup>+</sup> using ammonium hexafluorophosphate, but unsuccessfully, while RuT<sup>+</sup> was readily obtained in these conditions; although with a lower yield (79% vs 87%), this methodology avoids the manipulation of dangerous thallium salts.

Interestingly, both iron<sup>15</sup> and ruthenium<sup>17</sup> monocyclopentadienyl complexes are efficient catalysts for the (3 + 2)cycloaddition of azide to electro-deficient nitriles in mild conditions, affording the corresponding organometallic tetrazolates. On the basis of these procedures, the tetrazolate complexes **FeT**<sup>0</sup> and **RuT**<sup>0</sup> were also obtained by a one-pot reaction of the corresponding parent neutral complexes with thallium hexafluorophosphate, sodium azide, and 4-nitrobenzonitrile, in dichloromethane at room temperature (Scheme 2), with yields of 83 and 85%, respectively.



New compounds **T-H**, **FeT**<sup>0</sup>, **RuT**<sup>0</sup>, and **RuT**<sup>+</sup> were fully characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectroscopies, and their formulations and purity were confirmed by elemental analysis. Even though it was acquired in dry DMSO- $d_6$ , the <sup>1</sup>H NMR spectrum of **T-H** revealed only two doublets at 8.30 and 8.44 ppm ( $J_{\rm HH} = 8.8$  Hz), attributed to phenyl protons (Scheme 3), and no signal of the tetrazole proton was observed, due to rapid exchange between 1*H* and 2*H* tautomers which exist as a near 1:1 ratio; <sup>12</sup> addition of D<sub>2</sub>O led to the disclosure of a low-field shifted water residual signal, consistent with media acidity.

Compounds  $\mathbf{FeT}^0$  and  $\mathbf{RuT}^0$  revealed similar NMR spectra, as expected given their structural analogy, with <sup>1</sup>H and <sup>13</sup>C cyclopentadienyl chemical shifts and dppe <sup>31</sup>P resonances similar to the ones found for analogous [CpM(dppe)(4-C $\equiv$ C-C<sub>6</sub>H<sub>4</sub>-NO<sub>2</sub>)] neutral compounds.<sup>6f,g</sup>

Tetrazolate Ct <sup>13</sup>C NMR chemical shifts (Scheme 3) of 161.8 and 160.9 ppm for FeT<sup>0</sup> and RuT<sup>0</sup>, respectively, confirm the expected M-N2 coordination of the tetrazolate ring.<sup>18</sup> In FeT<sup>0</sup>,  $C_t$  is shielded by 2-3 ppm when compared to compounds  $[CpFe(CO)(L)(N_4C-C_6H_4-CN)] (L = CO, PPh_3, P (OCH_3)_3, \delta(CS) = 164.2 - 165.1 \text{ ppm})^{15}$  despite the superior electron-withdrawing ability of the  $-NO_2$  group over  $-C \equiv N$ , evidencing the donor ability of the [CpFe(dppe)]<sup>+</sup> organometallic moiety. Also, comparison of the <sup>1</sup>H NMR spectra of T-H with  $FeT^0$  and  $RuT^0$  shows that the phenyl protons are significantly shielded upon coordination, with  $\Delta(H_{2.6}Ph)$ downfield shifts of ~0.8 and 0.9 ppm (superimposed) and  $\Delta(H_{3.5}Ph)$  shifts of 0.37 and 0.41 ppm, respectively for RuT<sup>0</sup> and FeT<sup>0</sup>. These results agree with increased electronic density on the phenyl ring upon coordination, due to  $\pi$ -backdonation from the electron-rich metal centers extended throughout the hyperconjugated chromophore.

<sup>1</sup>H NMR spectrum of  $\mathbf{RuT}^+$  in DMSO- $d_6$  revealed differences when compared with the  $\mathbf{RuT}^0$  spectrum, namely, a broad resonance at  $\delta = 5.93$  ppm attributed to the tetrazole proton 1*H* coupled with residual water. Addition of D<sub>2</sub>O led to the upfield shift of the water coupled 1*H* signal, while the remaining signals are coincident with the  $\mathbf{RuT}^0$  spectrum, as confirmed by <sup>1</sup>H NMR after addition of the neutral analogue (Figure S1). In dry CD<sub>2</sub>Cl<sub>2</sub>, the <sup>1</sup>H NMR spectra of  $\mathbf{RuT}^+$  and  $\mathbf{RuT}^0$  presented significant differences, namely, a  $\delta(\mathbf{H}_{3.5}\text{Ph})$  low-field shift of 0.13 ppm ( $RuT^0$  to  $RuT^+$ ), in agreement with the presence of tetrazole and tetrazolate complexes, respectively, and evidencing hyperconjugation loss in  $RuT^+$  upon N4 protonation (Figure S2).

The protic switchability of  $\mathbf{RuT}^+/\mathbf{RuT}^0$  complexes was studied in dry dichloromethane, one of the solvents commonly used in hyper-Rayleigh scattering experiments (HRS).  $\mathbf{RuT}^0$ was first quantitatively obtained from  $\mathbf{RuT}^+$ , by reaction with an equivalent amount of triethylamine (Et<sub>3</sub>N) and silica filtration (Scheme 4). Reversibly, when  $\mathbf{RuT}^0$  was reacted with an equivalent amount of trifluoromethanesulfonic acid (triflic acid, F<sub>3</sub>CSO<sub>3</sub>H),  $\mathbf{RuT}^+$  was readily obtained in 89% yield, as the corresponding triflate salt (Figure S3).

We studied also the RuT<sup>+</sup>/RuT<sup>0</sup> conversion in "wet" conditions (Scheme 4). First, a dichloromethane solution of RuT<sup>+</sup> was vigorously stirred with an equivalent volume of water, in the presence of a catalytic amount of tetrabutylammonium bromide as phase transfer catalyst. After 15 min, RuT<sup>0</sup> was recovered from the crude product by extraction with dry ethyl ether (Et<sub>2</sub>O) with 20% yield, and unreacted  $RuT^+$ (insoluble in Et<sub>2</sub>O) was recovered by extraction of the crude product with dry dichloromethane with 75% yield, demonstrating some stability of RuT<sup>+</sup> in "wet" dichloromethane. When the experiment was repeated in basic conditions, using an equivalent volume of NaOH 35% solution and in the presence of the same phase transfer catalyst, RuT<sup>0</sup> was efficiently obtained with 78% yield (Scheme 4). The reverse conversion of  $RuT^{0}$  in  $RuT^{+}$  in acid phase transfer conditions was unsuccessful using 50% fluoroboric acid solution (HBF<sub>4</sub>), with RuT<sup>0</sup> being quantitatively recovered even after reaction times up to 2 h; nonetheless, when RuT<sup>+</sup> was stirred with 50%  ${\rm HBF}_4$  solution for 15 min, no formation of  $RuT^0$  was noticed, which indicates that tetrazole deprotonation of RuT<sup>+</sup> is inhibited in these acidic conditions (Scheme 4). Since no signs of decomposition were found during the referred experiments, these demonstrate also the stability of the Ru-N bonds toward hydrolysis.

Given the unsuccessful synthesis of FeT<sup>+</sup> (described above), we studied the evolution of the <sup>1</sup>H and <sup>31</sup>P NMR spectra of  $FeT^0$  in DMSO- $d_6$  over time in the presence and absence of trifluoroacetic acid, TFA (Figure S4). After 1 h of incubation with TFA (Figure S4-B), free T-H was already perceptible by <sup>1</sup>H NMR, indicating that protonation leads to decoordination of the tetrazole ligand, evidencing FeT<sup>+</sup> instability. After 24 h, the T-H/FeT<sup>0</sup> proportion is  $\sim 5/4$  (Figure S4-C), and the formation of free cyclopentadiene (C<sub>5</sub>H<sub>6</sub>,  $\delta_{\rm H}$  = 1.97, 6.40, and 6.49 ppm) and of free dppe ( $\delta_{\rm H}$  = 7.23–7.26 ppm;  $\delta_{\rm P}$  = -14.0 ppm) are noticed (Figure S4-C). After 3 days of acidic incubation, FeT<sup>0</sup> was completely decomposed, and only T-H, cyclopentadiene and free dppe could be identified by <sup>1</sup>H and <sup>31</sup>P NMR in the now colorless solution (Figure S4-D). In the absence of TFA, FeT<sup>0</sup> was stable over the same period, with no signs of decomposition. Overall, these experiments suggest that the formation of  $FeT^+$  leads to T-H decoordination and

Scheme 3. Numbering Scheme for the Ligand T-H (left), RuT<sup>+</sup> (Middle), and MT<sup>0</sup> Complexes (Right)



Scheme 4. Evaluation of the RuT<sup>+</sup>/RuT<sup>0</sup> Protic Switch in Dichloromethane in Dry (Top) and Wet Conditions (Bottom)<sup>a</sup>



<sup>*a*</sup>In wet conditions, tetrabutylammonium bromide was used as phase transfer catalyst.



Figure 1. Molecular diagrams of compounds  $FeT^0$  (left) and  $RuT^+$  (right), with numbering scheme (C1 = C<sub>t</sub>); thermal ellipsoids are drawn at a 50% probability. Hydrogen atoms have been omitted for clarity, except for H4 in  $RuT^+$ .

bond lengths (Å)	FeT <sup>0</sup>	RuT <sup>+</sup>	bond angles (deg)	FeT <sup>0</sup>	RuT <sup>+</sup>
M-Cp <sup>a</sup>	1.7070(6)	1.865 (15)	N2-M-Cp <sup>a</sup>	123.95(11)	123.1 (3)
M-P1	2.205(1)	2.301(1)	P1-M-Cp <sup>a</sup>	127.21(4)	131.2(4)
M-P2	2.203(1)	2.297(1)	$P2-M-Cp^{a}$	126.26(4)	127.4 (4)
M-N2	1.964(3)	2.081(4)	P1-M-P2	87.07(5)	82.85(5)
N1-N2	1.340(4)	1.345(7)	P1-M-N2	90.4(1)	89.4(1)
N2-N3	1.334(5)	1.305(7)	P2-M-N2	90.2(1)	89.3(1)
N3-N4	1.338(5)	1.346(7)	N1-N2-N3	111.0(3)	112.1(4)
N4-C1 <sup>b</sup>	1.342(5)	1.335(8)	N2-N3-N4	107.8(3)	104.4(4)
C1 <sup>b</sup> -N1	1.344(5)	1.326(6)	N3-N4-C1 <sup>b</sup>	105.8(3)	110.1(5)
			$N4-C1^{b}-N1$	111.7(3)	107.6(5)
			$C1^{b}$ -N1-N2	103.7(3)	105.8(4)
			M-N2-N1	122.4(2)	125.3(3)
			M-N2-N3	126.4(3)	122.4(3)

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Compounds  $\mbox{FeT}^0$  and  $\mbox{RuT}^+$ 

<sup>*a*</sup>Centroid. <sup>*b*</sup>C1 =  $C_t$ .

subsequent decomposition of the [CpFe(dppe)]<sup>+</sup> organometallic moiety, despite successfully modeling by density functional theory (DFT) computational methods (see below).

**Structural Studies.** Compounds  $FeT^0$  and  $RuT^+$  were further characterized by single crystal X-ray diffraction studies. Suitable crystals of  $RuT^+$  were obtained by slow diffusion of Et<sub>2</sub>O in a DCM solution of the compound, and of *n*-hexane in DCM for  $FeT^0$ . Compound  $FeT^0$  crystallizes in the orthorhombic crystal system, *Pbcn* space group (centrosymmetric), while compound  $RuT^+$  crystallizes in the monoclinic crystal system, space group *Cc* (non-centrosymmetric). Molecular diagrams of  $FeT^0$  and  $RuT^+$  are presented in Figure 1, and selected bond lengths and angles of  $FeT^0$  and  $RuT^+$  are presented in Table 1.

Compounds  $FeT^0$  and  $RuT^{\scriptscriptstyle +}$  present the usual "three-legged piano stool" ligand distribution around the metal centers with bond distances and angles within the range found for [CpM(dppe)(L)] analogues (M = Fe, Ru).<sup>10,11,15,19-23</sup> The Ru-N length is shorter than the respective lengths in similar  $[CpRu(dppe)(1-BuIm)]^+$  analogues (1-BuIm = 1-butyl-imidazole, 2.131(2) to 2.141(3)).<sup>19</sup> Also, the Fe-N bond is shorter in FeT<sup>0</sup> than in an analogue tetrazolate compound (2.007(7)).<sup>15</sup> The different electronic environment within the tetrazolate/tetrazole rings in compounds FeT<sup>0</sup>/RuT<sup>+</sup> is reflected in the respective conformations of the heterorings. The main differences are found in the N3-N4-C1 angle, larger in RuT<sup>+</sup> by  $\sim$ 5°, and in the N4–C1–N1, which is  $\sim$ 5° smaller. Overall, the structural features fully align with examples of tetrazolate/tetrazole ruthenium(II) and iron(II) analogue complexes found in the literature.<sup>15,20–23</sup> Significantly,  $RuT^+$  is one of the few examples of an X-ray structure of a Ru-tetrazole complex, following the structures of  $[Ru(tpy) (bpy)L]^+$  (tpy = 2,2':6',2''-terpyridine, bpy = 2,2'-bipyridyl, L = 2-(1H-tetrazol-5-yl)thiophene)<sup>21</sup> and  $[Ru(tpy) (bpy)(L)]^+$  (L = 4-(1Htetrazol-5-yl)benzonitrile).<sup>23</sup>

Contrary to what would be expected, based on spectroscopic evidence for interannular conjugation (vide supra) and the DFT-optimized structures of the complexes (see below), in complex RuT<sup>+</sup> a quasi-planarity is verified between the phenyl and the tetrazole rings, with a torsion angle  $\tau$  of 4.5°, while in FeT<sup>0</sup> these rings present a significant deviation from planarity  $(\tau = 31.9^{\circ})$ . This apparent disagreement was easily rationalized for both compounds by close inspection of the supramolecular interactions in solid state packing. The large deviation from planarity in compound FeT<sup>0</sup> (see Figure S5) can be attributed to a series of very weak intermolecular interactions of the type C-H…O between nitro group oxygens and Ph hydrogens of neighbor molecules, both from dppe (C212-H212···O2 {2.611 Å}, C213–H213…O2 {2.597 Å}, C213–H213…O1 {2.514 Å}) and the tetrazolate ligand (C4-H4...O2 {2.628 Å}). In compound RuT<sup>+</sup>, the planar interannular conformation adopted by the tetrazole ligand in this compound (see Figure S6) is mostly explained by the stronger C-H…O intermolecular interactions established between nitro group oxygens and Cp and dppe ligands of consecutive cationic complexes  $(C24-H24...O2 \{2.414 \text{ Å}\}, C113-H113...O1 \{2.571 \text{ Å}\}),$ with some "reinforcement" from short contacts of the type N-H…F and C-H…F between tetrazole ligand hydrogens and fluorine atoms of neighbor anions (N4-H4--F3 {1.878 Å}, N4–H4…F1 {2.640 Å}, C3–H3…F1 {2.532 Å}, C7–H7…F2 {2.496 Å}).

As referred above, compound  $\mathbf{RuT}^+$  crystallizes in the monoclinic crystal system, in a non-centrosymmetric space group (*Cc*), which can be a key feature for SHG response in the solid state.<sup>1</sup> Analysis of the crystal packing of  $\mathbf{RuT}^+$  shows that despite the dipole cancel along the *b* axis, the monocationic complex molecules are aligned along the (a, -c) direction (Figure S7).

Even more important than the perfect alignment of the molecular dipoles is the angle between the molecular charge transfer axis, normally along the donor–acceptor axis, and the polar crystal axis.<sup>1a</sup> The optimum value of this angle depends on the crystallographic system, in order to allow quadratic phase-matched interactions.<sup>6d</sup> This angle in complex **RuT**<sup>+</sup> is 86.8°, which deviates significantly from the optimum value of 54.74° for the monoclinic system.<sup>1a</sup> Therefore, and contrary to **FeT**<sup>0</sup> in which the centrosymmetric crystallization leads to the

macroscopic cancel of the SONLO response of the individual molecules, compound  $RuT^+$  is expected to have a nonzero SHG response in the solid state.<sup>60</sup>

UV-vis Spectroscopic Studies. The optical absorption spectra of complexes  $FeT^0$ ,  $RuT^0$ ,  $RuT^+$ , and ligand T-H, recorded in  $10^{-3}$  to  $10^{-5}$  mol dm<sup>-3</sup> dimethylformamide (DMF) solutions, are presented in Figure 2. Additionally, for the



Figure 2. UV–vis spectra of compounds FeT<sup>0</sup>, RuT<sup>0</sup>, RuT<sup>+</sup>, and T-H, recorded in DMF.

organometallic complexes, spectra were acquired in solvents with different polarities, i.e., toluene ( $RuT^+$  is insoluble), dichloromethane (DCM), tetrahydrofuran (THF), and dimethyl sulfoxide (DMSO) to unveil the solvatochromic behavior of the UV–vis absorption bands. These results are summarized in Table 2.

Table 2. UV-Vis Spectral Data of FeT<sup>0</sup>, RuT<sup>0</sup>, RuT<sup>+</sup>, and T-H

solvent	toluene	DCM	THF	DMF	DMSO
compound	v	vavelength (n	m) { $\varepsilon \times 10^{-3}$	$^{3}$ (M <sup>-1</sup> cm <sup>-1</sup> )	}
T-H				349 {15.0}	
FeT <sup>0</sup>	458 {2.9}	479 {3.5}	477 {3.3}	495 {2.3}	502 {3.2}
	309 {11.6}	313 {15.6}	314 {14.8}	315 {11.4}	314 {14.8}
RuT <sup>0</sup>	392 {6.3}	396 {7.0}	401 {7.0}	404 {4.7}	409 {5.0}
	300 {11.6}	305 {11.7}	304 {14.7}	306 {12.4}	306 {13.8}
RuT <sup>+</sup>	а	380 <sup>b</sup>	397 {6.6}	408 {5.1}	412 {5.0}
		305 <sup>b</sup>	302 {16.6}	302 {15.0}	305 {15.0}
<sup><i>a</i></sup> Insoluble.	<sup>b</sup> Shoulder.				

The UV-vis spectrum of T-H in DMF presents only an intense  $\pi - \pi^*$  absorption band at 349 nm. Spectra of the organometallic compounds  $FeT^0$ ,  $RuT^0$ , and  $RuT^+$  also present an intense band in the UV region (302-315 nm) attributed to the same  $\pi - \pi^*$  ligand absorption, which suffers a significant blue-shift upon coordination (Figure 2, Table 2). The complexes show also a less intense absorption band in the visible region, at 495 nm for FeT<sup>0</sup>, 404 and 408 nm for RuT<sup>0</sup> and RuT<sup>+</sup>, respectively, which are red-shifted with increasing solvent polarity, up to 44 nm for  $FeT^0$  and 17 nm for  $RuT^0$ (toluene-DMSO, Table 2), consistent with metal-to-ligand charge transfer (MLCT) bands. This assignment is supported also by their low energy, low intensity, their absence in the spectra of the T-H ligand and parent complexes, and by timedependent DFT calculations, TD-DFT (see below). These band red-shifts are characteristic of electronic transitions with an increase of the dipole moment upon photoexcitation. The

lower energy of the  $FeT^0$  MLCT band can be rationalized based on the lower oxidation potential of the iron center in relation to ruthenium (see below). The lower intensity of the  $FeT^0$  MLCT spectral band might be explained by its decreased proximity of the  $\pi - \pi^*$  band when compared to the ruthenium counterparts, and its larger-base Gaussian shape; this shape may also indicate that more than one electronic transition contributes to the MLCT band (see Computational Studies below).

Compounds  $RuT^0$  and  $RuT^+$  present quite similar UV-vis spectra in THF, DMF, and DMSO, but not in DCM, as depicted in Figure 3 for DMSO and DCM, and in Figure 2 for



Figure 3. UV–vis spectra of compounds  $RuT^0$  and  $RuT^+$  recorded in DCM and DMSO.

DMF. In DCM, complex  $\mathbf{RuT}^+$  displays both  $\pi - \pi^*$  and MLCT bands as shoulders, while  $\mathbf{RuT}^0$  displays Gaussian-shaped

bands. These data indicate that the photoactive species originated by **RuT**<sup>+</sup> is different in DMSO and DCM solutions. In DCM, the protonated tetrazole form is stable even in the presence of water, as demonstrated by solution studies (vide supra), and hence the different optical behavior in this solvent in relation to the tetrazolate RuT<sup>0</sup>. Comparison of the spectra in this solvent shows also that tetrazole-tetrazolate deprotonation leads to a significant intensity increase and a bathochromic shift of the MLCT band, with both band features anticipating improved second order NLO properties for RuT<sup>0</sup> over the protonated analogue, as initially expected. In DMSO, the deprotonated tetrazolate form  $(RuT^{0})$  is easily formed from RuT<sup>+</sup> in the presence of water, as evidenced by <sup>1</sup>H NMR experiments in DMSO- $d_6$ . Given that, despite preparation from dry solvents, UV-vis spectra were acquired in atmospheric conditions and in (new) nonflamed glassware; we are here led to conclude that RuT<sup>+</sup> is switched to RuT<sup>0</sup> due to water absorbed by the hydrophilic solvents during the experiments.

According to the two-level model (TLM),<sup>24</sup> the secondorder nonlinearity can be described as

$$\beta \propto \frac{\Delta \mu_{\rm eg} f_{\rm eg}}{E_{\rm eg}^3} \tag{1}$$

where  $\Delta \mu_{\rm eg}$  is the difference between the dipole moments of the ground (g) and the excited state (e),  $f_{\rm eg}$  is the oscillator strength and  $E_{\rm eg}$  is the transition energy. This model assumes that only one excited state is coupled strongly enough to the ground state by the applied electric field for the contribution to  $\beta$  and that only one tensor component dominates the NLO response (i.e., a unidirectional charge-transfer transition) and has been used to compute  $\beta_0$  values for analogue acetylide

Table 3. Summary of Electrochemical Data for T-H and Complexes FeT <sup>0</sup> , Ru	T <sup>0</sup> , and RuT <sup>+</sup>
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			-			
compound	$E_{\rm pa}$ (V)	$E_{\rm pc}$ (V)	$E_{1/2}$ (V)	$E_{\rm pa}-E_{\rm pc}~({\rm mV})$	$I_{\rm c}/I_{\rm a}$	HOMO-LUMO (V) <sup>a</sup>
			Acetonitr	ile <sup>c</sup>		
T-H		-0.70				
		-0.89				
	-1.12	-1.21	-1.17	90	1 <sup>b</sup>	
FeT <sup>0</sup>	0.30	0.22	0.26	80	1	1.47
		-0.88				
	-1.07	-1.17	-1.12	100	1 <sup>b</sup>	
RuT <sup>0</sup>	0.70	0.62	0.66	80	1	1.89
		-0.98				
	-1.07	-1.19	-1.13	120	1 <sup>b</sup>	
RuT <sup>+</sup>	1.21	1.10				
	1.03					
	0.75					
		0.73				
	-1.03	-1.13	-1.18	100	1 <sup>b</sup>	
			Dichloromet	hane <sup>d</sup>		
FeT <sup>0</sup>	0.37	0.27	0.32	100	1	1.60
		-0.92				
	-1.03	-1.23		200		
RuT <sup>0</sup>	0.77	0.69	0.73	80	1	2.07
	-0.98	-1.30				
RuT <sup>+</sup>	1.18	1.03		150	0.6	
		0.70				
		-0.80				
	-0.99	-1.26				

 ${}^{a}E_{\rm pa}({\rm M}^{2+}/{\rm M}^{3+}) - E_{\rm pc}({\rm NO}_{2}/{\rm NO}_{2}^{-}). {}^{b}I_{\rm a}/I_{\rm c}. {}^{c}E_{1/2} ({\rm Fc/Fc^{+}}) = 0.40 \text{ V}, \Delta E = 80-100 \text{ mV}. {}^{d}E_{1/2} ({\rm Fc/Fc^{+}}) = 0.46 \text{ V}, \Delta E = 100-110 \text{ mV}.$ 



Figure 4. Cyclic voltammograms of  $FeT^0$  and  $RuT^0$  in dichlorometane (left), and of  $RuT^0$ ,  $FeT^0$  (only Fe(II)/Fe(III) process) and T-H in acetonitrile (right) ( $\nu = 200 \text{ mV} \cdot \text{s}^{-1}$ ). A full voltammogram of  $FeT^0$  in acetonitrile is presented in Figure S8.

compounds.<sup>6f,g,n</sup> Although computational results showed that more than one excited state contributed to the MLCT bands of  $MT^0$  and  $RuT^+$  complexes (see below), it allows a first intuitive prediction of the first hyperpolarizabilities of these complexes in relation to acetylide analogues. On the basis of this simple model, one can anticipate (i) lower first hyperpolarizabilities for  $MT^0$  in relation to the corresponding acetylide analogues, due to the lower intensity of the MLCT bands of  $MT^0$  complexes and (ii) lower first hyperpolarizability for  $RuT^+$  in relation to  $RuT^0$ , due to lower intensity of the MLCT band of  $RuT^+$ . Despite its simplicity and limitations,<sup>25</sup> these trends fully align with our first hyperpolarizabilities results, obtained by DFT calculations (see below).

**Electrochemical Studies.** The redox behavior of the organometallic complexes  $FeT^0$ ,  $RuT^0$ , and  $RuT^+$  was investigated in DCM and acetonitrile (ACN) at room temperature by cyclic voltammetry (CV), using a Pt wire as working electrode and a Ag wire as pseudoreference electrode; T-H was only characterized in ACN due to its insolubility in DCM. All potentials are collected in Table 3.

The electrochemical behavior of **T-H** is characterized by two irreversible processes, at  $E_{pc} = -0.70$  V and  $E_{pc} = -0.89$  V (low intensity), showing no anodic counterparts even when potential was reversed at -1.00 V. It displays also a quasi-reversible process at  $E_{1/2} = -1.17$  V attributed to the NO<sub>2</sub>/NO<sub>2</sub><sup>-</sup> redox process.

The electrochemical behavior of  $\mathbf{FeT}^0$  in DCM is characterized by a reversible redox process at  $E_{1/2} = 0.32$  V, attributed to the Fe(II)/Fe(III) redox pair. At negative potentials, it displays a cathodic process at  $E_{pc} = -0.92$  V (very low intensity) and an irreversible process at  $E_{pc} = -1.23$ V ( $E_{pa} = -1.03$  V), attributed to the NO<sub>2</sub>/NO<sub>2</sub><sup>-</sup> redox process. In ACN, FeT<sup>0</sup> presented the same general electrochemical behavior, with a reversible redox process at  $E_{1/2} = 0.26$  V, attributed to the Fe(II)/Fe(III) redox pair, a small cathodic process at  $E_{pc} = -0.88$  V, and a quasi-reversible process at  $E_{1/2}$ = -1.12 V attributed to the NO<sub>2</sub>/NO<sub>2</sub><sup>-</sup> pair. Compound RuT<sup>0</sup> evidenced the same general electrochemical behavior as FeT<sup>0</sup> in DCM and ACN, except for the higher potentials verified for Ru(II)/Ru(III) redox processes (Figure 4).

Comparison of the electrochemical behavior of T-H,  $FeT^0$ , and  $RuT^0$  in ACN (Table 3, Figure 4) shows that the first T-H

reductive process ( $E_{\rm pc} = -0.70$  V), probably a tetrazole related reduction, is absent upon coordination to [CpM(dppe)]<sup>+</sup> metal centers, while the second ( $E_{\rm pc} = -0.89$  V, low intensity) displays reduced intensities and is slightly shifted toward lower potentials, and although mostly unchanged in potential, the NO<sub>2</sub>/NO<sub>2</sub><sup>-</sup> redox processes display a more irreversible character in complexes **MT**<sup>0</sup> (M = Fe and Ru) than in **T-H**. These differences agree with NMR evidence for d(metal)- $\pi$ (chromophore) hyperconjugation and the increased chromophore electronic density upon coordination.

The electrochemical behavior of  $\mathbf{MT}^{0}$  compounds is quite similar to the one revealed by  $[CpM(dppe)(4-C\equiv C-C_{6}H_{4}-NO_{2})]$  analogues, which unveiled slightly lower M(II)/M(III)redox potentials in DCM ( $E_{1/2}$  of 0.29 and 0.67 V for M = Fe and Ru, respectively).<sup>6g</sup> Nonetheless, while  $[CpFe(dppe)(4-C\equiv C-C_{6}H_{4}-NO_{2})]$  unveiled an irreversible redox process ( $I_{c}/I_{a} = 0.6$ ), compound **FeT**<sup>0</sup> displays reversible Fe(II)/Fe(III) redox waves, with  $I_{c}/I_{a}$  ratios of 1 (Figure 4) in both solvents tested.

As demonstrated below in Computational Studies, for complexes MT<sup>0</sup>, the highest occupied molecular orbital (HOMO) is essentially located in the metal fragment, with some contribution of the Cp ligand and tetrazolate ring, while the lowest unoccupied molecular orbital (LUMO) is mostly a Ph-NO<sub>2</sub> orbital. It is thus fair to assume that the M(II)/M(III)oxidation and the  $\mathrm{NO_2/NO_2^-}$  reduction potential can be related, respectively, to the relative magnitude of HOMO and LUMO energies. Therefore, we calculated the HOMO-LUMO gaps for compounds MT<sup>0</sup>, expressed as the potential differences between M(II)/M(III) and  $NO_2/NO_2^-$  redox processes.<sup>6j,n</sup> The results (Table 3) show that the HOMO-LUMO gaps depend significantly on the metal fragment, with smaller gaps for FeT<sup>0</sup> than for RuT<sup>0</sup>. This effect is mainly due to the relative stabilization of the HOMO orbital in RuT<sup>0</sup>, since LUMO orbitals are mostly unaffected by the change of metal fragment and solvent, and agrees with the better donor character of the iron(II) fragment. For both compounds, the calculated HOMO-LUMO gaps are higher in DCM than in ACN, in agreement with the bathochromic shifts of the MLCT bands with increasing solvent polarity in the UV-vis spectra.

Compound  $RuT^+$  exhibited a quite interesting electrochemical behavior. At negative potentials in DCM, it presents two ligand-based reductive processes being the one at -1.26 V attributed to the  $NO_2/NO_2^-$  pair. At positive potentials, a ruthenium centered process (oxidation) at 1.18 V with a  $I_c/I_a$ ratio of 0.6 suggests some instability of the oxidized ruthenium species at the electrode surface. Scan rate studies showed that it became more reversible when the scan direction is immediately reverted after the oxidation potential. This behavior can be associated with a Ru<sup>II</sup>/Ru<sup>III</sup> oxidation, followed by fast decomposition. The higher potential for the Ru<sup>II</sup>/Ru<sup>III</sup> oxidation process agrees with the lower electronic density in the cationic ruthenium(II) center in relation to RuT<sup>0</sup>. Nevertheless, when the initial scan is directed toward the negative potentials range and reaches the NO2/NO2- redox process, a new oxidation wave at  $E_{pa} = 0.78$  V emerges and is probably related to the cathodic wave at 0.70 V, already present in the first scan (Figure S9). Moreover, the comparison between this new redox process with the one obtained for the  $RuT^0$  complex seems to indicate that the loss of the tetrazole proton is possible during the electrochemical time scale, being dependent on the NO2/NO2 process. In ACN the electrochemical behavior of RuT+ shows higher complexity with the presence of three oxidation processes  $(E_{pa} = 0.75 \text{ V}; 1.03 \text{ and})$ 1.21 V), the last one being attributed to the Ru(II)/Ru(III) pair and two cathodic processes ( $E_{pc} = 1.10$  and 0.73 V). In accordance with the behavior found in DCM, when the initial scanning direction to negative potentials was reversed after the NO<sub>2</sub> reduction, an increase in the anodic process at  $E_{pa} = 0.75$ V was observed.

**Computational Studies.** Given the experimental confirmation of the interesting electronic properties preconized for complexes FeT<sup>0</sup>, RuT<sup>0</sup>, and RuT<sup>+</sup> and the pH switchability of the RuT<sup>0</sup>/RuT<sup>+</sup>, DFT calculations<sup>26</sup> were employed to provide further insights into the experimental data and to calculate the theoretical SONLO response ( $\beta_{tot}$ ) of these organometallic complexes. Indeed, DFT calculations have been successfully employed in the study of these properties of analogue acetylide and nitrile organometallic complexes.<sup>9,27,28</sup>

Using the experimental X-ray data as a starting point, the geometries of complexes FeT<sup>0</sup>, RuT<sup>0</sup>, and RuT<sup>+</sup> were optimized at the DFT level of theory using the popular PBE1PBE functional, also known as PBE0,<sup>29</sup> and the hybrid exchange-correlation functional using the Coulomb-attenuating method (CAM-B3LYP)<sup>30</sup> which predicts more reliable, optical and hyperpolarizability data when compared with experimental results.<sup>9</sup> Since the UV-vis and NMR data showed the stability of RuT<sup>+</sup> in dichloromethane, all calculations used a polarizable continuum model to account this solvent (see Methods for further details). Although compound FeT<sup>+</sup> is experimentally unstable, it was successfully optimized, and structural details are summarized in Table S1, which presents a selection of distances and angles for the DFT-optimized structures compared with X-ray diffraction data, when available. Both functionals give excellent results in the prediction of the coordination sphere of the iron and ruthenium complexes. Nonetheless, CAM-B3LYP systematically yields longer M-L bond lengths when compared with PBE0 and the X-ray structures. This effect of stretched bond lengths for single bonds was previously observed for similar systems in gas-phase calculations.<sup>9</sup> The calculated bond angles fall in the experimental range, whereas the remaining calculated bond lengths for the tetrazole/tetrazolate are equivalent for both functionals. All the optimized structures of MT<sup>0</sup> complexes present a torsion angle au near 0°, whereas RuT<sup>+</sup> presents a auangle >24 $^{\circ}$ , contrasting with the X-ray structures of FeT<sup>0</sup> and  $RuT^+$  (vide supra). The presence of the N–H proton appears to induce the distortion to avoid an interaction with the ortho hydrogen of the phenyl ring. Torsion angles different from zero are common for uncoordinated 5-phenyl-1H-tetrazole derivatives, e.g., free 5-(4-aminophenyl)-1*H*-tetrazole  $(12.6^{\circ})^{31}$  and for coordinated tetrazoles,  $[TiCl_4(5-phenyltetrazole)_2]$  (24.10°,  $53.8^{\circ}$ ).<sup>32</sup> Indeed, for the related  $[Ru(tpy)(bpy)(L)]^+$  (L = 4-(1H-tetrazol-5-yl)benzonitrile) complex, a  $\tau$  torsion angle of  $27.2^{\circ}$  is found in the X-ray structure,<sup>23</sup> whereas for L = 2-(1Htetrazol-5-yl)thiophene, the torsion angle is close to  $0^{\circ}$  (3.9°).<sup>21</sup> As discussed above, packing forces are strong enough to overcome the steric repulsions between the ortho hydrogen and the N-H proton, allowing planarity, whereas our calculations are performed in a solvent continuum media, and a twisted structure is invariably obtained for all MT<sup>+</sup> complexes. A similar question was discussed for 4,4'-bipyridine bridging ligands in ruthenium complexes.33

The highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of complexes  $FeT^0$ ,  $FeT^+$ ,  $RuT^0$ , and  $RuT^+$ , calculated at the PBE0 level of theory, are depicted in Figure 5; the correspondent orbitals calculated using CAM-B3LYP are very similar (Figure S10).



Figure 5. HOMOs (left) and LUMOs (right) of complexes  $FeT^0$ ,  $FeT^+$ ,  $RuT^0$ , and  $RuT^+$ .

The HOMO of complexes  $\mathbf{MT}^0$  have essentially metal character with a considerable participation of the tetrazole moiety, defining a M–N  $\pi^*$  bond. A small contribution of the Cp ligand is also present. Upon protonation, the  $\pi$  system of the tetrazole ligand no longer contributes to the HOMO, essentially being a Cp-M based orbital. On the other hand, the LUMOs of  $\mathbf{MT}^0$  and  $\mathbf{MT}^+$  complexes are essentially located in the acceptor Ph-NO<sub>2</sub> moiety.

Using the optimized structures, we performed TD-DFT calculations for complexes  $FeT^0$ ,  $RuT^0$ , and  $RuT^+$  in dichloromethane, and the relevant calculated excitations are listed in

Table	4. Relevant TD-DFT Excitation Energies ( $\lambda$ ), Oscillator St	rengths (f)	and Compositions,	for Complexes	FeT <sup>0</sup> , RuT <sup>0</sup> ,	, and
$RuT^+$	Calculated at the PBE0 and CAM-B3LYP Level of Theor	y <sup>a</sup>				

	PBE0			CAM-B3LYP			
complex	$\lambda$ (nm)	f	composition	$\lambda$ (nm)	f	composition	$\lambda_{exp}$ (nm)
FeT <sup>0</sup>	441	0.1804	$H \rightarrow L (97\%)$	436	0.1597	$H \rightarrow L (97\%)$	479
	309	0.4421	$H-3 \rightarrow L (91\%)$	307	0.2601	$H-3 \rightarrow L (51\%)$	313
			H-18 $\rightarrow$ L (5%)	307	0.2047	$H \rightarrow L+2$ (41%)	
						$H-3 \rightarrow L (44\%)$	
						$H \rightarrow L+2$ (45%)	
RuT <sup>0</sup>	464	0.1742	$H \rightarrow L (99\%)$	462	0.1541	$H \rightarrow L (99\%)$	396
	310	0.5076	$H-3 \rightarrow L (87\%)$	307	0.428	$H-3 \rightarrow L (80\%)$	305
			$H-4 \rightarrow L (5\%)$			H-4 $\rightarrow$ L (7%)	
RuT <sup>+</sup>	474	0.0219	$H \rightarrow L (99\%)$	471	0.0178	$H \rightarrow L (99\%)$	380
	323	0.154	$H \rightarrow L+1$ (62%)	326	0.1557	$H \rightarrow L+1$ (63%)	305
						$H-2 \rightarrow L+4 (8\%)$	
						$H \rightarrow L+6 (8\%)$	

<sup>*a*</sup>The values are compared with experimental data ( $\lambda_{exp}$ ).



Figure 6. Electron density difference maps (EDDM) in complexes  $FeT^0$ ,  $RuT^0$ , and  $RuT^+$  for excitations presented in Table 4, calculated at the PBE0 (left) and CAM-B3LYP levels of theory (right). Green and brown correspond to a decrease and increase of electron density, respectively.

Table 4. To aid the visualization and the character assignment of the listed excitations, the electron density difference maps (EDDM), which represent the changes in electron density that occur for a given electronic transition, are presented in Figure 6.

For complex FeT<sup>0</sup>, the low-lying absorption observed at 479 nm in dichloromethane is blue-shifted in the TD-DFT spectra with a calculated excitation at 441 nm (PBE0) or 436 nm (CAM-B3LYP). This excitation is assigned to a MLCT since it corresponds to a transition from an iron centered orbital with some tetrazole contribution, to the  $\pi$  system of the Ph-NO<sub>2</sub> moiety, as depicted in Figure 6. The experimental higherenergy absorption observed at 313 nm is calculated at 309 or 307 nm for PBE0 and CAM-B3LYP, respectively. Although there is some metal contribution, this transition corresponds mainly to an intraligand charge transfer (ILCT) as it transfers electron density from the tetrazole ring to the nitrobenzene group. Despite the blue shift observed for the low-energy band, the TD-DFT calculations are in very good agreement with the experimental results. This agreement is clearly observed in Figure 7 were a superposition of the experimental spectra with the calculated excitations is shown.

Complex  $RuT^0$  shows two maxima in the experimental UVvis spectra in dichloromethane at 396 and 305 nm. The calculated TD-DFT results also show the existence of two main excitations, and the agreement between the experimental and calculated spectra is satisfactory (see Figure 7). As for FeT<sup>0</sup>, the calculated low-energy excitation at 464 nm (PBE0) or 462 nm (CAM-B3LYP) is assigned to a MLCT corresponding to an excitation from the metal-tetrazolate group (with some Cp participation) to PhNO<sub>2</sub>; contrary to the iron analogue, this band is significantly red-shifted when compared with the experimental value (396 nm), which is opposite to the trend found experimentally results,  $\lambda(FeT^0) > \lambda(RuT^0)$ . The agreement between calculated and experimental results is much better for the high-energy absorption (experimental, 305 nm) calculated at 310 nm (PBE0) or 307 nm (CAM-B3LYP). As for the iron analogue, this excitation is assigned as ILCT and as for the other complexes, this result is independent of the functional.

For compound  $\mathbf{RuT}^+$ , there is a low-energy excitation with moderate oscillator strength, calculated at 474 nm (PBE0) or 471 nm (CAM-B3LYP) which should account for the observed shoulder at 380 nm and is assigned to a ruthenium-tonitrophenyl MLCT. This MLCT is slightly different since the tetrazole ring is absent from the transition whereas in  $\mathbf{RuT}^0$ , a metal-tetrazole to nitrophenyl charge transfer is observed. At higher energies, a stronger excitation was calculated at 323 nm



Figure 7. TD-DFT excitations (blue, PBE0 and green, CAM-B3LYP) plotted against the UV–visible absorption spectra (red) in dichloromethane for complexes FeT<sup>0</sup>, RuT<sup>0</sup>, and RuT<sup>+</sup>.

(PBE0) or 326 nm (CAM-B3LYP) but contrarily to  $RuT^0$ , this excitation does not correspond to an ILCT, being better described as a MLCT from the metal to the 5-(4-nitrophenyl)-1*H*-tetrazole ligand as seen in the EDDMs depicted in Figure 6, accounting for the shoulder observed at 305 nm.

Our calculations further confirmed that there are relevant MLCT-attributed electronic transitions, especially for complexes  $FeT^0$  and  $RuT^0$ , which are a main contributor for SONLO properties (see below). To predict their SONLO properties, the static first hyperpolarizabilities of the complexes,  $\beta_{tot}$ , were calculated using both functionals and the results are presented in Table 5 (further details in Methods). For

Table 5. Calculated Static First Hyperpolarizabilities  $\beta_{tot}$  for FeT<sup>0</sup>, RuT<sup>0</sup>, RuT<sup>+</sup>, and Acetylide Analogue Compounds

	$\beta_{ m Tot}~(10^{-30}~{ m esu})$		
complex	PBE0	CAM-B3LYP	
FeT <sup>0</sup>	132.35	119.91	
RuT <sup>0</sup>	155.96	143.67	
RuT <sup>+</sup>	53.64	49.49	
$CpFe(dppe)(4-C \equiv C - C_6H_4 - NO_2)$	359.32	345.43	
$CpRu(dppe)(4-C \equiv C - C_6H_4 - NO_2)$	376.20	367.77	

comparison and experimental reference, the putative complexes  $[CpM(dppe)(4-C \equiv C-C_6H_4-NO_2)]$  (M = Fe, Ru) were studied along with the tetrazolate/tetrazole analogues.

The calculated static first hyperpolarizabilities ( $\beta_{tot}$ ) for compounds **FeT<sup>0</sup>** and **RuT<sup>0</sup>** were 132.35 × 10<sup>-30</sup> and 155.96 × 10<sup>-30</sup> esu (PBE0) and 119.91 × 10<sup>-30</sup> and 143.67 × 10<sup>-30</sup> esu (CAM-B3LYP), respectively (Table 5). These values are lower than the ones calculated here for the acetylide analogue complexes, and larger than the ones calculated for the [MCp(H<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PH<sub>2</sub>)L]<sup>+</sup> (L = 5-(3-(thiophen-2-yl)benzo-[c]thiophen-1-yl)-thiophene-2-carbonitrile) systems at the

CAM-B3LYP level of theory with a similar basis set.<sup>9</sup> The estimated  $\beta_{tot}$  values are approximately 1.2-fold larger for **RuT**<sup>0</sup> when compared with **FeT**<sup>0</sup> for both functionals, in agreement with the trend found experimentally<sup>6f,g</sup> and by our calculations for the acetylide analogs.

As noticed before, the  $\beta_{tot}$  values for acetylide complexes are higher than the values calculated for  $MT^0$  complexes, by 2.7fold and 2.9-fold for iron complexes and by 2.4-fold and 2.6fold for ruthenium analogues, respectively, for PBE0 and CAM-B3LYP functionals. The relative magnitudes of the Fe/Ru MLCT oscillator strength, calculated for the acetylide complexes, are also in good agreement with the ones obtained experimentally.<sup>6f,g</sup>

Compound **RuT**<sup>+</sup> revealed  $\beta_{tot}$  values of 53.64 × 10<sup>-30</sup> esu (PBE0) and 49.49 × 10<sup>-30</sup> esu (CAM-B3LYP). For both functionals the values are 2.9-fold lower than the ones calculated for the tetrazolate analogue, due to conjugation loss upon protonation of the tetrazolate ring, reflected by the low oscillator strengths calculated for the MLCT band (f = 0.0219 or 0.0178, for PBE0 or CAM-B3LYP, respectively) when compared with **RuT**<sup>0</sup>, and in agreement with the experimental results. Concerning the switchability of the **RuT**<sup>+/0</sup> complexes, the results confirm the potential of tetrazole/tetrazolate forms for use as pH SONLO switches, with a 2.9-fold increase in  $\beta_{tot}$  upon tetrazole deprotonation.

Compounds [CpM(dppe)(4-C=C-C<sub>6</sub>H<sub>4</sub>-NO<sub>2</sub>)] (M = Fe, Ru) have shown intense low-lying MLCT absorptions at ~500 nm (Fe) and ~450 nm (Ru) and revealed HRS-determined static first hyperpolarizabilities ( $\beta_0$ ) of 64 × 10<sup>-30</sup> esu and 161 × 10<sup>-30</sup> esu, respectively, when determined in THF;<sup>6g</sup> in chloroform, the iron complex had previously revealed a  $\beta_0$  of 92 × 10<sup>-30</sup> esu.<sup>6f</sup> These experimental results provide a basis for an evaluation of our DFT and TD-DFT calculations. Both functionals largely overestimate the experimentally determined  $\beta_0$ , yielding  $\beta_{tot}$  values of 359.32 × 10<sup>-30</sup> and 376.20 × 10<sup>-30</sup> esu (PBE0) and 345.43 × 10<sup>-30</sup> and 367.77 × 10<sup>-30</sup> esu (CAM-B3LYP) for M = Fe and Ru, respectively. The CAM-B3LYP functional produces systematically lower values. Although the trend for a larger response for [CpRu(dppe)(4-C=C-C<sub>6</sub>H<sub>4</sub>-NO<sub>2</sub>)] over the iron analogue is maintained, the experimentally determined values evidence a 2.5-fold  $\beta_0$  value for the ruthenium compound (THF), significantly larger than the calculated *ratio*. Nonetheless, the qualitative trends are generally correct, and therefore, DFT and TD-DFT calculations provide a reliable first evaluation of SONLO structure–activity relationships and a valuable insight into the electro-optical processes accounting for differences in  $\beta_{tot}$  verified for complexes with different metal linkers, [M-N<sub>4</sub>(H)C-R]<sup>+</sup> vs [M-N<sub>4</sub>C-R] vs [M-C=C-R], within the compounds here studied.

## CONCLUSIONS

We here first surveyed the second-order nonlinear optical properties (SONLO) of tetrazolate complexes of general formulas [CpM(dppe)(N<sub>4</sub>CC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>)] (M = Fe, Ru), and the tetrazole/tetrazolate complex pairs  $[CpM(dppe)(N_4(H) CC_6H_4NO_2$ ]<sup>+</sup>/[CpM(dppe)(N<sub>4</sub>CC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>)] as pH-switchable SONLO on/off forms, respectively. Our experimental and theoretical studies perspective the tetrazolate heteroring as a promising metal linker for the development of push-pull organometallic complexes with large first hyperpolarizabilities,  $\beta$ . These studies demonstrate also that the pair [CpRu(dppe)- $(N_4(H)CC_6H_4NO_2)]^+/[CpRu(dppe)(N_4CC_6H_4NO_2)]$  can be reversible and efficiently interconverted in solution by pH variation, predicting an approximate 3-fold increase in  $\beta_{tot}$  upon tetrazole deprotonation. The acidic "switch-off" of compound  $[CpFe(dppe)(N_4CC_6H_4NO_2)]$  was not possible, due to instability of the iron tetrazole complex  $[CpFe(dppe)(N_4(H) CC_6H_4NO_2)$ ]<sup>+</sup>.

Given that the SONLO structure–activity relationships depicted throughout the last 20 years for nitrile compounds of general formulas  $[CpM(PP)(N \equiv C-R)][X]$  (M = Fe, Ru; PP = mono/bidentate phosphine; R = phenyl-, thienylderivative chromophore; X = counterion), and that the respective tetrazolate neutral analogues can be directly obtained from those by self-catalyzed azide [3 + 2] cycloadditions, this work establishes a straight one-step route for target neutral tetrazolate complexes with improved, pH switchable SONLO properties. Although revealing lower  $\beta_{tot}$  values, our studies evidenced a remarkable stability of **RuT**<sup>0</sup> (and **RuT**<sup>+</sup>) when compared with acetylide analogues (known for some instability, e.g., vide ref 6n), thus evidencing organoruthenium(II) tetrazolate complexes as stable, efficient building blocks for the construction of SONLO materials.

#### METHODS

**General Procedures.** All experiments were carried out under inert atmosphere ( $N_2$ ) using standard Schlenk techniques. Commercial reagents were bought from Sigma-Aldrich and used without further purification; solvents were dried using standard methods.<sup>34</sup> Starting materials were prepared following the methods described in the literature for the synthesis of [CpRu(dppe)Cl]<sup>35</sup> and [CpFe(dppe)-I].<sup>6d 1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra were recorded on Bruker Avance II 400 spectrometer at probe temperature. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts are reported in parts per million (ppm) downfield from the residual solvent peak; <sup>31</sup>P NMR spectra are reported in ppm downfield from internal hexafluorophosphate anion standard (-144.2 ppm). Coupling constants are reported in Hz. Assignments of <sup>1</sup>H and <sup>13</sup>C NMR spectra were confirmed with the aid of <sup>1</sup>H-<sup>13</sup>C two-dimensional techniques (COSY, HSQC). Electronic spectra were recorded at room temperature on an Agilent Technologies Cary 60 UV–vis spectrophotometer in the range 200–900 nm. Combustion analyses were performed at Laboratório de Análises do Instituto Superior Técnico, using a Fisons Instruments EA1108 system, and data acquisition, integration, and handling were performed using the software package Eager-200 (Carlo Erba Instruments), confirming  $\geq$ 95% purity for all compounds.

Synthesis of 5-(4-Nitrophenyl)-1H-tetrazole. Hydroxylamine hydrochloride (1.04 g, 15.0 mmol) was added to a stirred pyridine solution (4 mL) of 4-nitrobenzaldehyde (1.51 g, 10.0 mmol). After 30 min, acetic anhydride (3 mL) was added, and the mixture was stirred at r.t. for a further 1 h. After pumping to dryness, the crude was dissolved in AcOEt (30 mL), washed with water ( $3 \times 10$  mL), rinsed with brine (10 mL), and dried over  $MgSO_4$ , and the solvent removed under reduced pressure. The crude product was then dissolved in DMF (10 mL), ammonium chloride (0.64 g, 12 mmol) and sodium azide (0.71 g, 11.0 mmol) were added, and the mixture was heated to 90 °C for 2 h. After being pumped to dryness, the crude was dissolved in AcOEt (30 mL), washed with water  $(3 \times 10 \text{ mL})$ , rinsed with brine (10 mL), and dried over MgSO<sub>4</sub>, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (AcOEt/n-hexane 1:1 to AcOEt), affording pure 5-(4-nitrophenyl)-1*H*-tetrazole as a white crystalline solid;  $\eta = 82\%$ . <sup>1</sup>H NMR (DMSO- $d_{61}$  400 MHz): 8.30 (d, 2H, J = 8.8,  $H_{2.6}$ Ph), 8.44 (d, 2H, J = 8.8,  $H_{3.5}Ph$ ); <sup>13</sup>C NMR (DMSO- $d_6$ , 100 MHz): 124.6 (C<sub>3.5</sub>Ph), 128.2 (C<sub>2.6</sub>Ph), 130.6 (C<sub>1</sub>Ph), 148.7 (C<sub>4</sub>Ph), 155.4 (C<sub>t</sub>). Anal. Calcd for C<sub>7</sub>H<sub>5</sub>N<sub>5</sub>O<sub>2</sub>·0.04C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>: C, 44.17; H, 2.75; N, 35.97. Found: C, 44.47; H, 2.60; N, 36.17.

Synthesis of Complexes  $MT^0$  (M = Fe, Ru). To Schlenk tubes charged with THF solutions (20 mL) of 5-(4-nitrophenyl)-1*H*-tetrazole (105 mg, 0.55 mmol) was added thallium ethoxide (39  $\mu$ L, 0.55 mmol). After being stirred for 30 min at r.t., complexes [CpM(dppe)X] were added (0.50 mmol), and the mixtures were stirred at r.t. for further 4 h. The solutions were double filtered to eliminate thallium chloride and pumped to dryness, and the crude compounds were washed with *n*-hexane and recrystallized by slow diffusion of *n*-hexane in dichloromethane solutions, affording crystalline products.

Compound **FeT**<sup>0</sup>: purple;  $\eta = 78\%$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 2.72–2.86 (m, 2H,  $-(CH_2)_2$ –, dppe) 3.09–3.23 (m, 2H,  $-(CH_2)_2$ –, dppe), 4.34 (s, 5H,  $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>), 7.12 (s (br), 6H, Ph, dppe), 7.28 (s (br), 4H, Ph, dppe), 7.37-7.44 (comp., 12H, H<sub>2.6</sub>Ph + Ph, dppe), 7.97 (d, 2H, J = 8.4,  $H_{3.5}$ Ph). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): 30.1 (t,  $J_{CP} = 20.8$ ,  $-(CH_2)_2$ -, dppe), 79.5 ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>), 123.6 (C<sub>3.5</sub>Ph), 126.1 (C<sub>2.6</sub>Ph), 128.1 (t,  $J_{CP}$  = 4.5,  $C_{meta}$ , dppe), 128.6 (t,  $J_{CP}$  = 4.2,  $C_{meta}$ , dppe), 129.3, 129.7 ( $C_{para}$ Dppe,  $C_1$ Ph), 131.2 (t,  $J_{CP}$  = 4.2,  $C_{ortho}$ , dppe), 132.6 (t,  $J_{CP} = 4.6, C_{ortho}, dppe), 134.5 (t, J_{CP} = 20.0, C_{ipsor} dppe), 136.4 (C_{ipsor} dppe), 141.9 (t, J_{CP} = 20.1, C_{ipsor} dppe), 146.9 (C_4Ph), 161.8 (C_t). <sup>31</sup>P$ NMR (CDCl<sub>3</sub>, 162 MHz): 106.9 (dppe). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz): 2.94 (s (br), 2H, -(CH<sub>2</sub>)<sub>2</sub>-, dppe) 3.11 (s (br), 2H,  $-(CH_2)_2$ -, dppe), 4.27 (s, 5H,  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>), 7.13 (s (br), 6H, Ph, dppe), 7.30 (s (br), 4H, Ph, dppe), 7.42 (comp. (br), 8H, Ph, dppe + H<sub>2.6</sub>Ph), 7.53 (s (br), 4H, Ph, dppe), 8.03 (s (br), 2H, H<sub>3.5</sub>Ph). <sup>31</sup>P NMR (DMSO-d<sub>6</sub>, 162 MHz): 105.9 (dppe). Anal. Calcd for C38H33N5O2P2Fe: C, 64.33; H, 4.69; N, 9.87. Found: C, 63.94; H, 4.69; N, 10.04.

Compound **RuT**<sup>0</sup>: orange;  $\eta = 89\%$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 2.61–2.75 (m, 2H,  $-(CH_2)_2-$ , dppe) 3.11–3.27 (m, 2H,  $-(CH_2)_2-$ , dppe), 4.73 (s, 5H,  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>), 7.09 (s (br), 6H, Ph, dppe), 7.23 (s (br), 4H, Ph, dppe), 7.34 (s (br), 6H, Ph, dppe), 7.42 (s (br), 4H, Ph, dppe), 7.46 (d, 2H, J = 8.5, H<sub>2,6</sub>Ph), 8.00 (d, 2H, J = 8.4, H<sub>3,5</sub>Ph). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): 29.0 (t,  $J_{CP} = 22.5$ ,  $-(CH_2)_2-$ , dppe), 82.3 ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>), 123.6 (C<sub>3,5</sub>Ph), 126.3 (C<sub>2,6</sub>Ph), 128.0 (t,  $J_{CP} = 4.8$ , C<sub>meta</sub>, dppe), 128.5 (t,  $J_{CP} = 4.6$ , C<sub>meta</sub>, dppe), 132.7 (t,  $J_{CP} = 5.3$ , Corthor dppe), 133.6 (t,  $J_{CP} = 23.0$ , C<sub>ipsor</sub> dppe), 136.7 (C<sub>ipsor</sub>, dppe), 141.7 (t,  $J_{CP} = 20.5$ , C<sub>ipsor</sub> dppe), 146.9 (C<sub>4</sub>Ph), 160.9 (C<sub>1</sub>). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 162 MHz): 86.1 (dppe). <sup>1</sup>H NMR (DMSO- $d_6$ , 400 MHz): 2.77–2.81 (m, 2H,  $-(CH_2)_2-$ , dppe) 3.16–3.23 (m, 2H,  $-(CH_2)_2-$ , dppe), 4.69 (s, SH,  $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>), 7.12 (s (br), 6H, Ph, dppe), 7.23–7.27 (m, 4H, Ph, dppe), 7.37–7.41 (m, 6H, Ph, dppe), 7.48–7.50 (comp., 6H, H<sub>2,6</sub>Ph + Ph, dppe), 8.07 (d, 2H, J = 8.1, H<sub>3,5</sub>Ph). <sup>31</sup>P NMR (DMSO- $d_{6}$ , 162 MHz): 85.1 (dppe). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz): 2.72 (s (br), 2H,  $-(CH_2)_2-$ , dppe) 3.21 (s (br), 2H,  $-(CH_2)_2-$ , dppe), 4.73 (s, 5H,  $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>), 7.12 (s (br), 6H, Ph, dppe), 7.24 (s (br), 4H, Ph, dppe), 7.35 (s (br), 6H, Ph, dppe), 7.24 (s (br), 4H, Ph, dppe), 7.35 (s (br), 6H, Ph, dppe), 7.46 (s (br), 4H, Ph, dppe), 7.55 (s (br), 2H, H<sub>2,6</sub>Ph), 8.02 (s (br), 2H, H<sub>3,5</sub>Ph). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>, 162 MHz): 86.0 (dppe). Anal. Calcd for C<sub>38</sub>H<sub>33</sub>N<sub>5</sub>O<sub>2</sub>P<sub>2</sub>Ru·(0.4CH<sub>2</sub>Cl<sub>2</sub>, 0.3C<sub>6</sub>H<sub>14</sub>): C, 59.27; H, 4.70; N, 8.59. Found: C, 58.89, H, 4.87; N, 8.45.

**One-Pot Catalytic Synthesis of Complexes MT**<sup>0</sup> (**M** = **Fe**, **Ru**). To Schlenk tubes charged with [CpM(dppe)X] (0.10 mmol), 4nitrobenzonitrile (148 mg, 0.10 mmol), thallium hexafluorophosphate (35 mg, 0.10 mmol) and sodium azide (65 mg, 0.10 mmol) was added dichloromethane (5 mL). After stirring overnight, at r.t., the solutions were double filtered and pumped to dryness, and the crude compounds were washed with *n*-hexane and recrystallized by slow diffusion of *n*-hexane in dichloromethane solutions, affording crystalline products;  $\eta = 83\%$  (M = Fe),  $\eta = 85\%$  (M = Ru).

**Synthesis of RuT**<sup>+</sup>. To a Schlenk tube charged with [CpRu-(dppe)Cl] (300 mg, 0.50 mmol), thallium hexafluorophosphate (175 mg, 0.50 mmol) and 5-(4-nitrophenyl)-1*H*-tetrazole (96 mg, 0.55 mmol), was added dichloromethane (20 mL) and the mixture was stirred overnight at room temperature, under inert atmosphere. The solution was double filtered to eliminate thallium chloride and pumped to dryness, and the crude was washed with *n*-hexane and recrystallized by slow diffusion of ethyl ether in dichloromethane solution of the compound;  $\eta = 87\%$ . Using ammonium hexafluorophosphate (82 mg, 0.50 mmol) instead of thallium hexafluorophosphate, **RuT**<sup>+</sup> was obtained in 79% yield.

Bright yellow; <sup>i</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz): 2.72-2.93 (m, 2H,  $-(CH_2)_2$ , dppe) 3.10–3.21 (m, 2H,  $-(CH_2)_2$ , dppe), 4.71 (s, 5H, η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), 5.93 (s (br), 1H, H<sub>4</sub>Tet) 7.11 (s (br), 6H, Ph, dppe), 7.24– 7.28 (m, 4H, Ph, dppe), 7.38-7.42 (m, 6H, Ph, dppe), 7.49 (comp., 6H,  $H_{2.6}Ph$  + Ph, dppe), 8.10 (d, 2H, J = 8.7,  $H_{3.5}Ph$ ). <sup>13</sup>C NMR (DMSO-d6, 100 MHz): 28.0 (t,  $J_{CP} = 22.6$ ,  $-(CH_2)_2 -$ , dppe), 82.3 ( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>), 124.3 (C<sub>3,5</sub>Ph), 126.4 (C<sub>2,6</sub>Ph), 128.2 (t,  $J_{CP} = 4.7$ , C<sub>meta</sub>, dppe), 129.0 (t,  $J_{CP}$  = 4.5,  $C_{meta'}$  dppe), 129.7, 129.8 ( $C_{para'}$  dppe,  $C_1$ Ph), 130.9 (t,  $J_{CP}$ = 4.8,  $C_{ortho}$ , dppe), 132.9 (t,  $J_{CP}$  = 5.0,  $C_{ortho}$ , dppe), 134.2 (t,  $J_{CP}$  = 22.5,  $C_{ipso'}$  dppe), 135.6 ( $C_{ipso'}$  dppe), 141.3 (t,  $J_{CP}$  = 21.1,  $C_{ipso'}$  dppe), 147.1 ( $C_4$ Ph), 159.5 (C1). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 162 MHz): -144.2 (qt,  $J_{PF} = 712.8$ ,  $PF_6^-$ ), 84.9 (dppe). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz): 2.73 (s (br), 2H, -(CH<sub>2</sub>)<sub>2</sub>-, dppe) 3.05 (s (br), 2H,  $-(CH_2)_2$ -, dppe), 4.82 (s, 5H,  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>), 7.18 (s (br), 6H, Ph, dppe), 7.29 (s (br), 4H, Ph, dppe), 7.43-7.49 (comp., 12H, H<sub>2,6</sub>Ph + Ph, dppe), 8.15 (s (br), 2H, H<sub>3,5</sub>Ph). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>, 162 MHz): -144.2 (qt,  $J_{PF} = 712.2$ ,  $PF_6^{-}$ ), 83.8 (dppe). Anal. Calcd for  $C_{38}H_{34}F_6N_5O_2P_3Ru$ : C, 50.67; H, 3.80; N, 7.78. Found: C, 50.65, H, 3.90: N. 7.45%

pH Switch Studies for RuT<sup>+</sup>/RuT<sup>0</sup>. All pH switch experiments were made using 0.1 mmol of  $RuT^+$  (90 mg) or  $RuT^0$  (75 mg) dissolved in 10 mL of dichloromethane. The experiments in dry conditions were performed in flamed Schlenk tubes and under inert atmosphere.  $Ru\hat{T}^0$  was obtained in 97% yield (73 mg) after silica filtration, by addition of triethylamine (14  $\mu$ L, 0.10 mmol) to RuT<sup>+</sup>. RuT<sup>+</sup> was obtained (as triflate salt) in 89% yield (80 mg) by addition of triflic acid (9  $\mu$ L, 0.10 mmol) to RuT<sup>0</sup>; after washing of the crude product with ethyl ether  $(3 \times 10 \text{ mL})$ . The experiments in wet conditions were performed in atmospheric conditions, and tetrabutylammonium bromide (catalytic, 2 mg) was dissolved in dichloromethane solutions of the compounds. Water, or aqueous solutions of sodium hydroxide (35 wt %) or of fluoroboric acid (50 wt %), were used. After intense stirring for 15 min the phases were separated, the organic phase was dried with anhydrous magnesium sulfate, filtered, and pumped to dryness. RuT<sup>0</sup> was recovered by crude extraction with ethyl ether  $(3 \times 10 \text{ mL})$  and (posteriorly) RuT<sup>+</sup> was recovered by crude extraction with dichloromethane (2  $\times$  5 mL). RuT<sup>0</sup> was obtained in 20% yield (15 mg) from RuT<sup>+</sup> after stirring with water (67 mg of RuT<sup>+</sup> recovered) and in 78% yield from RuT<sup>+</sup> after stirring with

sodium hydroxide solution. No conversions were verified when  $RuT^0$  (2 h) or  $RuT^+$  (15 min) were stirred with fluoroboric acid solutions, with quantitative recovery of the starting products.

**Electrochemical Studies.** Electrochemical experiments were performed using an EG&G Princeton Applied Research model 273A potentiostat/galvanostat and monitored using Electrochemistry PowerSuite v2.51 software (Princeton Applied Research). Cyclic voltammograms were obtained in 0.2 M/0.1 M solutions of  $[NBu_4][PF_6]$  in dried DCM/CH<sub>3</sub>CN, respectively. Experiments were carried out using a three-electrode configuration cell, with a platinum-disk work electrode (1.0 or 0.7 mm diameter) probed by a Luggin capillary connected to a silver-wire pseudoreference electrode; a Pt wire auxiliary electrode was employed. The redox potentials were measured in the presence of ferrocene (internal standard) and normally quoted relative to SCE using the ferrocenium/ferrocene redox couple ( $E_{1/2} = 0.46$  and 0.40 V versus SCE for DCM or CH<sub>3</sub>CN, respectively).

X-ray Crystallographic Procedures. Crystals were mounted with protective oil on a cryo-loop and X-ray single diffraction was conducted on Bruker D8 and X8 Apex II diffractometers equipped with MoK $\alpha$  X-ray sources and graphite monochromators. The X-ray generators were operated at 50 kV and 30 mA, and the X-ray data collection were monitored using the APEX2 program.<sup>36</sup> Psi-scan absorption correction was applied using SAINT and SADABS programs.<sup>37</sup> Structures were solved by direct methods with the program SHELXS<sup>38</sup> and SIR2004,<sup>39</sup> and refined by full-matrix leastsquares on F<sup>2</sup> with SHELXL,<sup>38</sup> all included in the package of programs WINGX-V2014.1.40 Non-hydrogen atoms were refined with anisotropic thermal parameters, with H atoms placed in idealized positions and allowed to refine riding on the parent C atom. PLATON<sup>41</sup> was used to calculate bond distances and angles as well as intermolecular interactions. Graphical representations (ESI) were prepared using Mercury 3.5.1.42 Further crystallographic information for all determined structures are given in Table S2. CCDC 1526279 and 1526280 contain the supplementary crystallographic data for FeT<sup>0</sup> and RuT<sup>+</sup>, respectively; these data can be obtained free of charge via www. ccdc.cam.ac.uk/data request/cif.

**Computational Details.** All DFT calculations were performed with Gaussian09<sup>43</sup> using the PBE1PBE functional, also known as PBE0<sup>29</sup> and the hybrid exchange–correlation functional using the Coulomb-attenuating method (CAM-B3LYP).<sup>30</sup> The triple- $\zeta$  basis set with one polarization function LANL2TZ(f) (ruthenium and iron) and LANL08(d) (phosphorus) were used with the associated effective core potential (ECP)<sup>44</sup> downloaded from the EMSL Basis Set Library.<sup>45</sup> For the other elements, the standard 6-311G\*\* basis set was employed. Geometry optimizations were performed in dichloromethane, without symmetry constraints, using a polarizable continuum model described with the integral equation formalism variant (IEFPCM).<sup>46</sup>

The static first hyperpolarizabilities  $\beta_{tot}$  were calculated using the finite field (FF) method by double numerical differentiation of the energy using the following equation.

$$\beta_{\text{tot}} = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2} \tag{2}$$

calculating the individual static components

$$\beta_{i} = \beta_{iii} + \frac{1}{3} \sum_{i \neq j} (\beta_{ijj} + \beta_{jij} + \beta_{jji})$$
(3)

The same procedure was employed for the calculation of NLO properties of  $\eta^5$ -monocyclopentadienylmetal complexes.<sup>9</sup> TD-DFT calculations were also performed using the same functionals and basis sets. The scripts to plot the electron density difference maps (EDDMs) were retrieved from the GaussSum package.<sup>47</sup>

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#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b00138.

NMR spectra of  $MT^0$  and  $RuT^+$ . Supramolecular analysis, and further crystallographic data for  $FeT^0$  and  $RuT^+$ . Cyclic voltammograms of  $FeT^0$  and  $RuT^+$ . HOMO and LUMO of complexes  $MT^0$  and  $MT^+$ , and further computational data (PDF)

#### **Accession Codes**

CCDC 1526279–1526280 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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#### DEDICATION

Dedicated to Prof. Maria Helena Garcia on her retirement.

# **REFERENCES**

(1) (a) Zyss, J.; Chemla, D. S. Quadratic nonlinear optics and optimization of the second-order nonlinear optical response of molecular crystals. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D.S.; Zyss, J., Eds.; Academic Press, 1987; Vol. *I*, Chapter II, pp 23–191. (b) Prasad, N. P.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley, New York, 1991. (c) Dalton, L.; Steier, W.; Robinson, B.; Zhang, C.; Ren, A.; Garner, S.; Chen, A.; Londergan, T.; Irwin, L.; Carlson, B.; Fifield, L.; Phelan, G.; Kincaid, C.; Amend, J.; Jen, A. From molecules to optochips: Organic electro-optic materials. *J. Mater. Chem.* **1999**, *9*, 1905–1920. (d) Goovaerts, E.; Wenseleers, W.; Garcia, M. H.; Cross, G. H. Design and characterization of organic and organometallic molecules for second order nonlinear optics. *Handbook of Advanced Electronic and Photonic Materials*; Nalwa, H.S., Ed.; Academic Press, 2001, Vol. *9*, Chapter 3, pp 127–191.

(2) (a) Coe, B. J. Molecular materials possessing switchable quadratic nonlinear optical properties. *Chem. - Eur. J.* 1999, *5*, 2464–2671.
(b) Coe, B. J.; Houbrechts, S.; Asselberghs, I.; Persoons, A. Efficient, reversible redox-switching of molecular first hyperpolarizabilities in ruthenium(II) complexes possessing large quadratic optical non-linearities. *Angew. Chem., Int. Ed.* 1999, *38*, 366–369. (c) Delaire, J. A.;

Nakatani, K. Linear and nonlinear optical properties of photochromic molecules and materials. Chem. Rev. 2000, 100, 1817-1846. (d) Berkovic, G.; Krongauz, V.; Weiss, V. Spiropyrans and spirooxazines for memories and switches. Chem. Rev. 2000, 100, 1741-1753. (e) Asselberghs, I.; Clays, K.; Persoons, A.; Ward, M. D.; McCleverty, J. Switching of molecular second-order polarisability in solution. J. Mater. Chem. 2004, 14, 2831-2839. (f) Guerchais, V.; Ordronneau, L.; Le Bozec, H. Recent developments in the field of metal complexes containing photochromic ligands: Modulation of linear and nonlinear optical properties. Coord. Chem. Rev. 2010, 254, 2533-2545. (g) Green, K. A.; Cifuentes, M. P.; Samoc, M.; Humphrey, M. G. Metal alkynyl complexes as switchable NLO systems. Coord. Chem. Rev. 2011, 255, 2530-2541. (h) Roberto, D.; Di Bella, S.; Oliveri, I. P.; Colombo, A.; Dragonetti, C.; Righetto, S. An unprecedented switching of the second-order nonlinear optical response in aggregate bis(salicylaldiminato)zinc(II) Schiff-base complexes. Dalton Trans. 2012, 41, 7013-7016. (i) Castet, F.; Rodriguez, V.; Pozzo, J.-L.; Ducasse, L.; Plaquet, A.; Champagne, B. Design and Characterization of Molecular Nonlinear Optical Switches. Acc. Chem. Res. 2013, 46, 2656-2665. (j) Boixel, J.; Guerchais, V.; Le Bozec, H.; Jacquemin, D.; Amar, A.; Boucekkine, A.; Colombo, A.; Dragonetti, C.; Marinotto, D.; Roberto, D.; Righetto, S.; De Angelis, R. Secondorder NLO switches from molecules to polymer films based on photochromic cyclometalated platinum(II) complexes. J. Am. Chem. Soc. 2014, 136, 5367-5375. (k) Beaujean, P.; Bondu, F.; Plaquet, A.; Garcia-Amorós, J.; Cusido, J.; Raymo, F. M.; Castet, F.; Rodriguez, V.; Champagne, B. Oxazines: a new class of second-order nonlinear optical switches. J. Am. Chem. Soc. 2016, 138, 5052-5062.

(3) (a) Tessore, F.; Roberto, D.; Ugo, R.; Mussini, P.; Quici, S.; Ledoux-Rak, I.; Zyss, J. Large, concentration-dependent enhancement of the quadratic hyperpolarizability of  $[Zn(CH_3CO_2)_2(L)_2]$  in CHCl<sub>3</sub> on substitution of acetate by triflate. *Angew. Chem., Int. Ed.* **2003**, 42, 456–459. (b) Maury, O.; Le Bozec, H. Molecular engineering of octupolar NLO molecules and materials based on bipyridyl metal complexes. *Acc. Chem. Res.* **2005**, 38, 691–704. (c) Cariati, E.; Pizzotti, M.; Roberto, D.; Tessore, F.; Ugo, R. Coordination and organometallic compounds and inorganic–organic hybrid crystalline materials for second-order non-linear optics. *Coord. Chem. Rev.* **2006**, 250, 1210–1233. (d) Coe, B. J. Switchable nonlinear optical metallochromophores with pyridinium electron acceptor groups. *Acc. Chem. Res.* **2006**, 39, 383–393. (e) Morrall, J. P.; Dalton, G. T.; Humphrey, M. G.; Samoc, M. Organotransition metal complexes for nonlinear optics. *Adv. Organomet. Chem.* **2007**, 55, 61–136.

(4) Green, M. L. H.; Marder, S. R.; Thompson, M. E.; Bandy, J. A.; Bloor, D.; Kolinsky, P. V.; Jones, R. J. Synthesis and structure of (cis)-[1-ferrocenyl-2-(4-nitrophenyl)ethylene], an organotransition metal compound with a large second-order optical nonlinearity. *Nature* **1987**, 330, 360–362.

(5) Barlow, S.; Marder, S. R. Electronic and optical properties of conjugated group 8 metallocene derivatives. *Chem. Commun.* 2000, 1555–1562.

(6) (a) Whittall, I. R.; Cifuentes, M. P.; Humphrey, M. G.; Luther-Davies, B.; Samoc, M.; Houbrechts, S.; Persoons, A.; Heath, G. A.; Hockless, D. C. R. J. Organomet. Chem. 1997, 549, 127-137. (b) Wenseleers, W.; Gerbrandij, A. W.; Goovaerts, E.; Garcia, M. H.; Robalo, M. P.; Mendes, P. J.; Rodrigues, J. C.; Dias, A. R. Hyper-Rayleigh scattering study of  $\eta^5$ -monocyclopentadienyl-metal complexes for second order non-linear optical materials. J. Mater. Chem. 1998, 8, 925-930. (c) Wu, I.-Y.; Lin, J. T.; Luo, J.; Li, C.-S.; Tsai, C.; Wen, Y. S.; Hsu, C.-C.; Yeh, F.-F.; Liou, S. Syntheses and Second-Order Optical Nonlinearity of ruthenium  $\sigma$ -acetylides with an endcapping organic electron acceptor and thienyl entity in the conjugation chain. Organometallics 1998, 17, 2188-2198. (d) Garcia, M. H.; Rodrigues, J. C.; Dias, A. R.; Piedade, M. F. M.; Duarte, M. T.; Robalo, M. P.; Lopes, N. Second harmonic generation of  $\eta^5$ -monocyclopentadienyl ruthenium p-benzonitrile derivatives by Kurtz powder technique. Crystal and molecular structure determinations of [Ru- $(\eta^{5}-C_{5}H_{5})((+)-DIOP)(p-NCC_{6}H_{4}NO_{2})][X], X = PF_{6}^{-}, CF_{3}SO_{3}^{-} and$  $[\operatorname{Ru}(\eta^5-\operatorname{C}_5\operatorname{H}_5)((+)-\operatorname{DIOP}) (\operatorname{NCCH}_3)][\operatorname{PF}_6]$ . J. Organomet. Chem.

2001, 632, 133-144. (e) Garcia, M. H.; Robalo, M. P.; Dias, A. R.; Piedade, M. F. M.; Galvão, A.; Duarte, M. T.; Wenseleers, W.; Goovaerts, E. Organometallic complexes for second-order non-linear optics: synthesis and molecular quadratic hyperpolarizabilities of  $\eta^5$ monocyclopentadienyliron(II) nitrile derivatives with different phosphines. X-ray crystal structure of [FeCp(DPPE)(p-NCC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>)]-[PF<sub>6</sub>]·CH<sub>2</sub>Cl<sub>2</sub>. J. Organomet. Chem. 2001, 619, 252–264. (f) Garcia, M. H.; Robalo, M. P.; Dias, A. R.; Duarte, M. T.; Wenseleers, W.; Aerts, G.; Goovaerts, E.; Cifuentes, M. P.; Hurst, S.; Humphrey, M. G.; Samoc, M.; Luther-Davies, B. Synthesis and nonlinear optical properties of  $\eta^5$ -monocyclopentadienyliron(II) acetylide derivatives. X-ray crystal structures of  $[Fe(\eta^5-C_5H_5) (DPPE)(p-C \equiv CC_6H_4NO_2)]$ and  $[Fe(\eta^5-C_5H_5) (DPPE)((E)-p-C \equiv CC_6H_4C(H) = C(H)-$ C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>)]. Organometallics 2002, 21, 2107–2118. (g) Powell, C. E.; Cifuentes, M. P.; McDonagh, A. M.; Hurst, S. K.; Lucas, N. T.; Delfs, C. D.; Stranger, R.; Humphrey, M. G.; Houbrechts, S.; Asselberghs, I.; Persoons, A.; Hockless, D. C. R. Organometallic complexes for nonlinear optics. Part 27. Syntheses and optical properties of some iron, ruthenium and osmium alkynyl complexes. Inorg. Chim. Acta 2003, 352, 9-18. (h) Powell, C. E.; Humphrey, M. G. Nonlinear optical properties of transition metal acetylides and their derivatives. Coord. Chem. Rev. 2004, 248, 725-756. (i) Cifuentes, M. P.; Humphrey, M. G. Alkynyl compounds and nonlinear optics. J. Organomet. Chem. 2004, 689, 3968-3981. (j) Garcia, M. H.; Mendes, P. J.; Robalo, M. P.; Dias, A. R.; Campo, J.; Wenseleers, W.; Goovaerts, E. Compromise between conjugation length and charge-transfer in nonlinear optical  $\eta^5$ -monocyclopentadienyliron(II) complexes with substituted oligo-thiophene nitrile ligands: Synthesis, electrochemical studies and first hyperpolarizabilities. J. Organomet. Chem. 2007, 692, 3027-3041. (k) Garcia, M. H.; Florindo, P.; Piedade, M. F. M.; Duarte, M. T.; Robalo, M. P.; Heck, J.; Wittenburg, C.; Holtmann, J.; Licandro, E. Synthesis of organometallic Ru(II) and Fe(II) complexes containing fused rings hemi-helical ligands as chromophores. Evaluation of non-linear optical properties by HRS. J. Organomet. Chem. 2008, 693, 2987-2999. (1) Florindo, P.; Garcia, M. H. Second Order Nonlinear Optical Properties of Group 8 Half-Sandwich Organometallic Complexes. Organometallic Compounds: Preparation, Structure and Properties; Nova Science Publishers, Inc., New York, 2010; Chapter 9, pp 347-372. (m) Valente, A.; Royer, S.; Narendra, M.; Silva, T. J. L.; Mendes, P. J. G.; Robalo, M. P.; Abreu, M.; Heck, J.; Garcia, M. H. Synthesis of new Fe(II) and Ru(II) η5-monocyclopentadienyl compounds showing significant second order NLO properties. J. Organomet. Chem. 2013, 736, 42-49. (n) Silva, T. J. L.; Mendes, P. J.; Santos, A. M.; Garcia, M. H.; Robalo, M. P.; Ramalho, J. P. P.; Carvalho, A. J. P.; Büchert, M.; Wittenburg, C.; Heck, J. Mono( $\eta^5$ -cyclopentadienyl)metal(II) complexes with thienyl acetylide chromophores: synthesis, electrochemical studies, and first hyperpolarizabilities. Organometallics 2014, 33, 4655-4671. (o) Wenseleers, W.; Goovaerts, E.; Hepp, P.; Garcia, M. H.; Robalo, M. P.; Dias, A. R.; Piedade, M. F. M.; Duarte, M. T. High first hyperpolarizability and perfectly aligned crystal packing for an organometallic compound  $[Fe(\eta^5-C_5H_5)(R-PROPHOS)(p-$ NCC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>)][PF<sub>6</sub>]·CH<sub>2</sub>Cl<sub>2</sub>. Chem. Phys. Lett. 2003, 367, 390-397. (7) (a) Espa, D.; Pilia, L.; Marchiò, L.; Mercuri, M. L.; Serpe, A.; Barsella, A.; Fort, A.; Dalgleish, S. J.; Robertson, N.; Deplano, P. Redox-switchable chromophores based on metal (Ni, Pd, Pt) mixedligand dithiolene complexes showing molecular second-order nonlinear-optical activity. Inorg. Chem. 2011, 50, 2058-2060. (b) Coe, B. J.; Avramopoulos, A.; Papadopoulos, M. G.; Pierloot, K.; Vancoillie, S.; Reis, H. Theoretical modelling of photoswitching of hyperpolarisabilities in ruthenium complexes. Chem. - Eur. J. 2013, 19, 15955-15963. (c) Boixel, J.; Guerchais, V.; Le Bozec, H.; Jacquemin, D.; Amar, A.; Boucekkine, A.; Colombo, A.; Dragonetti, C.; Marinotto, D.; Roberto, D.; Righetto, S.; De Angelis, R. Second-order NLO switches from molecules to polymer films based on photochromic cyclometalated platinum(II) complexes. J. Am. Chem. Soc. 2014, 136, 5367-5375.

(8) Paul, F.; Costuas, K.; Ledoux, I.; Deveau, S.; Zyss, J.; Halet, J. F.; Lapinte, C. Redox-switchable second-order molecular polarizabilities with electron-rich Iron  $\sigma$ -aryl acetylides. *Organometallics* **2002**, *21*, 5229–5235.

(9) Mendes, P. J.; Silva, T. J. L.; Garcia, M. H.; Ramalho, J. P. P.; Carvalho, A. J. P. Switchable nonlinear optical properties of  $\eta^{5}$ monocyclopentadienylmetal complexes: a DFT approach. *J. Chem. Inf. Model.* **2012**, *52*, 1970–1983.

(10) (a) Garcia, M. H.; Morais, T. S.; Florindo, P.; Piedade, M. F. M.; Moreno, V.; Ciudad, C.; Noe, V. Inhibition of cancer cell growth by ruthenium(II) cyclopentadienyl derivative complexes with heteroaromatic ligands. J. Inorg. Biochem. 2009, 103, 354-361. (b) Moreno, V.; Lorenzo, J.; Aviles, F. X.; Garcia, M. H.; Ribeiro, J.; Morais, T. S.; Florindo, P.; Robalo, M. P. Studies of the Antiproliferative Activity of Ruthenium(II) Cyclopentadienyl-Derived Complexes with Nitrogen Coordinated Ligands. Bioinorg. Chem. Appl. 2010, ID 936834, 20101-11.10.1155/2010/936834 (c) Florindo, P. R.; Marques, I. J.; Nunes, C. D.; Fernandes, A. C. Synthesis, characterization and cytotoxicity of cyclopentadienyl ruthenium(II) complexes containing carbohydratederived ligands. J. Organomet. Chem. 2014, 760, 240-247. (d) Florindo, P. R.; Pereira, D. M.; Borralho, P. M.; Rodrigues, C. M. P.; Piedade, M. F. M.; Fernandes, A. C. Cyclopentadienylruthenium(II) and iron(II) organometallic compounds with carbohydrate derivative ligands as good colorectal anticancer agents. J. Med. Chem. 2015, 58, 4339-4347.

(11) Goncalves, A. C.; Morais, T. S.; Robalo, M. P.; Marques, F.; Avecilla, F.; Matos, C. P.; Santos, I.; Tomaz, A. I.; Garcia, M. H. Important cytotoxicity of novel iron(II) cyclopentadienyl complexes with imidazole based ligands. J. Inorg. Biochem. 2013, 129, 1–8.
(b) Valente, A.; Santos, A. M.; Côrte-Real, L.; Robalo, M. P.; Moreno, V.; Font-Bardia, M.; Calvet, T.; Lorenzo, J.; Garcia, M. H. New iron(II) cyclopentadienyl derivative complexes: synthesis and antitumor activity against human leukemia cancer cells. J. Organomet. Chem. 2014, 756, 52–60.

(12) Herr, R. J. 5-Substituted-1*H*-tetrazoles as carboxylic acid isosteres: medicinal chemistry and synthetic methods. *Bioorg. Med. Chem.* **2002**, *10*, 3379–3393.

(13) (a) Ostrovskii, V. A.; Koren, A. O. Alkylation and related electrophilic reactions at endocyclic nitrogen atoms in the chemistry of tetrazole. *Heterocycles* **2000**, *53*, 1421–1448. (b) Zhao, H.; Qu, Z. R.; Ye, H. Y.; Xiong, R. G. In situ hydrothermal synthesis of tetrazole coordination polymers with interesting physical properties. *Chem. Soc. Rev.* **2008**, *37*, 84–100. (c) Ma, L.; Qiu, Y.-C.; Peng, G.; Cai, J.-B.; Deng, H. In situ tetrazole ligand synthesis of two-fold interpenetrating zinc coordination frameworks. *Eur. J. Inorg. Chem.* **2011**, *2011*, 3446–3453.

(14) Ye, Q.; Li, Y.-H.; Song, Y.-M.; Huang, X.-F.; Xiong, R.-G.; Xue, Z. A second-order nonlinear optical material prepared through in situ hydrothermal ligand synthesis. *Inorg. Chem.* **2005**, *44*, 3618–3625.

(15) Palazzi, A.; Stagni, S.; Bordoni, S.; Monari, M.; Selva, S. Interannular conjugation in new iron(II) 5-aryl tetrazolate complexes. *Organometallics* **2002**, *21*, 3774–3781.

(16) Hurst, S. K.; Cifuentes, M. P.; Morrall, J. P.; Lucas, N. T.; Whittall, I. R.; Humphrey, M. G.; Asselberghs, I.; Persoons, A.; Samoc, M.; Luther-Davies, B.; Willis, A. C. Organometallic complexes for Nonlinear Optics. 22.<sup>1</sup> Quadratic and cubic hyperpolarizabilities of trans-bis(bidentate phosphine)ruthenium  $\sigma$ -arylvinylidene and  $\sigma$ arylalkynyl complexes. *Organometallics* **2001**, *20*, 4664–4675.

(17) Chang, C.-W.; Lee, G.-H. Synthesis of Ruthenium Triazolato and Tetrazolato Complexes by 1,3-Dipolar Cycloadditions of Ruthenium Azido Complex with Alkynes and Alkenes and Regiospecific Alkylation of Triazolates. *Organometallics* **2003**, *22*, 3107–3116.

(18) Butler, R. N.; McEvoy, T. M. A carbon-13 and proton nuclear magnetic resonance study of annular tautomerism and interannular conjugation in some substituted-5-aryl-tetrazoles. *J. Chem. Soc., Perkin Trans.* 2 1978, 1087–1090.

(19) Morais, T. S.; Garcia, M. H.; Robalo, M. P.; Piedade, M. F. M.; Duarte, M. T.; Villa de Brito, M. J.; Madeira, P. J. A. Synthesis and structural characterization of new piano-stool ruthenium(II) com-

#### **Inorganic Chemistry**

plexes bearing 1-butylimidazole heteroaromatic ligand. J. Organomet. Chem. 2012, 713, 112-122.

(20) Chang, K.-H.; Lin, Y.-C.; Liu, Y.-H.; Wang, Y. Reactions of ruthenium cyclopropenyl complexes with trimethylsilyl azide. *J. Chem. Soc., Dalton Trans.* **2001**, 3154–3159.

(21) Stagni, S.; Palazzi, A.; Brulatti, P.; Salmi, M.; Muzzioli, S.; Zacchini, S.; Marcaccio, M.; Paolucci, F. 5-(2-Thienyl)tetrazolates as ligands for Ru<sup>II</sup>–polypyridyl complexes: synthesis, electrochemistry and photophysical properties. *Eur. J. Inorg. Chem.* **2010**, 2010, 4643–4657.

(22) Bruce, M. I.; Fox, M. A.; Low, P. J.; Skelton, B. W.; Zaitseva, N. N. Some reactions of an  $\eta^3$ -tetracyanobutadienyl-ruthenium complex. *Dalton Trans.* **2010**, *39*, 3759–3770.

(23) Stagni, S.; Palazzi, A.; Zacchini, S.; Ballarin, B.; Bruno, C.; Marcaccio, M.; Paolucci, F.; Monari, M.; Carano, M.; Bard, A. J. New family of ruthenium(II) polypyridine complexes bearing 5-aryltetrazolate ligands as systems for electrochemiluminescent devices. *Inorg. Chem.* **2006**, 45, 695–709.

(24) Oudar, J. L.; Chemla, D. S. Hyperpolarizabilities of the nitroanilines and their relations to the excited state dipole moment. *J. Chem. Phys.* **1977**, *66*, 2664–2269.

(25) Concerns about dispersion, namely near-resonant enhancement, and limitations of the application of the TLM to analogue acetylide compounds are thoroughly discussed in ref 6h and ref 6n.

(26) Parr, R. G.; Yang, W. Density Functional Theory of Atoms and Molecules; Oxford University Press, New York, 1989.

(27) Mendes, P. J.; Carvalho, A. J. P.; Ramalho, J. P. P. Role played by the organometallic fragment on the first hyperpolarizability of iron-acetylide complexes: A TD-DFT study. *J. Mol. Struct.: THEOCHEM* **2009**, 900, 110–117.

(28) Mendes, P. J.; Silva, T. J. L.; Carvalho, A. J. P.; Ramalho, J. P. P. DFT studies on thiophene acetylide Ru(II) complexes for nonlinear optics: Structure-function relationships and solvent effects. *J. Mol. Struct.: THEOCHEM* **2010**, *946*, 33–42.

(29) Adamo, C.; Barone, V. Toward reliable density functional methods without adjustable parameters: The PBE0 model. *J. Chem. Phys.* **1999**, *110*, 6158–6169.

(30) Yanai, T.; Tew, D. P.; Handy, N. C. A new hybrid exchangecorrelation functional using the Coulomb-attenuating method (CAM-B3LYP). *Chem. Phys. Lett.* **2004**, 393, 51–57.

(31) Zou, Y.; Hong, S.; Park, M.; Chun, H.; Lah, M. S. Selective gas sorption property of an interdigitated 3-D metal–organic framework with 1-D channels. *Chem. Commun.* **200**7, 5182–5184.

(32) Hill, M. S.; Hitchcock, P. B.; Smith, N. Routes to titanium tetrazole complexes. *Polyhedron* **2004**, *23*, 801–807.

(33) Adams, H.; Costa, P. J.; Newell, M.; Vickers, S. J.; Ward, M. D.; Félix, V.; Thomas, J. A. Mixed Valence Creutz-Taube Ion Analogues Incorporating Thiacrowns: Synthesis, Structure, Physical Properties, and Computational Studies. *Inorg. Chem.* **2008**, *47*, 11633–11643.

(34) Perrin, D. D.; Amarego, W. L. F.; Perrin, D. R. Purification of Laboratory Chemicals, 2nd ed.; Pergamon, New York, 1980.

(35) Ashby, G. S.; Bruce, M. I.; Tomkins, I. B.; Wallis, R. C. Cyclopentadienyl-ruthenium and -osmium chemistry. VII. Complexes containing nitriles, tertiary phosphines or phosphites formed by addition or displacement reactions. *Aust. J. Chem.* **1979**, *32*, 1003–1008.

(36) APEXII, Bruker AXS Inc.: Madison, Wisconsin, USA, 2012.

(37) SABADS, Area detector Absorption Correction; Bruker AXS Inc.: Madison, WI, 2004.

(38) Sheldrick, G. M. SHELXL 97: An Integrated System for Solving and Refining Crystal Structures from Diffraction Data, Revision 5.1; University of Göttingen: Germany, 1997.

(39) Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; De Caro, L.; Giacovazzo, C.; Polidori, G.; Spagna, R. SIR2004: an improved tool for crystal structure determination and refinement. J. Appl. Crystallogr. 2005, 38, 381–388.

(40) Farrugia, L.J. WinGX suite for small molecule single crystal crystallography. J. Appl. Crystallogr. 1999, 32, 837–838.

(41) Spek, A. L. Structure validation in chemical crystallography. *Acta Crystallogr., Sect. D: Biol. Crystallogr.* **2009**, *65*, 148–155.

(42) Macrae, C. F.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Shields, G. P.; Taylor, R.; Towler, M.; Van de Streek, J. Mercury: visualization and analysis of crystal structures. *J. Appl. Crystallogr.* **2006**, 39, 453–457.

(43) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09; Gaussian, Inc.: Wallingford, CT, 2009.

(44) Roy, L. E.; Hay, P. J.; Martin, R. L. Revised basis sets for the LANL effective core potentials. *J. Chem. Theory Comput.* **2008**, *4*, 1029–1031.

(45) (a) Feller, D. The role of databases in support of computational chemistry calculations. J. Comput. Chem. 1996, 17, 1571–1586.
(b) Schuchardt, K. L.; Didier, B. T.; Elsethagen, T.; Sun, L.; Gurumoorthi, V.; Chase, J.; Li, J.; Windus, T. L. Basis Set Exchange: a community database for computational sciences. J. Chem. Inf. Model. 2007, 47, 1045–1052.

(46) Tomasi, J.; Mennucci, B.; Cammi, R. Quantum mechanical continuum solvation models. *Chem. Rev.* 2005, *105*, 2999–3093.

(47) O'Boyle, N. M.; Tenderholt, A. L.; Langner, K. M. cclib: A library for package-independent computational chemistry algorithms. *J. Comput. Chem.* **2008**, *29*, 839–845.