Synthesis and Second-Order Nonlinear Optical Properties of New Palladium(II) and Platinum(II) Schiff-Base Complexes

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The second harmonic generations of the dimeric complexes $[M_2(\mu\text{-}X)(\mu\text{-}SC_nH_{2n+1})(RC_6H_3\text{-}CH{=}NC_6H_4R')]$ (M = Pd, Pt; X = Cl, CH_3COO, (*R*)-$CH_3CHClCOO$; R, R′ = NO_2 and OC_8H_{17} or $N(C_4H_9)_2$; $n = 4$ or 8) and the monomeric complexes $[Pd(RC_6H_3CH{=}NC_6H_4R')L]$ (L = C_5H_5 (Cp), $CH_3COCHCOCH_3$ (acac)) and $[Pd(RC_6H_3CH{=}NC_6H_4R')(CNC_6H_4R'')Cl]$ (R″ = NO_2, OC_nH_{2n+1}, $N(C_mH_{2m+1})_2$; $n = 4$ or 8; $m = 1$ or 4) have been measured, and the influence of the position of donor and acceptor groups is discussed and compared with that of the free imine ligands. The value of the hyperpolarizability (β) is raised only when a strong donor group is located in the cyclometalated ring. Moreover, the β value has been enhanced, too, in the cyclopentadienyl monomer complex by as much as 80% with respect to the β value of the corresponding free imine. The molecular structure of $[Pd_2(\mu\text{-}Cl)(\mu\text{-}SC_4H_9)(N(C_4H_9)_2C_6H_3\text{-}CH{=}NC_6H_4NO_2]$ has been determined by an X-ray diffraction analysis.

Introduction

There is currently considerable interest in the development of new molecular materials with nonlinear optical properties.[1,2] The first-order hyperpolarizability (β) of a molecule is associated with the donor−acceptor characteristics of the substituents and with the nature of the conjugation path linking these substituents. The introduction of a metal center as a donor or acceptor subunit may lead to large nonlinear responses.[3] However, there are very few studies concerning the influence of a metal located in the conjugation path.

Benzilideneanilines are very polarizable systems that can be easily derivatized by the introduction of donor and acceptor groups at the ends of the molecule, thus making them suitable for second harmonic generation. However, their nonlinear optical activity is reduced by a loss of conjugation derived from the noncoplanarity of the arylic rings and the iminic double bond.

Imine orthometalation is a well-known reaction frequently used in our research group. The cyclometalation forces the metalated ring and the iminic bond to be coplanar, resulting in a more planar molecule, with a higher degree of conjugation and, thus, more polarizable. This effect has been already used in our previous

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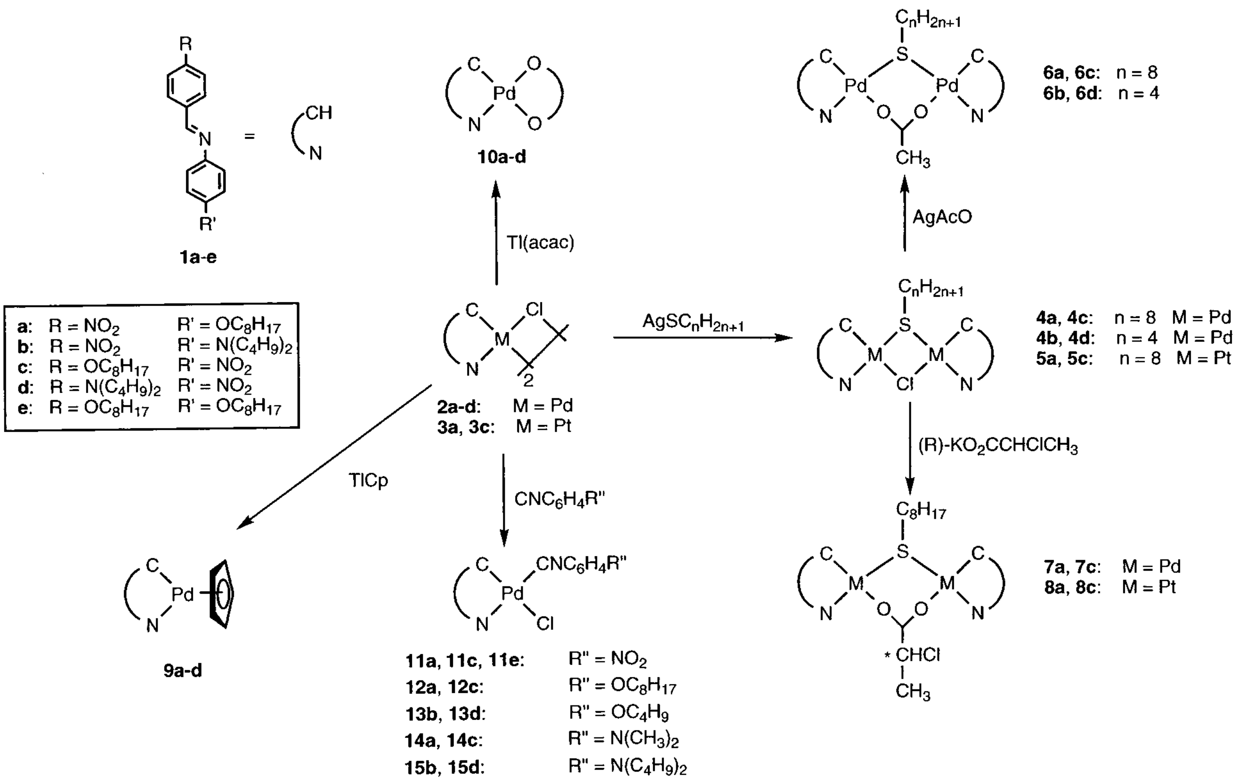
Scheme 1



work for the synthesis of liquid crystals,[4] and we can reasonably expect that such "planarization" can be advantageous to obtain molecules with increased first-order hyperpolarizability.

We have therefore synthesized a new series of dimeric palladium and platinum complexes with mixed bridges (chloro–thiolato or thiolato–carboxylato). In these derivatives the two imine moieties in the dimer have a cisoid disposition, which leads to positive addition of the nonlinear effects from each moiety. Moreoever, we have studied the influence of the introduction of a new ligand in the orthopalladated imine system on the nonlinear optical behavior. To this end, we have obtained monomeric complexes with cyclopentadienyl, acetylacetonato, and isonitrile ligands.

Synthesis and Structures

The compounds studied in this work were synthesized starting from the corresponding chloro-bridged complexes as shown in Scheme 1.

Reaction of **2** and **3** with silver alkanethiolate leads to the dinuclear complexes containing mixed chloro–thiolato bridges. The palladium chloro–thiolato-bridged complexes **4** react with silver acetate (1:1) or potassium (*R*)-2-chloropropionate (1:1.1) yielding the mixed-bridge thiolato–carboxylato complexes **6** and **7**. The platinum thiolato–chloropropionato-bridged complexes **8** have been prepared in a similar way, but the thiolato–acetato complexes were unstable.

The ^1H NMR resonances of the orthometalated imine ligand in the dimeric complexes **4**–**8** indicate their isomeric purity and a cis arrangement of the two imine moieties in these complexes.

The mixed-bridge thiolato–carboxylato complexes with an alkoxy or amino group attached to the cyclometalated ring show a broad signal (or even two signals separated by ca. 0.3 ppm in the case of the complexes with the dibutylamino group) for the first methylene of the chains, as expected for these protons being diastereotopic as a consequence of the folded structure of this kind of complexes, as discussed below (see Figure 1). An upfield shift (0.3–0.5 ppm) of the signals for the aromatic protons next to the dibutylamino group is observed in each case because of the strong electron-releasing properties of this group.

The molecular structure of **6d** was studied by X-ray diffraction (Figure 1, Table 1). The cyclometalated carbon coordinates trans to the oxygen atoms of the bridging carboxylate (in agreement with the usual antisymbiotic behavior of the soft metal atom).[5] The angle between the palladium coordination planes in this structure is 74°, somewhat more opened than that reported for $[Pd_2(CH_2C_9H_6N)_2(\mu\text{-}O_2CCF_3)(\mu\text{-}SBu^t)]$ ($CH_2C_9H_6N$ = 8-quinolylmethyl) of 55°.[6] The distance between the two palladium atoms is 3.3 Å, so that there is no interaction between the metal centers. The palladium–carbon distances are very similar to those found in other imine orthopalladated complexes.[7,8] Selected bond distances and angles are given in Table 2.

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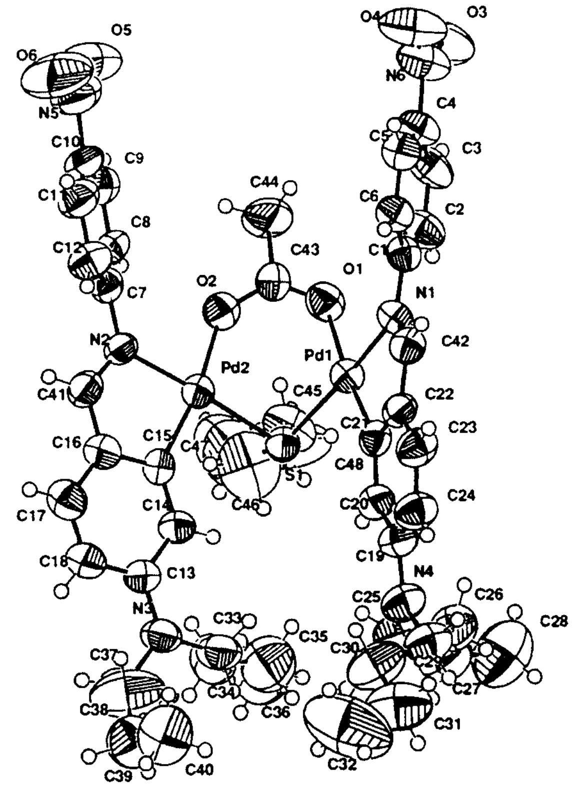

Figure 1. Molecular structure of **6d**, showing the labeling scheme.

Table 1. Details of the Crystal Structure Determination of 6d

chem formula: $C_{48}H_{64}N_6O_6Pd_2S$
cryst syst: triclinic
$a = 11.401(5)$ Å
$b = 13.678(9)$ Å
$c = 17.988(10)$ Å
$\alpha = 74.37(8)°$
$\beta = 81.42(3)°$
$\gamma = 66.34(5)°$
$V = 2471(2)$ Å^3
$Z = 2$

fw = 1065.91
space group: $P\bar{1}$
$T = 293(2)$ K
$\lambda = 0.710\ 73$ Å
$D_x = 1.432$ Mg m^{-3}
$\mu = 0.822$ mm^{-1}
$F(000) = 1100.0$
$R1 = 0.0384$
$wR2 = 0.0793$

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 6d

Pd(1)–C(21)	1.960(8)	Pd(2)–C(15)	1.973(7)
Pd(1)–N(1)	2.098(6)	Pd(2)–N(2)	2.094(6)
Pd(1)–O(1)	2.130(6)	Pd(2)–O(2)	2.112(13)
Pd(1)–S(1)	2.277(3)	Pd(2)–S(1)	2.295(2)
S(1)–C(45)	1.818(8)		
C(21)–Pd(1)–N(1)	81.5(3)	C(15)–Pd(2)–N(2)	82.5(3)
C(21)–Pd(1)–O(1)	173.6(3)	C(15)–Pd(2)–O(2)	166.2(6)
C(21)–Pd(1)–S(1)	92.3(3)	C(15)–Pd(2)–S(1)	93.3(2)
N(1)–Pd(1)–O(1)	92.6(2)	N(2)–Pd(2)–O(2)	91.8(4)
N(1)–Pd(1)–S(1)	167.6(2)	N(2)–Pd(2)–S(1)	174.4(2)
O(1)–Pd(1)–S(1)	94.0(2)	O(2)–Pd(2)–S(1)	93.2(4)
Pd(1)–S(1)–Pd(2)	92.45(10)		

Table 3. Linear and Nonlinear Optical Properties of the Imine Ligands $RC_6H_4CH{=}NC_6H_4R'$ (1)

compd	λ_{max} (nm)	ϵ (L mol^{-1} cm^{-1})	μ (D)	β (10^{-30} cm^5 esu^{-1})	$\beta(0)$ (10^{-30} cm^5 esu^{-1})
1a	383	21 400	4.4	36 ± 5	22 ± 3
1b	474	32 400	6.6	187 ± 11	82 ± 5
1c	345	37 000	5.7	35 ± 4	24 ± 3
1d	416	34 200	7.9	69 ± 6	38 ± 3

The chloro–thiolato-bridged complexes must be planar in the solid state, assuming that their structure is similar to that determined by X-ray diffraction for the analogous complex without the nitro group.[8] However, some chloro–thiolato complexes (**4d** with palladium and **5c** with platinum, both with the corresponding donor group located in the cyclometalated ring) also show the first methylene protons of the chains as diasterotopic, because at room temperature the dynamic process that averages the molecule to planar is slow on the NMR time scale. High-temperature (320 K) NMR experiments on a similar complex without a nitro group ($[Pt_2(\mu\text{-}SC_6H_{13})(\mu\text{-}Cl)(L_6)_2]$, $L_6 = H_{13}C_6OC_6H_3CH{=}NC_6H_4\text{-}OC_6H_{13}$)[9] show the signal of the first methylene as a virtual triplet, confirming the above statement.

The mononuclear species **9**–**15** are obtained by reaction of the dinuclear chloro complexes with [TlCp], [Tl(acac)], and the corresponding isonitrile.

Their ^{1}H NMR spectra are very similar to those of the dimeric complexes. They display the characteristic signals of the aromatic protons of the cyclometalated ring, the arylic ring attached to the iminic nitrogen and the alkyl chains, and the corresponding signals of the introduced ligand. Thus, for the acetylacetonato complexes a singlet at ca. 5.4 ppm corresponding to the α proton and two singlets at ca. 2.1 and 1.9 ppm (that integrate as 3 H) for the inequivalent methyl groups are observed. For the cyclopentadienyl derivatives a singlet at ca. 5.8 ppm that integrates as 5 H is observed as expected. In the isonitrile derivatives two pseudodoublets appear, corresponding to the AA′XX′ system of the isonitrile. When the isonitrile has an alkoxy group, the corresponding signals of the aliphatic chains are observed. To elucidate the position of the isonitrile moiety in the complexes, a NOE experiment was performed on compound **14a**. With irradiation of the H^3 signal of the cyclometalated ring, a NOE effect on one pseudodoublet of the aromatic ring of the isonitrile can be observed. This allows us to assign a trans disposition of the isonitrile with respect to the iminic nitrogen, as can be expected from the antisymbiotic behavior usually found in palladium complexes.

Nonlinear Optical Properties

The linear and nonlinear optical properties of the free imines and the imine palladium and platinum complexes are collected in Tables 3–6.

The imine ligands (Table 3) display higher values of the hyperpolarizability (β) when the donor–acceptor substituents of π-conjugated rings are strong (derivatives **1b,d**). Moreover their β values are greater when the strong donor group is located in the ring joined to the iminic nitrogen (**1b**), as expected according to Dewar's rules.[10] The same tendency is observed when the imine ligands are orthometalated to give dimeric (Table 4) and monomeric (Tables 5 and 6) palladium and platinum complexes.

If the β values of metal complexes are compared with those corresponding to the free imines, it is observed that complexation produces a slight decrease of β per imine unit for the dimeric compounds except in some complexes containing the strong donor–acceptor groups NBu_2 and NO_2 situated respectively in the aldehydic

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Table 4. Linear and Nonlinear Optical Properties of the [$M_2(\mu\text{-}SC_nH_{2n+1})(\mu\text{-}X)(RC_6H_3CH{=}NC_6H_4R')_2$] Complexes (4–8)

compd	λ_{max} (nm)	ϵ (L mol^{-1} m^{-1})	μ (D)	β (10^{-30} cm^5 esu^{-1})	% var^a	$\beta(0)$ (10^{-30} m^5 esu^{-1})	% var $\beta(0)^a$
4a	378	21 300	6.3	56 ± 1	−22	35 ± 1	−20
4b	501	39 100	13.1	260 ± 17	−30	99 ± 6	−40
4c	400	24 900	7.7	52 ± 3	−26	30 ± 2	−37
4d	464	153 100	17.1	217 ± 45	+57	99 ± 10	+30
5a	377	22 800	10.8	42 ± 4	−42	26 ± 2	−41
5c	349	26 400	9.5	54 ± 12	−23	37 ± 8	−23
6a	375	20 700	7.7	54 ± 3	−25	34 ± 2	−22
6b	498	27 200	15.7	212 ± 20	−43	82 ± 8	−50
6c	404	26 300	8.6	52 ± 6	−26	30 ± 3	−37
6d	466	104 200	13.1	192 ± 23	+39	87 ± 10	+10
7a	375	21 100	8.6	41 ± 2	−43	26 ± 1	−41
7c	400	27 500	9.4	47 ± 2	−33	27 ± 1	−44
8a	373	20 700	12.5	26 ± 7	−64	16 ± 4	−63
8c	349	32 200	10.0	59 ± 11	−16	40 ± 7	−17

[a] % var β refers to the change of β values as compared to $2\beta_{imine}$.

Table 5. Linear and Nonlinear Optical Properties of the [$ML(RC_6H_3CH{=}NC_6H_4R')$] (L = Cp or acac) Complexes (9, 10)

compd	λ_{max} (nm)	ϵ (L mol^{-1} cm^{-1})	μ (D)	β (10^{-30} cm^5 esu^{-1})	% var β^a	$\beta(0)$ (10^{-30} cm^5 esu^{-1})	% var $\beta(0)^a$
9a	405	22 800	6.6	32 ± 11	−11	18 ± 6	−18
9b	494	54 700	9.8	154 ± 13	−18	61 ± 5	−25
9c	413	45 100	5.6	43 ± 23	+23	24 ± 13	0
9d	483	68 100	7.7	167 ± 7	+142	70 ± 3	+84
10a	396	13 500	6.3	27 ± 3	−25	16 ± 2	−27
10b	502	20 000	9.1	135 ± 14	−28	51 ± 5	−38
10c	418	14 400	3.6	21 ± 2	−40	12 ± 1	−50
10d	486	60 700	7.7	141 ± 10	+104	58 ± 4	+53

[a] % var β refers to the change of β values as compared to β_{imine}.

Table 6. Linear and Nonlinear Optical Properties of the [$M(RC_6H_3CH{=}NC_6H_4R')Cl(CNC_6H_4R'')$] Complexes (11–15)

compd	λ_{max} (nm)	ϵ (L mol^{-1} cm^{-1})	μ (D)	β (10^{-30} cm^5 esu^{-1})	% var β^a	$\beta(0)$ (10^{-30} cm^5 esu^{-1})	% var $\beta(0)^a$
11a	414	16 100	4.7	48 ± 17	33	27 ± 9	+23
11c	390	15 900	9.2	17 ± 1	−51	10 ± 1	−58
11e	384	11 900	8.1	24 ± 15		15 ± 9	
12a	415	12 800	3.1	10 ± 2	−72	6 ± 1	−74
12c	392	21 900	11.3	29 ± 2	−17	17 ± 1	−29
13b	530	31 400	2.4	263 ± 39	40	83 ± 12	+1
13d	464	59 000	13.2	88 ± 4	27	40 ± 2	+5
14a	382	13 500	2.3	27 ± 7	−25	17 ± 4	−23
14c	385	20 000	12.3	37 ± 6	6	23 ± 4	−4
15b	528	25 400	3.7	111 ± 19	−40	35 ± 6	−57
15d	464	45 100	15.4	83 ± 7	20	38 ± 3	0

[a] % var β refers to the change of β values as compared to β_{imine}.

and the anilinic rings (**4d**, **6d**, **9d**, and **10d**). These last complexes show a clear enhancement of the β values.

The understanding of how molecular design is related to β has been provided by the two-level model:[11]

$$\beta = \frac{3e^2}{16\hbar m\pi^3 c^3} f\Delta\mu\lambda^3{}_0 \frac{1}{(1-(2\lambda_0/\lambda)^2)(1-(\lambda_0/\lambda)^2)} = \beta(0)\frac{1}{(1-(2\lambda_0/\lambda)^2)(1-(\lambda_0/\lambda)^2)}$$

where e and m are the charge and the mass of the electron, respectively, c is the velocity of light, f is the oscillator strength of the charge-transfer transition, $\Delta\mu$ is the difference between excited- and ground-state dipole moments, λ_0 is the wavelength corresponding to the charge-transfer transition, and λ is the fundamental wavelength of the laser beam.

This model predicts that β increases with the wavelength of the charge-transfer absorption. Although the two-level model is an oversimplification for molecule-based second nonlinear optical chromophores, it does provide some qualitative insight into the second-order nonlinear optical properties of organic and organometallic compounds.

The orthometalation of these ligands in the dinuclear metal complexes produces in general a red shift for λ_{max}, except for the derivatives with the donor group OC_8H_{17} located in the anilinic ring (**4a**, **5a**, **6a**, **7a**, and **8a**). Although some care has to be exercised when these kinds of results are discussed, because nonlinear behavior is influenced by several electron factors, a red shift upon complexation implies lower energy difference between the LUMO and HOMO orbitals of the complexed imine group, and consequently, an enhancement of the β value is to be expected. Such a behavior can be easily predicted by considering that the orthometalation forces coplanarity of the aldehydic ring with the imine double bond, then increasing the conjugation on the molecule. This effect can be reinforced by participation of the metal orbitals: It has been shown recently that there is a certain level of aromaticity within the five-membered palladacycle of orthopalladated imines.[12] Thus, an increase of the intraligand charge transfer should produce an enhancement of λ_{max}, in agreement with the general trend observed.

Another factor that influences the magnitude of the molecular hyperpolarizability is the extinction coefficient ϵ_{max}, related to oscillator strength f and mainly governed by the extent of overlap between the HOMO and LUMO orbitals.[13] Thus, the metal complexes that display greater ϵ_{max} values respect to the free imine ligands (**4d** and **6d**) should show the more important increasing of hyperpolarizability, as observed.

On the other hand, the Pd atom acts as an electron acceptor, mainly through its bond with the iminic nitrogen, as it has been proved in orthopalladated ferrocenylimines by means of Mössbauer spectroscopy.[14] This withdrawal of electron density by the palladium atom should make the charge-transfer more difficult and therefore diminish the β value.

This compensation of the induced coplanarity of the aldehydic ring and the iminic double bond by the withdrawal of electron density by the palladium atom, as well as other effects that may be produced, is responsible for the relative decrease of β values per imine units upon complexation in the case of dimers. Only the presence of the strong donor group NBu_2 attached to the aldehydic ring leads to a significant increase of β as compared to the free imine.

The nonlinearity of the system may be improved by increasing the electronic density on the Pd atom, thus reducing its undesired acceptor behavior, or by the introduction of a new chelate ring in order to extend

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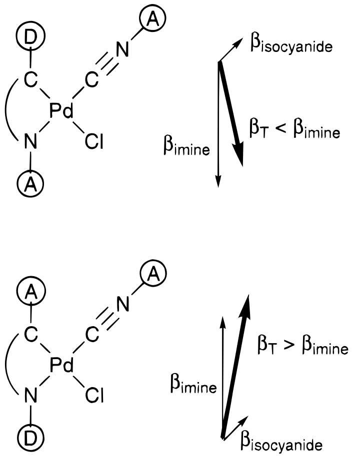

Figure 2. Sketches of the relative orientations of the first-order hyperpolarizability β vectors for isocyanide-substituted compounds (**11**).

the electronic delocalization. With this ideas in mind we have synthesized a new series of derivatives with the good π-donor cyclopentadienyl group (**9a**−**d**) or acetylacetonato ligand (acac) (**10a**−**d**) and measured their optical properties (Table 5).

The relationship between the β value of the monomeric complexes and the free imines follows the same trend observed in the dimeric complexes: β enhancement is observed only when the donor group is dibutylamino and is located in the cyclometalated ring, reaching a value 80% higher than β_{imine} in the cyclopentadienyl complex **9d** and 50% higher than β_{imine} in the acetylacetonato complex **10d**.

However, in the Cp and acac derivatives it must be taken into account that the EFISH experiment measures the vector projection of the β tensor along the molecular dipole axis, μ. In these monomeric complexes, the charge transfer and dipole axes are not parallel to each other, resulting in experimentally determined β_μ values that are smaller than the contribution of β along the CT axis.[15]

The last series of compounds synthesized (**11**−**15**) contains an isonitrile substituted with appropriate donor and acceptor groups that introduces a new charge transfer in the system. In a first approach one can consider the total effect as a vectorial addition of the imine and isonitrile contributions.

The experimental values of the linear and nonlinear optical properties (Table 6) show that in some cases the β value of the complex is higher than the corresponding value of the free imine. The fact that the other compounds show a smaller β value may be explained by the nonparallelism of dipole moment and β vectors as discussed previously for Cp and acac derivatives.

The behavior observed in this series of compounds may be summarized as follows: When the angle between the charge transfer in the imine and in the isonitrile is less than 90°, the two contributions add positively and $\beta_{measured}$ is higher than β_{imine}. On the contrary, when the angle between the two charge transfers is higher than 90°, the hyperpolarizabilities are subtracted and $\beta_{measured}$ is smaller than β_{imine} (Figure 2).

The replacement of Pd in the dimeric complexes with Pt does not change significantly the magnitude of the molecular hyperpolarizability. This behavior has also been observed for the series $M(CO)_4$(1,10-phenantroline) (M = Cr, Mo, W) despite the MLCT nature of the relevant CT excited state.[16] However EFISH measurements of complexes bearing a ferrocene donor group and a metal halide acceptor group reported by Balavoine indicate that β slightly increases along the series Ni(II) < Pd(II) < Pt(II).[17] Eisenberg also reported a series of M(diimine)(dithiolate) complexes in which Pt(II) complexes display enhanced β values over Pd(II) analogues.[18] These different trends indicate that an understanding of how metal d orbitals affect molecular hyperpolarizabilities requires further studies on organometallic chromophores.

Experimental Section

Literature methods were used to prepare bis(μ-chloro)bis(η^3-(2-methylallyl)platinum),[19] potassium (*R*)-2-chloropropionate,[20] $AgSC_nH_{2n+1}$,[21] thallium cyclopentadienyle,[22] and thallium acetylacetonate.[23]

The imines used to prepare the complexes were synthesized by *p*-toluenesulfonic acid-catalyzed condensation of the corresponding aldehyde and amine in toluene.[24] They were reacted with palladium acetate to prepare the acetato-bridged complexes from which the chloro-bridged derivatives (**2**) can be obtained by reaction with HCl by following literature methods.[25]

The dinuclear platinum chloro-bridged complexes **3** are prepared directly by reaction of the corresponding imine with $[Pt_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_4H_7)_2]$ by following a method already reported by us.[9]

Column chromatography was performed with silica gel (230−400 mesh ASTM). Infrared spectra were run on a Perkin-Elmer 883 or 1720 X spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker AC 300 and on an ARX 300 spectrometer at room temperature. Chemical shifts are expressed in parts per million upfield from $Si(CH_3)_4$. UV−vis spectra were run on a Shimadzu UV-160A spectrophotometer. Combustion analyses were made with a Perkin-Elmer 2400 CHN elemental analyzer.

EFISH Measurements. Second-order molecular hyperpolarizability analyses were performed using a Q-switched mode-locked Nd:YAG laser operating at 1.34 μm by the electric field induced second harmonic generation method.[26] The laser delivers 60 ns pulses focused onto a liquid cell and synchronized with a dc field applied to a solution containing the chromophore. By translation of the cell perpendicularly to the incident beam, the variation of the propagation length in the

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solution creates Maker fringes, whose amplitude and periodicity are related to the nonlinearity of the solution. The experiment was performed for each compound, by using solutions of increasing concentrations ($x = 10^{-4}-5 \times 10^{-3}$ mol/L) in chloroform.

The ground-state dipole moment was determined by the standard method of Guggenheim.[27] Further details of the experimental methodology and data analyses are reported elsewhere.[28]

Representative preparation procedures are given below as the syntheses were similar for the rest of the complexes. Spectral and analytical data for all compounds have been included as Supporting Information.

[$M_2(\mu\text{-SR})(\mu\text{-Cl})(L_n)_2$] (4, 5). To a suspension of **2** or **3** (0.296 mmol) in 30 mL of dichloromethane was added the corresponding AgSR (0.300 mmol). The mixture was stirred in the dark for 12 h at room temperature. After the AgCl precipitate was filtered off, ethanol (10 mL) was added, and the resulting solution was concentrated to a small volume on a rotary evaporator. A solid appeared which was filtered off, washed with ethanol (2 × 3 mL), and air-dried.

[$Pd_2(\mu\text{-}SC_8H_{17})(\mu\text{-OAc})(L_n)_2$] (6). To a solution of **2** (0.192 mmol) in 20 mL of dichloromethane was added silver acetate (0.320 g, 0.192 mmol). The workup was as described above affording compounds **6a**−**d**.

[$M_2(\mu\text{-}SC_8H_{17})(\mu\text{-}(R)\text{-ClPr})(L_n)_2$] (7, 8). A mixture of **2** (0.115 mmol) and potassium (*R*)-2-chloropropionate (0.126 mmol) in dichloromethane/acetone (2:1, 30 mL) was stirred for 24 h at room temperature. After removal of the precipitate by filtration, the resulting solution was concentrated to dryness. The residue was triturated in a mixture of dichloromethane/methanol (1:3) to obtain a solid, which was filtered out, washed with 2 × 3 mL of methanol, and air-dried.

[PdCpLn] (9). TlCp (0.030 g, 0.111 mmol) was added to a suspension of **2** (0.101 mmol) in 20 mL of dichloromethane. The mixture was stirred in the dark for 10 h at room temperature. The solution was filtered through Kieselguhr and evaporated to ca. 3 mL under reduced pressure. Addition of ethanol afforded **9** as an orange-red solid, which was filtered out and washed with 2 × 3 mL of ethanol.

[Pd(acac)L_n] (10). To a suspension of **2** (0.192 mmol) in 20 mL of dichloromethane was added the stoichiometric amount of [Tl(acac)] (0.384 mmol). After the mixture was stirred for 2 h, the white precipitate of TlCl was filtered off, the solution was evaporated to dryness, and the residue was stirred with 10 mL of ethanol to give the complexes.

[PdL_n(CNR)Cl] (11−15). To a suspension of **2** (0.101 mmol) in 20 mL of dichloromethane was added the corresponding isonitrile CNR (0.212 mmol). The precipitate immediately disappeared, and the resulting solution was stirred for 15 min. The solvent was taken off under reduced pressure, and the residue was stirred with ethyl ether to obtain a solid, which was filtered off, washed with 2 × 3 mL of ethyl ether and air-dried.

X-ray Crystallographic Analysis of 6d. Details of the structure analysis are listed in Table 1. X-ray diffraction measurements were performed on a single crystal of size 0.17 × 0.26 × 0.10 mm. Throughout the experiment Mo Kα radiation was used with a graphite crystal monochromator on an Enraf-Nonius CAD4 single-crystal diffractometer (λ = 0.710 73 Å). The unit cell dimensions were determined from the angular settings of 25 reflections with θ between 7 and 10°. The space group was determined to be $P\bar{1}$, from the structure determination. The intensity data of 7208 reflections, in *hkl* range (−12, −14, 0) to (12, 15, 19) and θ limits $0 < \theta < 23°$ were measured, using the $\omega-2\theta$ scan technique and a variable scan rate with a maximum scan time of 60 s per reflection. The intensity of the primary beam was checked throughout the data collection by monitoring three standard reflections every 60 min. The final drift correction factors were between 0.983 and 1.048. On all reflections a profile analysis was performed.[29,30] Some double measured reflections were averaged $R_{\text{int}} = \sum I - \langle I \rangle / \sum I = 0.0394$ resulting in 6863 "unique" reflections of which only 3289 were observed with $I > 2\sigma(I)$. Lorentz and polarization corrections were applied, and the data were reduced to $\Omega F_o \Omega$ values. The structure was solved by Patterson methods and phase expansion using DIRDIF.[31] Isotropic least-squares refinement on F^2 was made using SHELXL93.[32] At this stage an empirical absorption correction was applied using XABS.[33] The relative maximum and minimum transmision factors were respectively 0.595 and 1.000.

During the final stages of the refinement the positional parameters and the anisotropic thermal parameters of the non-H atoms were refined. All non-hydrogen atoms were anisotropically refined. All hydrogen atoms were geometrically placed. The final conventional agreement factors were R = 0.0384 and wR2 = 0.080 for the 3289 "observed" reflections and 580 variables. The function minimized was $[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, with $w = 1/[\sigma^2(F_o^2) + (0.0315P)^2 + 2.59P]$, $\sigma(F_o^2)$ from counting statistics, and $P = (\text{Max}(F_o^2,0) + 2F_c^2)/3$. The final difference Fourier map showed no peaks higher than 0.458 e Å^{-3} nor deeper than −0.578 e Å^{-3}. Figure 1 shows the atomic numbering scheme.[34]

Atomic scattering factors were taken from ref 35. Geometrical calculations were made with PARST.[36] All calculations were made at the University of Oviedo on the Scientific Computer Center and X-ray group VAX computers.

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Supporting Information Available: Tables of yields, elemental analyses, and IR and NMR data and, for the crystal structure of **6d**, complete tables of atomic coordinates, thermal parameters, bond distances and angles, and least-squares planes and atomic deviations therefrom (20 pages). Ordering information is given on any current masthead page.

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