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Quadratic Hyperpolarizability Enhancement of *para*-Substituted Pyridines upon Coordination to Organometallic Moieties: The Ambivalent Donor or Acceptor Role of the Metal

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Coordination of *para*-substituted pyridines 4-X-C_5H_4N (where X = NMe_2, CMe_3, H, COMe, CN) to metal carbonyl moieties such as "*cis*-$M(CO)_2Cl$" (M = Rh(I), Ir(I)) and "*fac*-$Os(CO)_3Cl_2$" produces an enhancement up to about 2 orders of magnitude of the quadratic hyperpolarizability β_λ of the free pyridine. This effect is due either to a red shift of the intraligand charge-transfer (ILCT) transition upon coordination (when X is a strong electron donor) or to a significant effect on the metal-to-ligand charge-transfer (MLCT) transitions (when X is a strong electron acceptor). In this latter case the quadratic hyperpolarizability may assume a negative sign, due to the negative value of $\Delta\mu_{eg}$ upon excitation. Therefore we confirmed that as already shown by metal carbonyl moieties such as "$M(CO)_5$" (M = Cr, W), a soft metal center displays, from the point of view of the perturbation of the quadratic hyperpolarizability of pyridines, an ambivalent acceptor or donor role. The quadratic hyperpolarizability of complexes of more π-delocalized *para*-substituted pyridine ligands (where X = *trans*- or *trans,trans*-$(CH{=}CH)_nC_6H_4$-4′-NMe_2 with $n = 1$ or 2) involving the same carbonyl Rh(I), Ir(I), and Os(II) moieties corresponds to an enhancement with respect to the free ligands of about 1.5−2.3 times that when $n = 1$ and 1.5−1.7 times that when $n = 2$. This enhancement, which is relatively low when compared to simple pyridines, is dependent upon the length of the π-delocalized bridge (it decreases with increasing n) and upon the nature of the metal center (oxidation state and ligand coordination sphere). Some of the complexes investigated show significant values (between 400×10^{-30} and 600×10^{-30} D cm^5 esu^{-1}) of the product $\mu\beta_0$.

Introduction

Although coordination and organometallic molecules may theoretically offer some advantages as compared with organic molecules for nonlinear optical applications,[1,2] basic molecular engineering schemes for the design of second-order nonlinear optical (NLO) organometallic molecules are not so well defined as for specific organic structures.[3] For instance in the latter case, pseudolinear π-delocalized organic systems substituted by donor and acceptor groups at the two ends show significant second-order NLO responses due to reduced energy gap between ground and intramolecular charge-transfer excited states, together with large oscillator strengths and a significant difference between ground and excited-state dipole moments.[4] These properties, which can be finely tuned by working on the details of the molecular structure, can lead to large quadratic hyperpolarizabilities described in first approximation by the so-called two-level model.[5]

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As the development of molecular engineering rules for purely organic systems has become more predictive, the investigation of the effects produced by the introduction of an organometallic or coordination chromophore has attracted increasing attention.[1,2] For instance in the past few years, many organometallic molecules or coordination compounds with ligands such as stilbazoles,[6−9] pyridines,[6,7,9] bipyridines,[10] Schiff bases,[11] and diimines,[12] or metal complexes with large π-delocalized ligands such as phthalocyanines[13] and porphyrins,[14] have been studied as potential second-order NLO materials. However, with the exception of some studies on complexes with pyridines and stilbazoles,[7] Schiff bases,[11] and porphyrins,[14] the understanding of the electronic origin of increased second-order NLO properties is still limited and far from being rationalized in terms of preferred molecular architectures. Therefore we have focused our investigation on an extended analysis of the role of the nature of a soft metal center and of its coordination sphere on the quadratic hyperpolarizability of metal-coordinated *para*-substituted pyridines. In particular, the effect of the versatility of the metal center (electron configuration and oxidation state) and of its coordination sphere was investigated by studying various carbonyl or organometallic Rh(I) ($4d^8$), Ir(I) ($5d^8$), and Os(II) ($5d^6$) complexes with *para*-substituted pyridines as one of the ligands.

A metal carbonyl or an organometallic fragment could act, when the ligand is covalently bonded and weakly coupled to the metal via its π-system, as an inductive electron-acceptor species, depending on the electron configuration of the metal, on its oxidation state, and on its ligand environment. However in the excitation process the metal can act as an electron donor via a $d \rightarrow \pi^*$ charge transfer.[7] These factors influence the nature of the charge-transfer processes between the metal and the pyridine ligands or even inside the ligands themselves, producing a significant effect on the quadratic hyperpolarizability of the pyridine ligands, as already shown in the case of some *para*-substituted pyridines or stilbazoles, when coordinated to organometallic or inorganic fragments, such as “$M(CO)_5$” (M = Cr, W)[6,7] or BR_3 (R = F, C_6F_5).[9] Only one report describes briefly the effect of coordination of *trans*-4-(*S*-(+)-2-methylbutoxy)-4′-stilbazole to the “$Rh(CO)_2Cl$” and “$Ir(CO)_2Cl$” moieties.[8a] In all these cases, β_{vec}, the vectorial projection of the quadratic hyperpolarizability tensor of the pyridine or stilbazole ligand along the ground-state molecular dipole moment (μ) direction, measured by the solution-phase dc electric-field-induced second-harmonic (EFISH) generation method,[15] increases upon coordination to a metal, although by a rather different extent depending on the kind of inorganic or organometallic chromophore.

Starting from the fundamental work of T. J. Marks et al.,[7] the aim of our work is to enrich by a rather systematic investigation the knowledge of what kind of molecular properties of coordination complexes or organometallic species with different *para*-substituted pyridines are necessary to tailor second-order NLO properties up to a maximum level.

Results and Discussion

1. Characterization of Some Ground-State Properties of the Organometallic Complexes. We investigated a series of complexes, (i) *cis*-[$M(CO)_2Cl(4\text{-}X\text{-}C_5H_4N)$] (M = Rh, Ir) (X = NMe_2, CMe_3, H, CN, *trans*-$CH{=}CHC_6H_4$-4′-NMe_2, *trans, trans*-$(CH{=}CH)_2C_6H_4$-4′-NMe_2) and (ii) [$Rh(COD)Cl(4\text{-}X\text{-}C_5H_4N)$] and *cis*-[$Ir(COT)_2Cl(4\text{-}X\text{-}C_5H_4N)$] (COD = cyclooctadiene; COT = cyclooctene; X = *trans*- or *trans,trans*-$(CH{=}CH)_nC_6H_4$-4′-NMe_2, where n = 1 or 2), readily prepared by room-temperature reaction of the pyridine ligand with the appropriate dimeric organometallic complex ($[Ir(CO)_2Cl]_2$,[16] $[Ir(COT)_2Cl]_2$,[17] $[Rh(CO)_2Cl]_2$,[18] $[Rh(COD)Cl]_2$[19]). We also investigated *fac*-[$Os(CO)_3Cl_2(4\text{-}X\text{-}C_5H_4N)$] (X = NMe_2, CMe_3, H, COMe, CN, *trans*- and *trans,trans*-$(CH{=}CH)_nC_6H_4$-4′-NMe_2, where n = 1 or 2) prepared by room-temperature reaction of the pyridine ligand with α-$[Os(CO)_3Cl_2]_2$[18b,20] followed by chromatographic purification of the *fac* isomer. The ligands 4,4′-*trans*- or *trans,trans*-$NC_5H_4(CH{=}CH)_nC_6H_4NMe_2$, where n = 1 or 2, and all complexes were characterized by elemental analysis, infrared (Table 1), ^1H NMR, and UV−visible spectroscopies; in some cases mass spectrometry and ^{13}C NMR spectroscopy (see Experimental Section) were used. Dipole moments were determined in $CHCl_3$ by the standard Guggenheim method[21] (Tables 2 and 3).

Infrared Spectra and Dipole Moments. For complexes *cis*-[$M(CO)_2Cl(4\text{-}X\text{-}C_5H_4N)$] (M = Rh, Ir) and *fac*-

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Table 1. Effect of the Nature of the Substituent X on the Carbonyl Stretching Frequencies of *cis*-[$M(CO)_2Cl(4\text{-}X\text{-}C_5H_4N)$] (M = Rh, Ir) and *fac*-[$Os(CO)_3Cl_2(4\text{-}X\text{-}C_5H_4N)$]

substituent X	"$Ir(CO)_2Cl$"[a] ν_{CO} (cm^{-1})	"$Rh(CO)_2Cl$"[b] ν_{CO} (cm^{-1})	"$Os(CO)_3Cl_2$"[b] ν_{CO} (cm^{-1})
NMe_2	2070(s) 1989(s)	2082(s) 2006(s)	2123(s) 2045(s) 2020(s)
4′-*trans*-$CH{=}CHC_6H_4NMe_2$	2074(s) 1994(s)	2086(s) 2011(s)	2126(s) 2049(s) 2023(s)
4′-*trans,trans*-$(CH{=}CH)_2C_6H_4NMe_2$	2074(s) 1994(s)	2086(s) 2011(s)	2126(s) 2050(s) 2024(s)
CMe_3	2076(s) 1995(s)	2087(s) 2013 (s)	2126(s) 2050(s) 2024(s)
H	2077(s) 1996(s)	2088(s) 2014(s)	2128(s) 2051(s) 2025(s)
COMe	2079(s) 2001(s)	2091(s) 2016(s)	2128(s) 2054(s) 2027(s)
CN	2080(s) 2002(s)	2092(s) 2018(s)	2120(s) 2055(s) 2028(s)

[a] In CH_3CN; for [$Ir(CO)_2Cl]_2$: ν_{CO} = 2084(s), 2008(s) cm^{-1}. [b] In CH_2Cl_2; for [$Rh(CO)_2Cl]_2$: ν_{CO} = 2109(w), 2092(s), 2036(s) cm^{-1}; for β-[$Os(CO)_3Cl_2]_2$: ν_{CO}= 2128(m), 2048(s), 2035(s) cm^{-1}.

Table 2. Dipole Moments and EFISH β_λ of Various *para*-Substituted Pyridines and Their Rh(I), Ir(I), Os(II), and W(0) Complexes

molecule	μ[a] (D)	$\mu\beta_{1.06}$[b] (10^{-30} D cm^5 esu^{-1})	$\beta_{1.06}$[b] (10^{-30} cm^5 esu^{-1})	$\beta_{1.91}$[c] (10^{-30} cm^5 esu^{-1})
4-NMe_2-C_5H_4N	3.5	0.25[d]	0.07[d]	0.06[d]
cis-[$Ir(CO)_2Cl(4\text{-}NMe_2\text{-}C_5H_4N)$]	6.4	58	9	6.5
cis-[$Rh(CO)_2Cl(4\text{-}NMe_2\text{-}C_5H_4N)$]	5.9	51	8.7	6.4
fac-[$Os(CO)_3Cl_2(4\text{-}NMe_2\text{-}C_5H_4N)$]	7.7	46	6	4.4
4-CMe_3-C_5H_4N	2.87[e]	0.40[f]	0.19[f]	0.17[f,g]
cis-[$Ir(CO)_2Cl(4\text{-}CMe_3\text{-}C_5H_4N)$]	4.9	0.49	0.1	
cis-[$Rh(CO)_2Cl(4\text{-}CMe_3\text{-}C_5H_4N)$]	4.0	ca. 0	ca. 0	
[$W(CO)_5(4\text{-}^nBu\text{-}C_5H_4N)$]	7.3[h]			−3.4[h]
C_5H_5N	2.20[e]	−0.35[f]	−0.17[f]	−0.13[f]
cis-[$Rh(CO)_2Cl(C_5H_5N)$]	4.8	12	2.6	
fac-[$Os(CO)_3Cl_2(C_5H_5N)$]	5.6	ca. 0	ca. 0	
[$W(CO)_5(C_5H_5N)$]	6.0[h]			−4.4[h]
4-MeCO-C_5H_4N	2.41[e]	−0.07[f]	−0.029[f]	−0.032[f]
fac-[$Os(CO)_3Cl_2(4\text{-}MeCO\text{-}C_5H_4N)$]	4.7	ca. 9	ca. 2	
[$W(CO)_5(4\text{-}MeCO\text{-}C_5H_4N)$]	4.5[h]			−9.3[h]
4-CN-C_5H_4N	1.63[e]	0.36[f]	0.33[f]	
cis-[$Ir(CO)_2Cl(4\text{-}CN\text{-}C_5H_4N)$]	3.4	−31	−9	
cis-[$Rh(CO)_2Cl(4\text{-}CN\text{-}C_5H_4N)$]	2.9	−12	−4.3	
fac-[$Os(CO)_3Cl_2(4\text{-}CN\text{-}C_5H_4N)$]	4.2	ca. 8	ca. 2	

[a] Experimental values in $CHCl_3$. [b] EFISH values measured in $CHCl_3$ at 1.06 μm, according to the "phenomenological convention".[29a] [c] $\beta_{1.06\,\mu m}$ converted to $\beta_{1.91\,\mu m}$ by the two-level expression (eq 2),[5] unless otherwise stated. [d] β measured by EFISH at 1.34 μm and converted to $\beta_{1.06\,\mu m}$ or $\beta_{1.91\,\mu m}$ with the two-level expression.[5] [e] Experimental values from ref 44; in C_6H_6, except 4-CMe_3-C_5H_4N determined in CCl_4. [f] Computed values by using the MNDO-CPHF methodology (see Table 4). [g] For 4-^nBu-C_5H_4N instead of 4-^tBu-C_5H_4N. [h] Experimental values from ref 6b; $\beta_{1.91\,\mu m}$ measured by EFISH in dioxane ([$W(CO)_5(4\text{-}^nBu\text{-}C_5H_4N)$]), toluene ([$W(CO)_5(C_5H_5N)$]), or $CHCl_3$ ([$W(CO)_5(4\text{-}MeCO\text{-}C_5H_4N)$]).

[$Os(CO)_3Cl_2(4\text{-}X\text{-}C_5H_4N)$], an increase of the electron-donating strength of the pyridine's X substituent leads, as expected, to a decrease of the IR carbonyl stretching frequencies (Table 1) and a parallel increase of the dipole moments (Table 2). These trends can be linked to the strong influence of the substituent X on the electron-donating properties of the pyridine toward the metal carbonyl moiety acting as an electron acceptor, as suggested by the good linear correlation of both carbonyl stretching frequencies and dipole moments with the σ_{para} Hammet constant[22] of the various X substituents (Figures1 and 2).

Interestingly, carbonyl stretching frequencies are lower for related complexes with 4-NMe_2-C_5H_4N than with 4,4′-*trans*- or *trans,trans*-$NC_5H_4(CH{=}CH)_nC_6H_4$-NMe_2 (n = 1 or 2), suggesting that the electron donation of the pyridine ligand decreases when the electron-donor NMe_2 substituent is not directly attached to the pyridine ring, as confirmed by the different increase of the dipole moment that occurs upon coordination of 4-NMe_2-C_5H_4N (for example, upon coordination to "$Os(CO)_3Cl_2$", experimental μ enhancement factor = 2.2, Table 3) or of 4,4′-*trans*- or *trans,trans*-$NC_5H_4(CH{=}CH)_nC_6H_4NMe_2$ (upon coordination to "$Os(CO)_3Cl_2$", experimental μ enhance-

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Table 3. Electronic Spectra, Dipole Moments, and EFISH β_λ of Rh(I), Ir(I), and Os(II) Complexes with 4-NMe$_2$-C$_5$H$_4$N, 4,4′-*trans*- or *trans,trans*-NC$_5$H$_4$(CH=CH)$_n$C$_6$H$_4$NMe$_2$ (n = 1 or 2)

molecule	λ_{max}[a] (nm)	μ[a] (D)	$\mu\beta_0$[b] (10^{-30} D cm^5 esu^{-1})	β_λ[c] (10^{-30} cm^5 esu^{-1})		$\beta_{1.34}$ EF[d]
				$\beta_{1.06}$	$\beta_{1.34}$	
4-NMe$_2$-C$_5$H$_4$N	260	3.5	0.18	0.07[b]	0.06	
[Ir(CO)$_2$Cl(4-NMe$_2$-C$_5$H$_4$N)]	291	6.4	38[e]	9	8[e]	ca. 1.5 × 10^2
[Rh(CO)$_2$Cl(4-NMe$_2$-C$_5$H$_4$N)]	289	5.9	53	8.7	12	ca. 2 × 10^2
				14[b]	8[e]	
[Os(CO)$_3$Cl$_2$(4-NMe$_2$-C$_5$H$_4$N)]	290	7.7	31[e]	6	5[e]	ca. 10^2
4,4′-*trans*-NC$_5$H$_4$CH=CHC$_6$H$_4$NMe$_2$	374	3.9	137	63	55	
				79[b]	44[e]	
[Ir(CO)$_2$Cl(4,4′-*trans*-NC$_5$H$_4$CH=CHC$_6$H$_4$NMe$_2$)]	431	6.0	402	242[b]	128	2.3
[Ir(COT)$_2$Cl(4,4′-*trans*-NC$_5$H$_4$CH=CHC$_6$H$_4$NMe$_2$)]	413	8.1	373	137[b]	82	1.5
[Rh(CO)$_2$Cl(4,4′-*trans*-NC$_5$H$_4$CH=CHC$_6$H$_4$NMe$_2$)]	421	7.0	427	177	111	2.0
				195[b]	101[e]	
[Rh(COD)Cl(4,4′-*trans*-NC$_5$H$_4$CH=CHC$_6$H$_4$NMe$_2$)]	397	6.7	308	119[b]	77	1.4
[Os(CO)$_3$Cl$_2$(4,4′-*trans*-NC$_5$H$_4$CH=CHC$_6$H$_4$NMe$_2$)]	435	7.4	318[e]	160	83[e]	1.5
4,4′-*trans,trans*-NC$_5$H$_4$(CH=CH)$_2$C$_6$H$_4$NMe$_2$	396	4.5	211	124[b]	80	
[Ir(CO)$_2$Cl(4,4′-*trans,trans*-NC$_5$H$_4$(CH=CH)$_2$C$_6$H$_4$NMe$_2$)]	449	8.8	580	285[b]	135	1.7
[Ir(COT)$_2$Cl(4,4′-*trans,trans*-NC$_5$H$_4$(CH=CH)$_2$C$_6$H$_4$NMe$_2$)]	430	7.2	576	280[b]	152	1.9
[Rh(CO)$_2$Cl(4,4′-*trans,trans*-NC$_5$H$_4$(CH=CH)$_2$C$_6$H$_4$NMe$_2$)]	442	6.7	442	262[b]	131	1.6
[Os(CO)$_3$Cl$_2$(4,4′-*trans,trans*-NC$_5$H$_4$(CH=CH)$_2$C$_6$H$_4$NMe$_2$)]	456	8.0	440	260[b]	116	1.5

[a] Experimental values in CHCl$_3$. [b] β measured by EFISH at 1.34 μm, according to the "phenomenological convention",[29a] and converted to β_0 or $\beta_{1.06}$ with the two-level expression (eq 2).[5] [c] $\beta_{1.06}$ and $\beta_{1.34}$ measured by EFISH in CHCl$_3$ at 1.06 and 1.34 μm, respectively, unless otherwise stated. [d] $\beta_{1.34}$ EF is $\beta_{1.34}$ enhancement factor = $\beta_{1.34}$ complex/$\beta_{1.34}$ corresponding free pyridine. [e] β measured by EFISH at 1.06 μm and converted to $\beta_{1.34}$ or β_0 with the two-level expression (eq 2).[5]

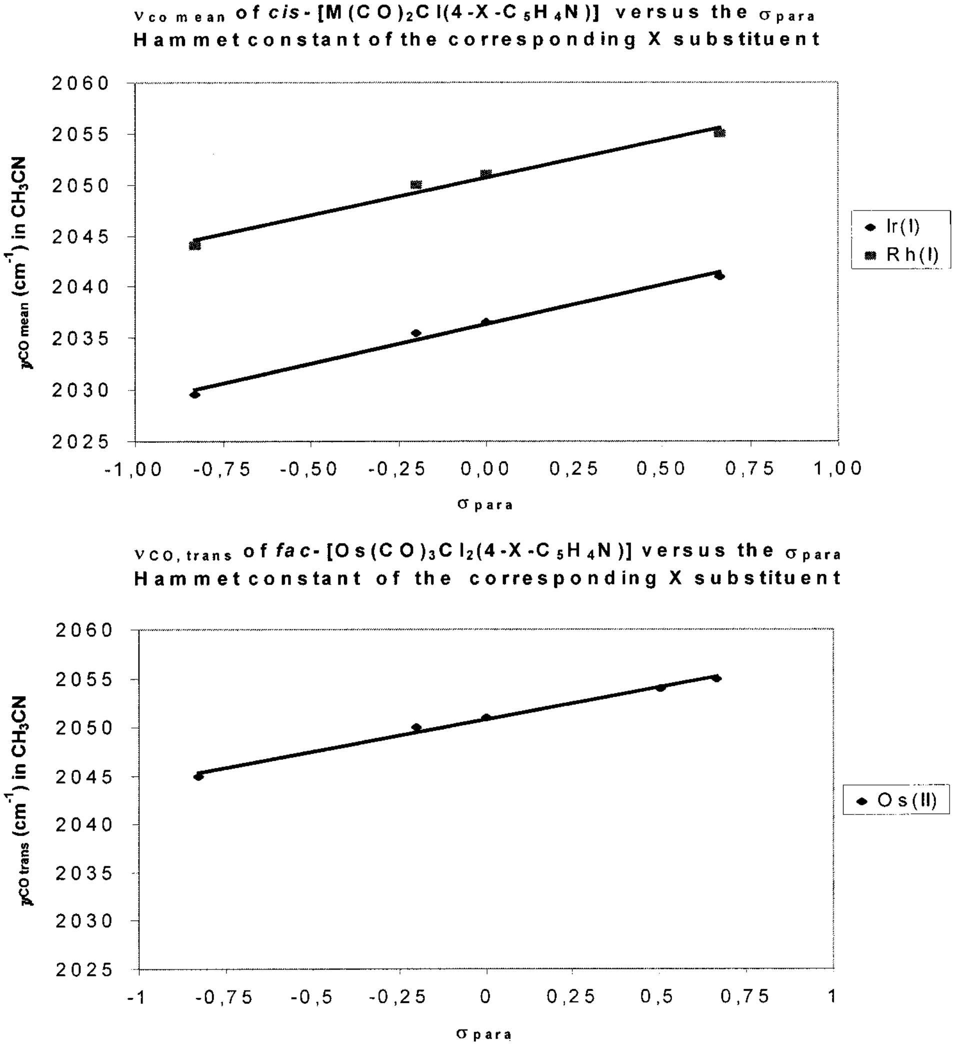

Figure 1. Effect of the pyridine's X substituent on the IR carbonyl stretching frequencies of *cis*-[M(CO)$_2$Cl(4-X-C$_5$H$_4$N)] (M = Rh, Ir) and *fac*-[Os(CO)$_3$Cl$_2$(4-X-C$_5$H$_4$N)].

ment factor = 1.9 (n = 1) and 1.8 (n = 2); Table 3). An increase of the dipole moment (ZINDO-derived μ enhancement factor = 2.6) was also reported to occur upon coordination of 4,4′-*trans*-NC$_5$H$_4$CH=CHC$_6$H$_4$NMe$_2$ to

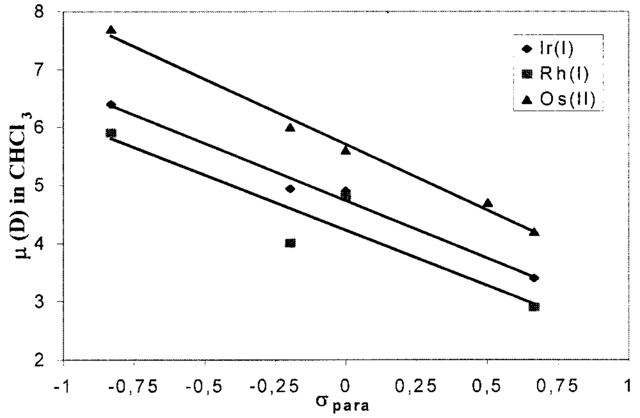

Figure 2. Effect of the pyridine's X substituent on the dipole moment of *cis*-[M(CO)$_2$Cl(4-X-C$_5$H$_4$N)] (M = Rh, Ir) and *fac*-[Os(CO)$_3$Cl$_2$(4-X-C$_5$H$_4$N)].

a softer acceptor center such as "Cr(CO)$_5$",[7] whereas, surprisingly enough, no significant increase was reported to occur upon interaction of this latter ligand or even of 4-NMe$_2$-C$_5$H$_4$N with a hard, strong Lewis acid such as B(C$_6$F$_5$)$_3$ or BF$_3$.[9]

^{1}H NMR Spectra. Comparison of the ^{1}H NMR data (see Experimental Section) of free pyridine ligands with that of the related complexes confirms the electron-accepting character of Rh(I), Ir(I), and Os(II) centers with pyridines bearing strong donor substituents. For example, coordination of 4-NMe$_2$-C$_5$H$_4$N to "M(CO)$_2$Cl" (M = Rh, Ir) and "Os(CO)$_3$Cl$_2$" causes a shift of the signal due to the NMe$_2$ protons (δ = 2.88 ppm) to lower fields (δ = 3.07−3.11 ppm), as expected for a significant increase of the electron donation from the NMe$_2$ group. However, the chemical shift due to the NMe$_2$ protons is similar in the free ligand 4,4′-*trans*-NC$_5$H$_4$CH=CHC$_6$H$_4$NMe$_2$ (δ = 3.04 ppm) and in its metal carbonyl complexes (δ = 3.03−3.05 ppm), adding further evidence to infrared and dipole moment findings which suggest a very limited perturbation of the donor properties of the NMe$_2$ group when these π-delocalized systems interact with Rh(I), Ir(I), or Os(II) metal centers.

The coupling between the *trans* olefinic hydrogens in 4,4′-*trans*-NC$_5$H$_4$CH=CHC$_6$H$_4$NMe$_2$ (J_{H-H} = 16.2 Hz) and 4,4′-*trans,trans*-NC$_5$H$_4$(CH=CH)$_2$C$_6$H$_4$NMe$_2$ (J_{H-H} = 15.4 Hz) is maintained in their metal complexes (see Experimental Section). Therefore the effective π-conjugated planar structure of the organic part is maintained in the metal complexes so that electronic properties can be compared between free and metal-coordinated ligands.

2. Charge-Transfer Bands in UV−Visible Spectra. Since low lying charge-transfer excitations are responsible for large second-order nonlinearities,[3−5] there should be a relationship between nonlinearity and properties of the UV−visible spectra, as was confirmed by the good correlation between the quadratic hyperpolarizability β and λ_{max} of the charge-transfer absorption band for various 4-donor,4′-acceptor-stilbenes.[4] The "W(CO)$_5$" organometallic moiety has been largely studied[6,7] because its complexes with pyridines and related ligands are known to have their metal-to-ligand or intraligand charge-transfer axis parallel to the dipole moment direction,[6b,23] making these systems ideal for studies of the effects on the second-order NLO properties of the ligands by the EFISH technique.[15] This kind of perfect parallelism cannot occur by coordination of the same ligands to "*cis*-M(CO)$_2$Cl" (M = Rh, Ir) and "*fac*-Os(CO)$_3$Cl$_2$" moieties, due to some contribution to the molecular dipole moment of the dipole moments of the "*trans*-(CO)MCl" (M = Rh, Ir, Os) bonds. However these latter contributions are small[24] when compared to that of "MNC$_5$H$_4$X" where X is a strong donor group; therefore their vectorial contribution to the total dipole moment vector should not produce a large deviation of its direction from the charge-transfer axis of the major metal-to-pyridine ligand or intraligand charge-transfer transitions. In agreement with this statement, the deviation angle was calculated to be about 18−19° by ab initio calculations (4-31G basis set) in the case of *cis*-[Ir(CO)$_2$Cl(4,4′-*trans*-NC$_5$H$_4$CHCHC$_6$H$_4$NH$_2$)].

The UV−visible spectra of pyridine or stilbazole ligands carrying the NMe$_2$ donor group and of their metal complexes (recorded in chloroform solution, see Table 3) show one major charge-transfer band, attributed to the intramolecular charge-transfer transition to the lowest energy excited state,[7] which is sensitive to the nature of the metal carbonyl or organometallic moiety. Since this transition emanates from the NMe$_2$ donor end of the molecule,[25] it must be sensitive to an increase in the strength of the acceptor end.

Complexes *cis*-[M(CO)$_2$Cl(4-NMe$_2$-C$_5$H$_4$N)] (M = Rh, Ir) and *fac*-[Os(CO)$_3$Cl$_2$(4-NMe$_2$-C$_5$H$_4$N)] show this relatively intense (log ϵ ca. 4.4) intraligand charge-transfer band (ILCT) in the region 289−291 nm red-shifted ($\Delta\lambda_{max}$ = 29−31 nm) when compared to the ILCT band of the corresponding free pyridine ligand (λ_{max} 260 nm; log ϵ 4.27). Coordination of more π-delocalized ligands such as 4,4′-*trans*- or *trans,trans*-NC$_5$H$_4$(CH=CH)$_n$C$_6$H$_4$-NMe$_2$ (for n = 1, λ_{max} 374 nm and log ϵ 4.50; for n = 2, λ_{max} 396 nm and log ϵ 4.58) to "M(CO)$_2$Cl" (M = Rh, Ir) and "Os(CO)$_3$Cl$_2$" leads to a more significant red shift ($\Delta\lambda_{max}$ = 46−61 nm) of the ILCT band, whereas coordination to "Ir(COT)$_2$Cl" and "Rh(COD)Cl" causes a less relevant red shift ($\Delta\lambda_{max}$ = 23−39 nm). The intensity of the ILCT band does not change significantly upon coordination (log ϵ ca. 4.5).

As just outlined, the red shift of its ILCT transition is consistent with an increased acceptor strength of the acceptor end of the ligand 4,4′-*trans*-NC$_5$H$_4$CH=CHC$_6$H$_4$-NMe$_2$; therefore $\Delta\lambda_{max}$ can be used as a way to estimate the relative acceptor strength of the metal center.[10b] The ordering is as follows: "Os(CO)$_3$Cl$_2$" ($\Delta\lambda_{max}$ = 61 nm) > "Ir(CO)$_2$Cl" ($\Delta\lambda_{max}$ = 57 nm) > "Rh(CO)$_2$Cl" ($\Delta\lambda_{max}$ = 47 nm) > "Ir(COT)$_2$Cl" ($\Delta\lambda_{max}$ = 39 nm) > "Rh(COD)-Cl" ($\Delta\lambda_{max}$ = 23 nm) (Table 3).

The red shift of ILCT bands produced upon coordination is consistent with a lower energy necessary to reach the lowest excited state of the ILCT process, which should induce an increase of the second-order NLO response of the pyridine ligands.[5] This suggestion is confirmed by a detailed solvatochromic investigation,

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which will be reported and discussed elsewhere,[26,27] of the quadratic hyperpolarizability of Rh(I), Ir(I), and Os(II) metal complexes with 4-NMe_2-C_5H_4N and 4,4′-*trans*- or *trans,trans*-$NC_5H_4(CH{=}CH)_nC_6H_4NMe_2$ ($n = 1$ or 2).

Related complexes with 4-X-C_5H_4N ligands carrying weak donor or strong acceptor substituents in the *para* position (X = CMe_3, H, COMe, CN) are characterized by more complex UV–visible spectra since both carbonyl and pyridine ligands may contribute with additional metal-to-ligand charge-transfer (MLCT) transitions, which, being of comparable energy to the ILCT transition,[7] produce more than one significant charge-transfer absorption band. Therefore the direct qualitative evaluation, also by the solvatochromic investigation, of the effects of coordination on the second-order NLO response of these latter pyridines is not so straightforward.[27]

3. The Investigation of Second-Order NLO Properties. 3.1. The Experimental Determination of Second-Order NLO Properties. We initially used Kurtz and Perry powder tests[28] for a preliminary evaluation of second-harmonic generation (SHG) efficiency in the crystalline state. It turned out that *cis*-[$Ir(CO)_2Cl$(4,4′-*trans*-$NC_5H_4CH{=}CHC_6H_4NMe_2$)] is SHG inactive, probably because it crystallizes in a centrosymmetric space group like BR_3(4-NMe_2-C_5H_4N) (R = H, F, C_6F_5) and $B(C_6F_5)_3$(4,4′-$NC_5H_4C{\equiv}CC_6H_4NMe_2$),[9] confirming that powder testing cannot be reliably used to probe molecular structure–property relations.[6b] Therefore, we investigated the molecular quadratic hyperpolarizabilities (β, defined according to the "phenomenological convention"[29a]) of complexes and free ligands (Tables 2 and 3) by the solution-phase dc electric-field-induced second-harmonic (EFISH) generation method,[15] which can provide direct information on the intrinsic molecular NLO properties through eq 1:

$$\gamma_{\mathrm{EFISH}} = (\mu\beta_{\mathrm{vec}}/5kT) + \gamma_0(-2\omega;\, \omega,\, \omega,\, 0) \qquad (1)$$

where $\mu\beta_{\mathrm{vec}}/5kT$ is the dipolar orientational contribution and $\gamma_0(-2\omega;\, \omega,\, \omega,\, 0)$, a third-order term at frequency ω of the incident light, is the electronic contribution to γ_{EFISH}, which is negligible for the kind of molecules here investigated.[7,9] In the following β_{vec}, which is the vectorial projection of the quadratic hyperpolarizability tensor along the dipole moment vector μ, will be reported as EFISH β_λ, where λ is the fundamental wavelength of the incident photon in the EFISH experiment.

Measurements were carried out in chloroform with radiation of sufficiently long wavelength (1.06 or 1.34 μm) to generate second-harmonic wavelength ($\lambda/2 = 530$ and 670 nm, respectively) quite far from any significant optical transition so that dispersive enhancement of the EFISH response should be minimized.[30]

Free ligands 4-NMe_2-C_5H_4N, 4,4′-*trans*- or *trans,*-*trans*-$NC_5H_4(CH{=}CH)_nC_6H_4NMe_2$ ($n = 1$ or 2), and their metal complexes show one major low-lying charge-transfer excited state (see UV–visible characterization);[7] therefore values of the zero-frequency quadratic hyperpolarizability β_0 were calculated from experimental EFISH β_λ using the two-level model,[5] which leads to the following expression:

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

where λ corresponds to the fundamental wavelength of the incident photon and λ_{max} is the maximum absorption λ value of the ILCT transition corresponding to the low lying excited state mainly responsible for the NLO response (Table 3).

To test experimentally the validity of the two-level model for the above molecules, β_λ values of 4,4′-*trans*-$NC_5H_4CH{=}CHC_6H_4NMe_2$, *cis*-[$Rh(CO)_2Cl$(4-$NMe_2$-$C_5H_4N$)], and *cis*-[$Rh(CO)_2Cl$(4,4′-*trans*-$NC_5H_4CH{=}CHC_6H_4NMe_2$)] were measured by EFISH both at 1.06 μm and at 1.34 μm. It turned out that $\beta_{1.06\,\mu\mathrm{m}}$, calculated with the two-level expression (eq 2) from experimental $\beta_{1.34\,\mu\mathrm{m}}$, is slightly enhanced (by a factor between 1.1 and 1.6) with respect to experimental $\beta_{1.06\,\mu\mathrm{m}}$ (Table 3). Also the values of β_0 are slightly different (by a factor between 1.1 and 1.5) if evaluated from experimental values determined at 1.34 or 1.06 μm (Table 3). Clearly the two-level model does not apply perfectly to these systems, but the observed differences between experimental and calculated values are small enough to allow the use of the two-level expression for qualitative comparative purposes and often remain within the range of experimental error (±10%). Therefore, we used this approach to calculate β_λ at 1.91 μm of the above molecules for comparison with literature data (Table 2). Interestingly such an acceptable agreement between experimental and calculated β_λ values seems to confirm that the axis of the major charge-transfer process is quite parallel to the dipole moment vector, because the two-level model applies well only when this limitation is satisfied.[5] As a consequence, other tensorial components inaccessible to EFISH experiments are probably not so relevant.

When more than one low lying charge-transfer process could contribute to the second-order NLO response, as it seems to occur from UV–visible spectra with complexes with 4-X-C_5H_4N (X = CMe_3, H, COMe, or CN),[27] we did not use the two-level approximation. Besides, the β_λ value of *cis*-[$Ir(CO)_2Cl$(4-X-C_5H_4N)] (X = H, COMe) could not be experimentally determined by EFISH due to their rather low solubility in chloroform.

3.2. The Evaluation of Second-Order NLO Properties of Pyridines by Various Theoretical Methodologies. To evaluate the effect of the coordination to a metal center on the second-order NLO response of *para*-substituted pyridines, it is necessary to have a satisfactory knowledge of their EFISH β_λ values. However, the quadratic hyperpolarizability of simple pyridines such as 4-X-C_5H_4N (X = NMe_2, CMe_3, H, COMe, or CN) is reported to be quite low;[6,7] therefore it can be affected by significant experimental errors when determined by the EFISH tecnique. Trying to define at least their order of magnitude, we calculated EFISH β_λ values of these pyridines using various computational methods also with the aim of comparing the reliability of the

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Table 4. Comparison of Various Theoretical Methodologies for the Determination of Dipole Moments and EFISH β_λ of Various 4-X-Pyridines[a]

substituent X		experimental[b]	MNDO-CPHF	ab initio-CPHF[d]
NMe_2	μ (D)	3.5	2.09	2.81[e]
	$\beta_{1.06}$[f]	0.07[g]	0.040	−0.136[e]
	$\beta_{1.34}$[f]	0.06	0.017	−0.129
	$\beta_{1.91}$[f]	0.06[g]	0.014 (2.6)[c]	−0.123
	β_0[f] ($\beta_{TOT,O}$[f])	0.05[g]	0.012 (0.153)	−0.118[e](0.314)
4′-*trans*-CH=CH$C_6H_4NMe_2$	μ (D)	3.9	4.57 (5.79)[c]	6.06
	$\beta_{1.06}$[f]	63 (28.2)[c,h]	25.5 (33.3)[c]	
	$\beta_{1.34}$[f]	55	16.4	
	β_0[f]($\beta_{TOT,O}$[f])	35[g]	10.4 (10.4)	13.61 (13.6)
4′-*trans,trans*-(CH=CH)$_2C_6H_4NMe_2$	μ (D)	4.5	4.8	
	$\beta_{1.34}$[f]	80	22.6	
	β_0[f]($\beta_{TOT,O}$[f])	47[g]	13.0 (13.0)	
CMe_3	μ (D)	2.87[i]	2.13	3.04
	$\beta_{1.06}$[f]		0.189	−0.003
	β_0[f] ($\beta_{TOT,O}$[f])		0.165 (0.173)	−0.016 (0.038)
H	μ (D)	2.20[i]	1.97	2.37
	$\beta_{1.06}$[f]		−0.173	−0.174[j]
	$\beta_{1.91}$[f]		−0.134 (−0.14)[c]	−0.168[j]
	β_0[f] ($\beta_{TOT,O}$[f])		−0.120 (0.125)	−0.105 (0.105)
COMe	μ (D)	2.41[i]	2.23	2.87
	$\beta_{1.06}$[f]		−0.029	−0.280[l]
	$\beta_{1.91}$[f]		−0.032 (−0.10)[c,k]	−0.273[l]
	β_0[f] ($\beta_{TOT,O}$[f])		−0.033 (0.239)	−0.272 (0.375)
CN	μ (D)	1.63[i]	1.08	2.20
	$\beta_{1.06}$[f]		0.334	−0.030
	β_0[f] ($\beta_{TOT,O}$[f])		0.178 (0.180)	−0.036 (0.036)

[a] For PNA, computed μ, β_0,$\beta_{TOT,O}$, and $\beta_{1.91}$ are: (MNDO): 7.64 D, 3.90, 3.9, and 4.63 × 10^{-30} cm^5 esu^{-1}; (HF/4-31G): 7.68 D, 4.24, 4.24, and 4.72 × 10^{-30} cm^5 esu^{-1}; (MP2/4-31G): 7.68 D, 4.35, 4.35, and 4.74 × 10^{-30} cm^5 esu^{-1}; the ZINDO-SOS computed $\beta_{1.91}$ value[7] is 10.7 × 10^{-30} cm^5 esu^{-1}, whereas the experimental value[4] 9.2 × 10^{-30} cm^5 esu^{-1} converted according to the “phenomenological convention”[29a] is 13.8 × 10^{-30} cm^5 esu^{-1}. [b] In $CHCl_3$. [c] ZINDO-SOS data.[7] [d] With HF/6-311++G**. [e] With either HF/4-31G or MP2/4-31G: $\mu = 3.02$ D; β_0 and $\beta_{1.06} = -0.295$ and -0.311×10^{-30} cm^5 esu^{-1}. [f] 10^{-30} cm^5 esu^{-1}. [g] Experimental EFISH $\beta_{1.34}$ converted to β_0 or $\beta_{1.06}$ or $\beta_{1.91}$ with eq 2.[5] [h] EFISH$\beta_{1.06}$ measured in dioxane. [i] Reference 44; in C_6H_6, except 4-CMe_3-C_5H_4N in CCl_4. [j] With HF/6-31G*. [k] X = COH instead of COMe. [l] With HF/4-31G.

various methodologies. Computations of quadratic hyperpolarizability tensors based on semiempirical methods have been reported in the literature,[29] mainly based on ZINDO approximate Hamiltonians for the determination of the ground-state wave function and for the characterization of excited states via a configuration interaction including only single excitations,[31] while frequency-dependent second-order NLO functions have been determined via a sum-over-states (SOS) perturbation approach.[30] ZINDO-SOS EFISH β_λ values for some of the *para*-substituted pyridines here investigated have been reported.[7]

We used a completely different theoretical approach that allows the determination of both β_0 and β_λ, not involving excited states and based on the coupled perturbed Hartree−Fock method (CPHF),[32−34] where the Hamiltonian is time dependent. Both an ab initio level (Hartree−Fock) and a semiempirical level, using the MNDO (modified intermediate neglect of differential overlap)[35] approximate Hamiltonian, have been used for determination of the ground-state properties. Details on the calculations are reported in the Experimental Section.

We calculated both $\beta_{VEC}(\omega)$ and $\beta_{TOT}(\omega)$ functions, defined as

$$\beta_{VEC}(\omega) = \frac{\sum_i \mu_i \beta_i}{\sqrt{\sum_i {\mu_i}^2}} \qquad \beta_{TOT}(\omega) = \sqrt{\sum_i (\beta_i)^2} \quad (3)$$

where $i = x, y, z$ and $\beta_i = \beta_{iii} + (1/3)\sum_{j \neq i}(\beta_{ijj} + \beta_{jij} + \beta_{jji})$. $\beta_{VEC}(\omega)$ corresponds to EFISH β_λ, and $\beta_{TOT}(\omega)$ is the intrinsic quadratic hyperpolarizability, at an incident light of frequency ω (and wavelength λ); β_i are the tensor components.

It follows that $\beta_{VEC}(\omega)$ is potentially affected by errors in both the computed dipole moment μ_i and the β_i tensor components. Therefore the reliability of computed values must be controlled, when possible, by comparison with experimental EFISH values.[7]

Values of β_i components, β_{VEC} and β_{TOT} (see eq 3), have been directly obtained from calculations of the induced dipole moments expressed as a Taylor expansion in terms of the applied electric field. Therefore, calculated $\beta_{VEC}(\omega)$ must be multiplied by a factor 0.5 to make it consistent with the “phenomenological” convention used in EFISH experimental measurements.[29a] Semiempirical and ab initio calculated EFISH β_λ values of *para*-substituted pyridines and *para*-nitroaniline (PNA) together with the available experimental EFISH values of some of these molecules are reported in Table 4; PNA was chosen as a reference term of our calculations because its experimental EFISH β_λ and dipole moment μ are well-known.[4]

Both experimentally (at least for 4-NMe_2-C_5H_4N) and theoretically, simple *para*-substituted pyridines 4-X-

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C_5H_4N show EFISH β_λ values on the order of 10^{-31}–10^{-32} cm^5 esu^{-1}, while PNA and more π-delocalized *para*-substituted pyridines such as 4,4′-*trans*-NC_5H_4-$CH{=}CHC_6H_4NMe_2$ show theoretical and experimental values of EFISH β_λ on the order of 10^{-30} and 10^{-29} cm^5 esu^{-1}, respectively.

From our investigation it appears that both ab initio-CPHF and semiempirical MNDO-CPHF calculations can predict correctly both the order of magnitude and the general trends of experimental EFISH β_λ only when the order of magnitude is higher than 10^{-30} cm^5 esu^{-1}, which appears to be also a limit for reliable experimental EFISH measurements.

It follows that only for molecular systems characterized by experimental EFISH β_λ values higher than 10^{-30} cm^5 esu^{-1} could comparison with ab initio-CPHF calculated values be a way to establish the validity and the limits of semiempirical methods such as MNDO-CPHF and ZINDO-SOS (see Table 4).

For PNA, MNDO-CPHF and ab initio-CPHF calculated dipole moments and EFISH β_λ values are similar when ab initio data are obtained either neglecting all the correlation effects at the HF level or partially considering the electron correlation at the MP2 level (see Experimental Section and Table 4). However the calculated value of EFISH $\beta_{1.91\,\mu m}$ is in all cases lower than the experimental one; a more satisfactory agreement is obtained with the ZINDO-SOS approach.[7]

For 4,4′-*trans*-$NC_5H_4CH{=}CHC_6H_4NMe_2$, both semiempirical MNDO-CPHF and ZINDO-SOS[7] calculated values of EFISH β_λ and β_0 are quite similar and comparable to values calculated using an ab initio-CPHF approach (Table 4). They are underestimated by a factor of 0.5–0.3 when compared to the experimental EFISH β_λ value obtained in this work, although it must be pointed out that an experimental EFISH $\beta_{1.06\,\mu m}$ value, measured in dioxane, not too far from the calculated theoretical values (see Table 4) was reported.[7]

As a general observation, we can conclude that when the experimental values of EFISH β_λ and β_0 are large enough, even a semiempirical method like MNDO-CPHF or ZINDO-SOS works remarkably well for semiquantitative purposes. This conclusion is confirmed by MNDO-CPHF calculations of μ and EFISH β_λ, including β_0, of 4,4′-*trans*,*trans*-$NC_5H_4(CH{=}CH)_2C_6H_4NMe_2$ which give values (Table 4) of μ quite similar to the experimental values and of $\beta_{1.34\,\mu m}$ or β_0 comparable although lower than the experimental ones. In this latter case ab initio calculations were not performed due to the size of the molecule.

On the contrary we observed a large disagreement between EFISH β_λ values calculated by ab initio-CPHF or MNDO-CPHF methods in the case of simple *para*-substituted pyridines, characterized by low values of EFISH β_λ, with the exception of pyridine itself (see Table 4). While calculated and experimental dipole moments are in acceptable agreement (with the exception of the MNDO values of 4-NMe_2-C_5H_4N and 4-CN-C_5H_4N), the difference in values of EFISH β_λ and β_0 calculated by ab initio-CPHF or by both MNDO-CPHF and ZINDO-SOS[7] semiempirical methods may be as large as 1 or 2 orders of magnitude and in some cases even the sign is opposite (see Table 4). The origin of such large differences is dependent on the nature of the molecule.

For instance, when 4-NMe_2-C_5H_4N and 4-CMe_3-C_5H_4N are taken into account (Table 4), EFISH β_λ obtained with ab initio-CPHF and MNDO-CPHF methods always differ in sign. The origin of this discrepancy involves the larger β_i component. Interestingly, the computed ab initio-CPHF absolute value of EFISH β_λ becomes smaller and smaller as the flexibility of the basis set increases, especially with the introduction of diffuse functions. In the case of 4-NMe_2-C_5H_4N, the calculated EFISH β_λ value using the MNDO-CPHF semiempirical method is closer to the experimental parameter than the corresponding ab initio-CPHF calculated value; however the experimental value is very low and therefore most likely to be affected by a significant error.

For 4-COMe-C_5H_4N and 4-CN-C_5H_4N (Table 4), ab initio-CPHF and MNDO-CPHF β_0 and EFISH β_λ values differ by factors in the range 4–8 and 9–11, respectively, due to significant differences in both the μ_i and β_i components.

However, it must be pointed out that there is a good agreement between EFISH β_λ values of these simple pyridines computed by the MNDO-CPHF method or by the ZINDO-SOS method[7] (Table 4). The MNDO-CPHF EFISH β_λ and the ZINDO-SOS β_λ values (in parentheses) are as follows: $\beta_{1.91}$ for C_5H_5N -0.13×10^{-30} cm^5 esu^{-1} (-0.14×10^{-30} cm^5 esu^{-1}), $\beta_{1.91}$ for 4-COMe-C_5H_4N -0.03×10^{-30} cm^5 esu^{-1} (-0.10×10^{-30} cm^5 esu^{-1} for the slightly different molecule 4-COH-C_5H_4N), $\beta_{1.06}$ for 4,4′-*trans*-$NC_5H_4CH{=}CHC_6H_4NMe_2$ 25.5×10^{-30} cm^5 esu^{-1} (33.3×10^{-30} cm^5 esu^{-1}).

Only in one case (Table 4) are the ZINDO-SOS and MNDO-CPHF values in apparent disagreement, the reported ZINDO $\beta_{1.91}$ value (2.6×10^{-30} cm^5 esu^{-1})[7] of 4-NMe_2-C_5H_4N being surprisingly high if compared to the MNDO-CPHF value (0.01×10^{-30} cm^5 esu^{-1}). However this discrepancy can be explained by a different choice of molecular geometries; ZINDO-SOS makes use sometimes of idealized geometries,[36] assuming a complete planarity of the conjugated chromophores including the NMe_2 moiety, while all the geometrical constraints are fully relaxed in our MNDO-CPHF calculations. In agreement with this hypothesis, the calculated $\beta_{1.91}$ value by the MNDO-CPHF method is equal to 1.80×10^{-30} cm^5 esu^{-1} when a planar geometry for 4-NMe_2-C_5H_4N is forced, as in ZINDO-SOS calculations.

It is worth pointing out that a simple semiempirical method such as MNDO-CPHF can be a useful way to predict the experimental quadratic hyperpolarizability of some substituted pyridine molecules, since a good linear relation (Figure 3; square correlation coefficients ≥ 0.99) of MNDO-CPHF EFISH β_λ versus experimental EFISH β_λ is obtained for 4-X-C_5H_4N (X = NMe_2, 4′-*trans*-$CH{=}CHC_6H_4NMe_2$, and 4′-*trans*,*trans*-$(CH{=}CH)_2C_6H_4NMe_2$; β_0 and $\beta_{1.34}$ are plotted) and PNA (β_0 and $\beta_{1.91}$ are plotted).

3.3. Second-Order NLO Properties of Complexes with 4-X-C_5H_4N Ligands (X = NMe_2, CMe_3, H, COMe, CN).

The EFISH $\beta_{1.06\,\mu m}$ values of complexes *cis*-[$M(CO)_2Cl(4\text{-}X\text{-}C_5H_4N)$] (M = Ir(I) (5d^8), Rh(I) (4d^8)) are strongly dependent upon the nature of X (Table 2):

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[36] Kanis, D. R.; Marks, T. J.; Ratner, M. A. *Int. J. Quantum Chem.* **1992**, *43*, 61.

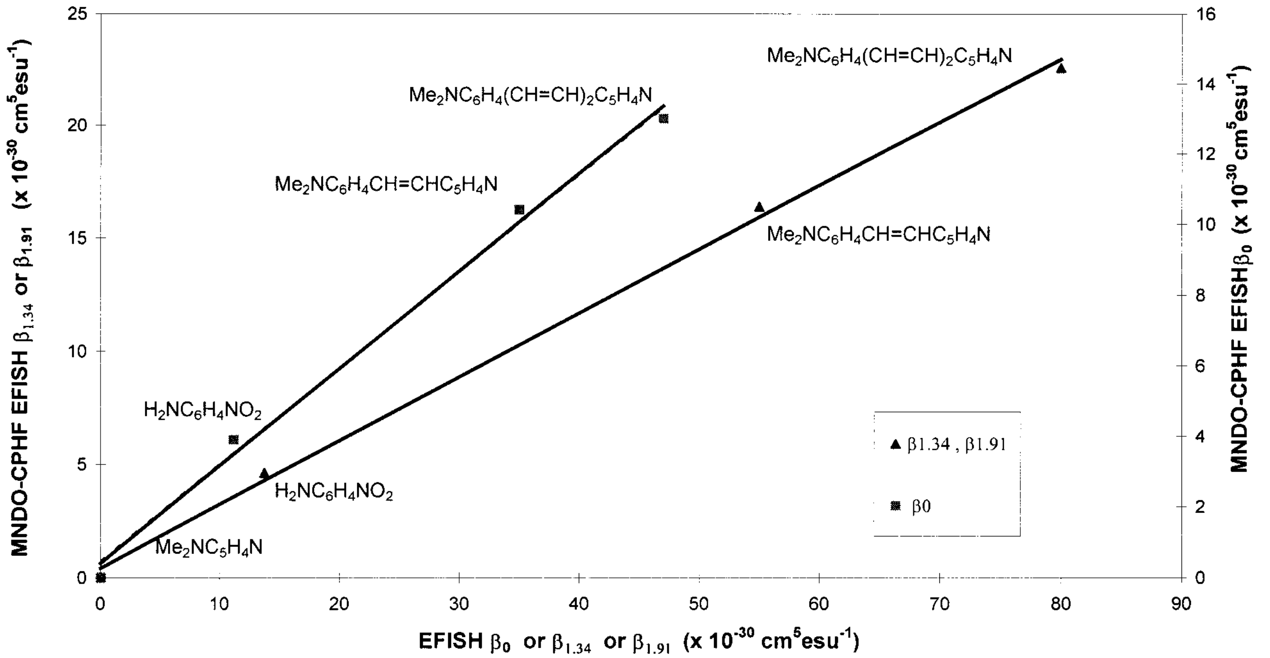

Figure 3. Comparison of experimental and computed MNDO-CPHF EFISH β_0 and $\beta_{1.34}$ (for 4-$NC_5H_4NMe_2$, 4,4′-*trans*-$NC_5H_4CH{=}CHC_6H_4NMe_2$, 4,4′-*trans,trans*-$NC_5H_4(CH{=}CH)_2C_6H_4NMe_2$) or $\beta_{1.91}$ (for 1,4-$H_2NC_6H_4NO_2$).

(i) $\beta > 0$ with strong electron-donating groups (e.g., X = NMe_2: M = Rh, $\beta_{1.06\,\mu m}$ 8.7 × 10^{-30} cm^5 esu^{-1}; M = Ir, $\beta_{1.06\,\mu m}$ 9 × 10^{-30} cm^5 esu^{-1});

(ii) β positive but very small with weak electron-donating groups (e.g., X = CMe_3: M = Rh, Ir $\beta_{1.06\,\mu m}$ ca. 0.1 × 10^{-30} cm^5 esu^{-1});

(iii) $\beta < 0$ with strong electron-withdrawing groups (e.g., X = CN: M = Rh, $\beta_{1.06\,\mu m}$ −4.3 × 10^{-30} cm^5 esu^{-1}; M = Ir, $\beta_{1.06\,\mu m}$ −9 × 10^{-30} cm^5 esu^{-1}).

This trend is less evident although similar in the related Os(II) ($5d^6$) complexes *fac*-[$Os(CO)_3Cl_2$(4-X-C_5H_4N)] (Table 2). In any case independently from the strong electron-donating or electron-withdrawing properties of the X groups, a significant enhancement of 1 or 2 orders of magnitude ($10-10^2$) of the absolute value of EFISH $\beta_{1.06\,\mu m}$ occurs upon coordination, if the order of magnitude of free pyridines, calculated by the above theoretical methods, is taken into account. It is not possible to discuss an exact enhancement factor based on experimental data because, as already pointed out, the experimental values of EFISH β_λ for simple *para*-substituted pyridines are low and therefore probably can be affected by significant errors.

The negative sign of $\beta_{1.06\,\mu m}$ for metal complexes when X is a strong electron-withdrawing group can be explained as the result of a reduction of the dipole moment upon excitation because, according to the two-level model for quadratic hyperpolarizabilities,[5] β_λ is dependent on the difference between excited-state and ground-state dipole moments ($\Delta\mu_{eg}$). A negative $\Delta\mu_{eg}$ upon excitation was also suggested as the origin of negative values of $\beta_{1.91\,\mu m}$ shown by related complexes with zerovalent metals such as [$M(CO)_5$(4-X-C_5H_4N)] (M = Cr, W; X is an electron-withdrawing group such as COH or 4′-*trans*-$CH{=}CHC_6H_4COH$).[7] The origin of such a reduction of the dipole moment upon excitation is attributed to a dominating metal-to-ligand charge-transfer (MLCT) transition which corresponds to an electron shift vectorially opposed to the electron donation of the pyridine nitrogen electrons into an empty metal orbital.[7]

We have now evidenced that when the substituent X is a strong electron-withdrawing group, even a relatively “soft” metal carbonyl center with an oxidation state different from zero can behave, through a metal-to-ligand charge-transfer process, as an electron donor toward the pyridine ring. Of course the effect becomes less relevant by increasing the oxidation state of the metal, as it can be inferred from the EFISH β_λ value of the Os(II) complex with 4-MeCO-C_5H_4N when compared to the value of the related W(0) complex where the metals have the same $5d^6$ electron configuration, (see Table 2).

Of course the same relatively “soft” metal centers act as better electron acceptors toward strong electron-donor pyridines; this latter type of metal-based chromophore can be compared to the conventional push−pull π-organic systems, where for a given donor, the strongest acceptor group would be expected to give the higher EFISH β_λ value.[3,4] The weak acceptor strength of the nitrogen atom of the pseudoaromatic pyridine ring is increased by coordination to a metallic center, producing a relevant increase of the EFISH β_λ value of the pyridine (Table 2) by about 1 or 2 orders of magnitude.

This effect is clearly modulated by the different acceptor strength of the various metal centers and therefore by their oxidation states. Coordination of 4-NMe_2-C_5H_4N to “*fac*-$Os(CO)_3Cl_2$” (Os(II) $5d^6$) and to “*cis*-$M(CO)_2Cl$” (M = Rh(I) $4d^8$ or Ir(I) $5d^8$) produces a larger increase of the EFISH β_λ value than coordination to “$M(CO)_5$” (M = Cr(0) $3d^6$). By using a two-level approach,[5] $\beta_{1.91\,\mu m}$ values calculated from $\beta_{1.06\,\mu m}$ are respectively 4.4 × 10^{-30} cm^5 esu^{-1} (Os(II)), 6.4 × 10^{-30} cm^5 esu^{-1} (Rh(I)), and 6.5 × 10^{-30} cm^5 esu^{-1} (Ir(I)), while the experimental EFISH $\beta_{1.91\,\mu m}$ value for Cr(0) is reported to be 0.55 × 10^{-30} cm^5 esu^{-1}.[7] The $\beta_{1.91\,\mu m}$ enhancement factor upon coordination is therefore, as expected, about 10 times higher for Os(II), Rh(I), and

Ir(I) moieties carrying three or two carbonyl ligands than for a Cr(0) moiety carrying five carbonyl ligands.

According to Marks et al.,[7] EFISH β_λ values of metal complexes with 4-X-C_5H_4N (X strong donor) are dominated by the red shift of an intraligand charge-transfer (ILCT) transition (also cited as ligand-to-ligand charge transfer (LLCT) by these authors),[7] which we have shown to be tuned by the increased electron-accepting properties of the metal center. At first sight it is quite unexpected that both EFISH β_λ and $\mu\beta_\lambda$ values at 1.34 μm of 4-NMe_2-C_5H_4N coordinated to the relatively soft "$Rh(CO)_2Cl$" moiety ($\beta_{1.34\,\mu m}$ 12 × 10^{-30} cm^5 esu^{-1}; $\mu\beta_{1.34\,\mu m}$ 71 × 10^{-30} D cm^5 esu^{-1}, Table 3) are similar to the corresponding values reported when this molecule interacts with a very strong Lewis acid such as BF_3 ($\beta_{1.34\,\mu m}$ 13.6 × 10^{-30} cm^5 esu^{-1}; $\mu\beta_{1.34\,\mu m}$ 69 × 10^{-30} D cm^5 esu^{-1}).[9] However, unlike BF_3, "$Rh(CO)_2Cl$" may show an ambivalent behavior where the acceptor metal may act also, by a limited electron charge transfer to the pyridine ring, as a weak donor.[7]

Accordingly with this ambivalent behavior, *fac*-[$Os(CO)_3Cl_2$(4-X-C_5H_4N)] complexes show a negligible but not negative EFISH β_λ value when X = CN or COMe ($\beta_{1.06\,\mu m}$ ca. 2 × 10^{-30} cm^5 esu^{-1}), suggesting that the effect on the MLCT charge transfer (negative β_λ values) is balanced by a comparable effect on the ILCT charge transfer (positive β_λ values) due to increased acceptor properties, as expected for the higher oxidation state and the lower number of d electrons (d^6 against d^8) of Os(II) when compared to Ir(I) and Rh(I) (for *cis*-[$Rh(CO)_2Cl$(4-CN-C_5H_4N)] and *cis*-[$Ir(CO)_2Cl$(4-CN-C_5H_4N)], $\beta_{1.06\,\mu m}$ −4.3 × 10^{-30} cm^5 esu^{-1} and −9 × 10^{-30} cm^5 esu^{-1}, respectively).

It follows that values of EFISH β_λ of 4-X-C_5H_4N upon coordination seem to be controlled by a very delicate balance: when X is a strong donor such as NMe_2, the increase is controlled mainly, but not only, by the increased acceptor properties of the metal fragment, while when X is a strong acceptor such as CN, an increased donor property of the metal fragment controls both the sign and the absolute values of EFISH β_λ.

Therefore by controlling the nature and properties of the metal center it is possible to tune the effects produced upon coordination of *para*-substituted pyridines. This latter statement is confirmed by the EFISH $\beta_{1.91\,\mu m}$ value of [$W(CO)_5$(4-MeCO-C_5H_4N)], which is large and negative (−9.3 × 10^{-30} cm^5 esu^{-1}),[6,7] even if MeCO is not a strong acceptor, because the donor properties of the "$W(CO)_5$" fragment are so good that they can induce negative EFISH $\beta_{1.91\,\mu m}$ values even of pyridine complexes containing weakly donating X substituents,[6,7] while the related complexes of Ir(I), Rh(I), and Os(II), with lower donor properties of the metal centers, show EFISH $\beta_{1.06\,\mu m}$ values positive although very low (see Table 2). Probably in these latter cases both MLCT and ILCT excitations (corresponding to two vectorially opposed charge-transfer processes) contribute in a similar but opposite extent, while in the much softer W(0) center the MLCT excitation dominates the second-order NLO response, therefore producing negative $\Delta\mu_{eg}$.

In summary we have added further evidence to the view[7] that a transition metal fragment may play, in the excitation processes, an ambivalent acceptor or donor role which is controlled by its intrinsic softness and by the presence in the pyridine ligand of an electron donor or acceptor group. As clearly shown by T. J. Marks et al., this delicate balance is related to the relative energy of d metal orbitals and π^* pyridine orbitals which can interact.[7]

3.4. Second-Order NLO Properties of Complexes with 4,4′-*trans*- or *trans,trans*-$NC_5H_4(CH{=}CH)_n$-$C_6H_4NMe_2$ (n = 1 or 2) Ligands. In the well-established push−pull π-organic molecules, an increase in the delocalized π-electron backbone between the donor and the acceptor groups can lead to a significant increase in the second-order NLO response.[3,4] Therefore, it was appealing to verify the effect of complexation on the quadratic hyperpolarizability of 4-X-pyridines, where X is an electron-donor group with a π-conjugated electron bridge between the electron-donor group and the *para* position of the pyridine ring such as in stilbazoles.

Coordination to "*cis*-$M(CO)_2Cl$" (M = Rh, Ir) or "*fac*-$Os(CO)_3Cl_2$" of 4′-*trans*- or *trans,trans*-$C_6H_4(CH{=}CH)_n$ (n = 1 or 2), causes an increase of EFISH β_λ ($\beta_{1.34\,\mu m}$ enhancement factor is 1.5 Os(II), 2.0 Rh(I), 2.3 Ir(I) for n = 1 or 1.5 Os(II), 1.6 Rh(I), 1.7 Ir(I) for n = 2; Table 3) which is not so significant when compared to the large increase produced on the related pyridine 4-NMe_2-C_5H_4N ($\beta_{1.34\,\mu m}$ enhancement factors on the order of 10^2). This behavior was already reported to occur even when 4,4′-*trans*-$NC_5H_4CH{=}CHC_6H_4NMe_2$ is bound to a weaker acceptor metal center such as the "$W(CO)_5$" moiety.[7] The enhancement factors caused by coordination of these pyridines with a π-delocalized bridge are slightly lower at 1.34 μm than at 1.06 μm and are even lower when β_0 is taken into account (Table 3), probably due to the correction of dispersion effects, although absorption bands are always far from second-harmonic wavelengths.

The enhancement factor of EFISH β_λ observed upon coordination to "*cis*-$M(CO)_2Cl$" (M = Rh, Ir) of 4,4′-*trans*-$NC_5H_4CH{=}CHC_6H_4$-X is higher when X = NMe_2 than when X = OR where R is 2-methylbutyl[8] (when X = NMe_2, by using the two-level approach[5] the $\beta_{1.91\,\mu m}$ enhancement factor is 1.8 and 2.1, whereas when X = OR[8a] the $\beta_{1.91\,\mu m}$ enhancement factor is 1.3 and 1.5 for Rh(I) and Ir(I) complexes, respectively), in agreement with the stronger donor properties of NMe_2. The effect due to coordination becomes less and less relevant by increasing the length of the π-delocalized bridge as when the effect of coordination on 4,4′-*trans*- or *trans,trans*-$NC_5H_4(CH{=}CH)_nC_6H_4NMe_2$ (n = 1 or 2; see Table 3) is compared.

Our observations are quite general and in agreement with previous findings; for instance by taking into account our experimental EFISH $\beta_{1.34\,\mu m}$ values for the free pyridines (Table 3), the $\beta_{1.34\,\mu m}$ enhancement factor upon coordination to strong Lewis acids such as BF_3 and $B(C_6F_5)_3$[9] is much lower with 4,4′-*trans*-$NC_5H_4CH{=}CHC_6H_4NMe_2$ (2.3 and 2.8, respectively) than with 4-NMe_2-C_5H_4N (order of about 10^2). In the former case, the slightly higher enhancement factors, when compared with those observed by coordination to W(0) or even Rh(I), Ir(I), and Os(II) metal centers (see Table 3), can be attributed to a higher perturbation on the ILCT transition due to coordination to the strong electron acceptor BF_3, as expected when the ILCT transition dominates the NLO response.

3.5. Effect of the Substitution of CO Ligands by Olefin Ligands. From the above observations it appears that the balance of the donor–acceptor properties of soft metal centers is relevant for tuning the second-order NLO response of coordinated 4-X-pyridines. Therefore, as an example, we investigated the substitution of CO by olefinic ligands, which should lead to an increase of the electron density on the ground state of Rh(I) and Ir(I) metal centers and therefore to an increase of their softness and to lower acceptor properties as shown by the relatively small red shift of the ILCT in the UV–visible spectra of olefin Rh(I) and Ir(I) complexes with 4,4′-*trans*-$NC_5H_4CH{=}CHC_6H_4NMe_2$ (see Table 3). According to the smaller red shift of the ILCT transition, EFISH $\beta_{1.34\ \mu m}$ decreases by a factor of ca. 0.7 upon substitution of the carbonyl ligands of *cis*-[$M(CO)_2Cl$(4,4′-*trans*-$NC_5H_4CH{=}CHC_6H_4NMe_2$)] (M = Ir, Rh) with two cyclooctene ligands (COT) or with cyclooctadiene (COD), respectively (Table 3). This effect becomes negligible when the length of the π-delocalized electron bridge (between the *para* position of the pyridine ring and the electron-donating group) is increased as with the ligand 4,4′-*trans*,*trans*-$NC_5H_4(CH{=}CH)_2C_6H_4NMe_2$ (Table 3).

Therefore we have evidence that a careful choice of the ligands of the coordination sphere can be used to modulate the second-order NLO response of metal-coordinated pyridines.

Conclusion

Several observations have emerged from this work, which confirms the main findings of previous investigations.[6–9] First of all, the quadratic hyperpolarizability EFISH β_λ of 4-X-pyridines (X = acceptor or donor group) is increased significantly even upon coordination to relatively soft metal centers such as “*cis*-$M^I(CO)_2Cl$” (M = Rh, Ir) or “*fac*-$Os^{II}(CO)_3Cl_2$” moieties. As confirmed also by a solvatochromic investigation,[26] when X is a strong donor group such as NMe_2, mainly the red shift produced upon coordination on the ILCT transition of the ligand contributes to the increase of EFISH β_λ, while when X is a strong acceptor group such as CN, new MLCT transitions dominate the second-order NLO response, still resulting in an increase of the absolute value of EFISH β_λ but often producing a negative sign of the latter. When X is a weak donor or a weak acceptor, both ILCT and MLCT transitions, which are vectorially opposite, can contribute to the second-order NLO response, producing a slightly positive or negative EFISH β_λ value, depending on the balance of the two donor (MLCT) or acceptor (ILCT) effects of the soft metal center to different excited states.[7] Therefore, even metal centers less soft than “$M(CO)_5$” (M = Cr(0), W(0))[7] such as Rh(I), Ir(I), or Os(II) carbonyl species display, in the excited states, electron-acceptor and electron-donor properties.

In our work we have shown that such a balance between acceptor and donor properties of a metal center is tuned by its oxidation state, d electron configuration, and coordination sphere. By controlling such factors it is possible to obtain different EFISH β_λ values for the same pyridine, when metal-coordinated. For instance, the increase of the donor efficiency in the order Os(II) (d^6) < Rh(I) ≅ Ir(I) (d^8) < W(0) (d^6) produces a parallel increase of absolute values of EFISH β_λ of metal-coordinated 4-X-pyridines, when X is an electron acceptor such as CN or COMe with a change of sign by decreasing the oxidation state because the MLCT transitions become more relevant. In addition, substitution of carbonyl ligands with olefinic ligands in Ir(I) and Rh(I) complexes decreases the acceptor properties of the metal centers, producing a slight decrease of EFISH β_λ values of metal-coordinated 4,4′-*trans*-$NC_5H_4CH{=}CHC_6H_4NMe_2$, which are dominated by the ILCT transition of the ligand. Therefore this kind of organometallic chromophore can behave, in the excitation processes, as donors or acceptors like organic groups in classical push–pull molecules: the comparison of EFISH $\beta_{1.91\ \mu m}$ of *cis*-[$M(CO)_2Cl$(4,4′-*trans*-$NC_5H_4CH{=}CHC_6H_4NMe_2$)] (M = Rh, 76×10^{-30} cm^5 esu^{-1}; M = Ir, 89×10^{-30} cm^5 esu^{-1}) with EFISH $\beta_{1.91\ \mu m}$ of the related push–pull organic molecule 4,4′-*trans*-$NMe_2C_6H_4CH{=}CHC_6H_4NO_2$ (73×10^{-30} cm^5 esu^{-1})[4] would suggest that the *cis*-[$NM(CO)_2Cl$] moiety [M = Rh(I), Ir(I)] is a slightly better electron-acceptor group than the strong electron-acceptor $C{-}NO_2$ fragment.[8a]

There is a buffering of the second-order NLO response when *para*-substituted pyridines are metal-coordinated. While by going from 4-NMe_2-C_5H_4N to 4,4′-*trans*-$NC_5H_4CH{=}CHC_6H_4NMe_2$ the $\beta_{1.34\ \mu m}$ enhancement factor is on the order of 10^3, by going from [$M(CO)_xCl_y$(4-NMe_2-C_5H_4N)] to [$M(CO)_xCl_y$(4,4′-*trans*-$NC_5H_4CH{=}CHC_6H_4NMe_2$)] (M = Rh or Ir, $x = 2$, $y = 1$; M = Os, $x = 3$, $y = 2$) the $\beta_{1.34\text{ or }1.91\ \mu m}$ enhancement factor is about 10. This behavior is not limited to an excitation process dominated by a ILCT transition. For instance even when the metal acts as a donor group, through an excitation process that involves mainly a MLCT transition,[7] a very modest increase of the quadratic hyperpolarizability was reported to occur by going from [$W(CO)_5$(4-COH-C_5H_4N)] to [$W(CO)_5$(4,4′-*trans*-COH-$C_6H_4CH{=}CHC_5H_4N$)] (the enhancement factor of $\beta_{1.91\ \mu m}$ is only 1.4).[6]

The positive effect on the quadratic hyperpolarizability EFISH β_λ upon coordination of 4-X-C_5H_4N ligands, when X is a donor group, to an acceptor metal center vanishes quickly by increasing the length of the π-delocalized bridge between the donor group and the pyridine ring. For instance EFISH $\beta_{1.34\ \mu m}$ increases on going from [$M(CO)_xCl_y$(4,4′-*trans*-$NC_5H_4CH{=}CHC_6H_4NMe_2$)] to [$M(CO)_xCl_y$(4,4′-*trans*,*trans*-$NC_5H_4(CH{=}CH)_2C_6H_4NMe_2$)] (M = Rh or Ir, $x = 2$, $y = 1$; M = Os, $x = 3$, $y = 2$) by a factor of 1.1–1.4, which is only slightly lower than the increase observed when the two free ligands are compared (enhancement factor of 1.5). These results nicely agree with the interpretation given by T. J. Marks et al. of this behavior when stilbazole ligands are bound to the softer, better donor and weaker acceptor “$W(CO)_5$” moiety.[7] The seemingly rather innocent pyridine ring serves as the most important acceptor group not only of MLCT but also of ILCT transitions. The excitation process remains rather unchanged regardless of the length of the π-network. Our work now confirms that these metal chromophores, independently from the nature and properties of the metal, cannot display the conjugation length dependence of their quadratic hyperpolarizability found in organic systems.[4] In addition, our results give a negative answer to the suggestion[7] that by increasing the oxidizing strength of the metal fragment the ILCT transition of a ligand such as 4,4′-*trans*-$NC_5H_4CH{=}CHC_6H_4NMe_2$ can be strongly enhanced.

Finally, it is worth noting that various complexes here investigated with ligands such as 4,4′-*trans*- or *trans*,-*trans*-$NC_5H_4(CH{=}CH)_nC_6H_4NMe_2$ ($n = 1, 2$) show $\mu\beta_0$ values between 400×10^{-30} and 600×10^{-30} D cm^5 esu^{-1}, comparable to those of organic materials such as Disperse Red 1 (*trans*-4,4′-$O_2NC_6H_4N{=}NC_6H_4NEt(CH_2CH_2OH)$, $\mu\beta_0 = 500 \times 10^{-30}$ D cm^5 esu^{-1}), which is currently used in electrooptic polymers.[37] Such excellent $\mu\beta_0$ values are due to two electronically related factors: an enhancement in the dipole moment μ generated by coordination to the metal center acting in the ground state always as an acceptor and in parallel an enhancement of β_0 due to a significant red shift of the ligand ILCT transition. Obviously the enhancement of the dipole moment is a factor that can be more easily increased by increasing the acceptor properties (or oxidizing strength) of the metal center.

Stilbazoles have been largely investigated as potential second-order NLO materials;[9] in particular it was reported that some of their salts with specific anions are characterized in the solid state by an enormous enhancement factor of the second-order NLO response.[3e] However due to their ionic nature, these materials cannot be used for generation of electrooptic polymers. Coordination of stilbazoles and of related π-delocalized pyridines to soft metal centers or to strong Lewis acids has shown in this and other investigations[6−9] to produce a significant, although less relevant, enhancement of the second-order NLO response. This latter effect is good enough, together with the parallel increase of the dipole moment, to consider these organometallic or coordination molecules, due to their non-ionic nature, interesting for further studies of their electrooptic polymers, taking into account also in some specific cases their higher thermal stability when compared to the stability of the free pyridine ligands.

Experimental Section

General Comments. $[Ir(CO)_2Cl]_2$,[16] $[Ir(COT)_2Cl]_2$ (COT = cyclooctene),[17] $[Rh(CO)_2Cl]_2$,[18b] $[Rh(COD)Cl]_2$ (COD = cyclooctadiene),[19] and α-$[Os(CO)_3Cl_2]_2$[18b,20b] were prepared according to the literature, whereas 4-X-pyridines (X = NMe_2, CMe_3, H, COMe, CN, and 4′-*trans*-$CH{=}CHC_6H_4NMe_2$) and 4-dimethylaminocinnamaldehyde were purchased from Sigma-Aldrich. 4,4′-*trans*-$NC_5H_4CH{=}CHC_6H_4NMe_2$ was also prepared as described below, along with 4,4′-*trans,trans*-$NC_5H_4(CH{=}CH)_2C_6H_4NMe_2$. The solvents (pentane, dichloromethane, 1,2-dichloroethane) were dried over molecular sieves (4 Å) prior to use. The general procedures for the preparation of *cis*-$[M(CO)_2Cl(4\text{-}X\text{-}C_5H_4N)]$ (M = Rh, Ir), $[Rh(COD)Cl(4\text{-}X\text{-}C_5H_4N)]$, $[Ir(COT)_2Cl(4\text{-}X\text{-}C_5H_4N)]$, and *fac*-$[Os(CO)_3Cl_2(4\text{-}X\text{-}C_5H_4N)]$ are described below. All complexes were characterized by infrared (by use of a Nicolet MX-1FT and a Bruker Vector 22 spectrometers), ^{1}H NMR (by use of a Bruker AC-200 and a Bruker Avance DRX 300 spectrometers), and UV−visible (by use of a Jasco V-570 spectrophotometer) spectroscopies. Elemental analysis were carried out in our department, and in a few cases also ^{13}C NMR spectroscopy and mass spectrometry (by use of a Bruker Avance DRX 300 spectrometer and a Varian VG-9090 spectrometer, respectively) were used. Dipole moments were determined by using a WTW-DM01 dipolmeter coupled with a Pulfrich Zeiss PR2 refractometer, to measure respectively the dielectric constant and the refractive index of the solutions in $CHCl_3$; from these experimental data the dipole moment can be calculated by using the Guggenheim method.[21]

Determination of the Second-Order NLO Responses. (i) EFISH Technique[15c]**.** EFISH measurements were carried out in chloroform solutions at a fundamental wavelength of 1.06 or 1.34 μm, using a Q-switched, mode-locked Nd^{3+}:YAG laser with pulse durations of 15 ns (90 ns) at a 10 Hz repetition rate. All our experimental EFISH β_λ values are defined according to the "phenomenological convention".[29a]

(ii) Theoretical Methods. The computational study of the quadratic hyperpolarizability of pyridines has been carried out with both semiempirical and ab initio methods; MNDO[35] and Hartree−Fock (HF) methods have been used in connection with the coupled perturbed HF procedure,[38] giving both static and frequency-dependent tensors, according to the theory developed by Sekino and Bartlett,[32] Karna and Dupuis,[33] and Ågren et al.[34] All the computed polarizability data refer to the optimum molecular geometry, determined in a consistent way per each model Hamiltonian and adopted basis set.

Semiempirical calculations have been carried out using a standard version of the MOPAC propagram[39] modified by us in order to include the CPHF equations. The code of the CPHF equations used is closely related to the form implemented in the HONDO8 program.[40]

Ab initio calculations have been carried out only at the HF level, thus neglecting all the correlation effects, although attempts of partially considering the electron correlation at the MP2 level have been done only for simple molecules such as 4-NMe_2-C_5H_4N and PNA (see Table 4). MP2 calculations, performed using a 4-31G basis,[41] give results for dipole moments and β tensors very close to the HF ones but appear to be much more expensive from a computational point of view. The consideration that the very high computational cost for a more advanced treatment of correlation would not produce more reliable results prompted us to limit our study to the HF level only.

The HF calculations have been carried out for different basis sets, ranging from the 4-31G to the 6-311++G**, that is, from a simple split valence quality to the basis including both diffuse and polarization functions.

As for the comparison between theoretical and experimental EFISH β_λ values, some considerations are in order. In our theoretical approach, use is made of a Taylor expansion of the energy (and of the induced dipole moment) in terms of the applied electric field. In addition, the frequency-dependent operators are all treated in an exponential form, instead of cosine expansion. Both aspects introduce specific constant numerical factors (e.g., a factor equal to 0.5), which must be carefully taken into consideration when theory is compared with experiment, the β_λ values of which are defined according to the so-called "phenomenological" convention.[29a]

Preparation of 4,4′-*trans*-$NC_5H_4CH{=}CHC_6H_4NMe_2$ and of 4,4′-*trans,trans*-$NC_5H_4(CH{=}CH)_2C_6H_4NMe_2$. (i) 4,4′-*trans*-$NC_5H_4CH{=}CHC_6H_4NMe_2$. This compound was prepared following a procedure reported in the literature:[42] yellow

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[37] Singer, K. D.; Sohn, E.; King, L. A.; Gordon, H. M.; Katz, H. E.; Dirk, P. W. *J. Opt. Soc. Am. B* **1989**, *6*, 1339.

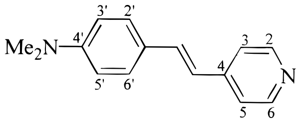
[38] Gerrat, J.; Mills, I. M. *J. Chem. Phys.* **1968**, *49*, 1719.

[39] *MOPAC Manual* (6th ed.), a program product of Stewart, J. J. P., and Seiler, F. J. Research Laboratory−United States Air Force Academy, 1990.

[40] Dupuis, M.; Farazdel, A.; Karna, S. P.; Maluendes, S. A. *HONDO-8 in Modern Techniques in Computational Chemistry; MOTECC-90*; Clementi, E., Ed.; ESCOM: Leiden, 1990.

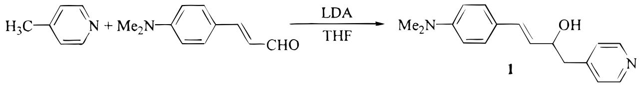
[41] Ditchfield, R.; Hehere, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.

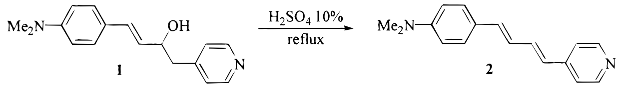
[42] Pentimelli, L. *Gazz. Chim. Ital.* **1961**, *XCI*, 991.



solid; ^{1}H NMR (CDCl$_3$)[43] δ (ppm) 8.52 (d, 2 H, H$_2$ and H$_6$, J = 6.2 Hz), 7.47 (d, 2 H, H$_{2'}$ and H$_{6'}$, J = 8.9 Hz), 7.37 (d, 2 H, H$_3$ and H$_5$, J = 6.2 Hz), 7.29 (d, 1 H, *CH*Ph, J_{trans} = 16.2 Hz), 6.83 (d, 1 H, Py*CH*, J_{trans} = 16.2 Hz), 6.73 (d, 2 H, H$_{3'}$ and H$_{5'}$, J = 8.9 Hz), 3.04 (s, 6 H, NMe$_2$); ^{13}C NMR (CDCl$_3$) δ (ppm) 151.3 (C$_{4'}$), 149.4 (C$_2$ and C$_6$), 146.9 (C$_4$), 134.6 (*C*HPh), 128.9 (C$_{2'}$ and C$_{6'}$), 124.4 (C$_{1'}$), 121.1 (*C*HPy), 120.9 (C$_3$ and C$_5$), 112.6 (C$_{3'}$ and C$_{5'}$), 40.7 (NMe$_2$). Anal. Calcd (found): C 80.32 (80.16), H 7.19 (7.30), N 12.49 (12.39).

(ii) 4,4′-*trans,trans*-NC$_5$H$_4$(CH=CH)$_2$C$_6$H$_4$NMe$_2$. This compound (**2**) was prepared by dehydration with H$_2$SO$_4$ of *trans*-4-[2-hydroxy-2(4′-dimethylaminostyryl)ethyl]pyridine (**1**), obtained by condensation of 4-methylpyridine with 4-dimethylaminocinnamaldehyde in the presence of lithium diisopropylamide (LDA).





(a) Synthesis of *trans*-4-[2-Hydroxy-2(4′-dimethylaminostyryl)ethyl]pyridine (1). A flame-dried round-bottomed flask equipped with thermometer and rubber septum, maintained under nitrogen atmosphere, was charged with 4-methylpyridine (2.71 g; 30 mmol) and dry tetrahydrofuran (THF; 30 mL). To this solution cooled at −78 °C and magnetically stirred was slowly added 16.5 mL of a 2 M THF solution of lithium diisopropylamide (LDA). When the addition was complete, the temperature was raised to −10 °C and the reaction mixture was stirred for 1 h, to allow carbanion formation. The resulting deep red reaction mixture was cooled to −40 °C, and a solution of 4-dimethylaminocinnamaldehyde (5.26 g; 30 mmol) in THF (100 mL) was added via syringe. The cooling bath was then removed, and the reaction mixture, warmed to room temperature, was magnetically stirred for a further 16 h. The mixture was quenched with NH$_4$Cl aqueous solution (50 mL), and the THF was evaporated under vacuum. The residue was taken up with H$_2$O (100 mL) and extracted with CH$_2$Cl$_2$ (3 × 80 mL). The organic phase was dried over MgSO$_4$ and evaporated to afford a red-brown thick residue, which was purified first by column chromatography over silica gel, using ethyl acetate as eluent, and then by crystallization with CH$_2$Cl$_2$/diethyl ether to afford a yellow-green solid (1.65 g; 20.5% yield). ^{1}H NMR (CDCl$_3$): δ (ppm) 8.50 (d, 2 H, H$_2$ and H$_6$, J = 6.0 Hz), 7.25 (d, 2 H, H$_{2'}$ and H$_{6'}$, J = 8.8 Hz), 7.20 (d, 2 H, H$_3$ and H$_5$, J = 6.0 Hz), 6.67 (d, 2H, H$_{3'}$ and H$_{5'}$, J = 8.8 Hz), 6.48 (d, 1 H, *CH*Ph, J_{trans} = 15.8 Hz), 6.00 (dd, 1 H, *CH*=CHPh, J_{trans} = 15.8 Hz; J = 7.0 Hz), 4.51 (q, 1 H, CHO, J = 6.6 Hz), 2.96 (s, 6 H, NMe$_2$), 2.90 (d, 2 H, *CH$_2$*Py, J = 6.4 Hz), 1.68 (broad s, 1 H, OH; it disappears by addition of D$_2$O).

(b) Dehydration of *trans*-4-[2-Hydroxy-2(4′-dimethylaminostyryl)ethyl]pyridine (1). A solution of **1** (393 mg; 1.46 mmol) in 10% H$_2$SO$_4$ aqueous (15 mL) was heated at reflux temperature under magnetic stirring for 1 h. The reaction mixture was then neutralized with 20% NaOH aqueous (30 mL) and extracted with CH$_2$Cl$_2$ (300 mL). The organic phase was washed with H$_2$O (100 mL), dried over MgSO$_4$, and evaporated to dryness to afford a yellow-brown solid residue (351 mg). Purification by crystallization with CH$_2$Cl$_2$/diethyl ether gave 4,4′-*trans,trans*-NC$_5$H$_4$(CH=CH)$_2$C$_6$H$_4$NMe$_2$ (306 mg; 84%). Solid-state color: yellow-brown. ^{1}H NMR (CDCl$_3$): δ (ppm) 8.50 (d, 2 H, H$_2$ and H$_6$, J = 6.0 Hz), 7.35 (d, 2 H, H$_{2'}$ and H$_{6'}$, J = 8.8 Hz), 7.24 (d, 2 H, H$_3$ and H$_5$, J = 6.4 Hz), 7.11 (dd, 1 H, *CH*=CHPh, J = 15.4 and 9.2 Hz), 6.79 (d, 1 H, Py*CH*, J_{trans} = 15.4 Hz), 6.73 (dd, 1 H, PyCH=*CH*, J = 15.4 and 9.2 Hz), 6.68 (d, 2 H, H$_{3'}$ and H$_{5'}$, J = 8.8 Hz), 6.46 (d, 1 H, *CH*Ph, J_{trans} = 15.4 Hz), 3.00 (s, 6 H, NMe$_2$). ^{13}C NMR (CDCl$_3$): δ (ppm) 150.9 (C$_4$), 150.2 (C$_2$ and C$_6$), 145.8 (C$_{4'}$), 136.9 (PyCH=*C*H), 135.1 (*C*H=CHPh), 128.4 (C$_{2'}$ and C$_{6'}$), 127.3 (*C*HPh), 125.4 (C$_{1'}$), 124.3 (*C*HPy), 120.8 (C$_3$ and C$_5$), 112.6 (C$_{3'}$ and C$_{5'}$), 40.7 (NMe$_2$). Anal. Calcd (found): C 81.56 (81.39), H 7.25 (6.87), N 11.19 (11.75).

General Procedure for the Preparation of *cis*-[Rh(CO)$_2$Cl(4-X-C$_5$H$_4$N)] Complexes. In a two-necked flask [Rh(CO)$_2$Cl]$_2$[18b] (0.189 g; 0.486 mmol) was dissolved in anhydrous pentane (40 mL) under nitrogen, and then, the desired substituted 4-X-pyridine (0.972 mmol) was added. Almost immediately, *cis*-[Rh(CO)$_2$Cl(4-X-C$_5$H$_4$N)] began to precipitate with concomitant decrease of the intensity of the ν_{CO} of [Rh(CO)$_2$Cl]$_2$ in the infrared spectrum of the solution. When the reaction was complete, about 3 h as shown by infrared spectroscopy of the solution, the mixture was filtered and the precipitate was washed with a few milliliters of pentane, affording pure *cis*-[Rh(CO)$_2$Cl(4-X-C$_5$H$_4$N)], which was stored in the dark under nitrogen.

X = NMe$_2$: yellow solid; ^{1}H NMR (CDCl$_3$) δ (ppm) 8.18 (d, 2 H, H$_2$ and H$_6$, J = 6.7 Hz), 6.50 (d, 2 H, H$_3$ and H$_5$, J = 6.7 Hz), 3.07 (s, 6 H, NMe$_2$). Anal. Calcd (found): C 34.15 (34.16), H 3.18 (3.23), N 8.85 (8.76). X = CMe$_3$: light brown solid; ^{1}H NMR (CDCl$_3$) δ (ppm) 8.59 (d, 2 H, H$_2$ and H$_6$, J = 6.5 Hz), 7.44 (d, 2 H, H$_3$ and H$_5$, J = 6.5 Hz), 1.34 (s, 9 H, CMe$_3$). Anal. Calcd (found): C 40.08 (40.16), H 3.95 (3.80), N 4.25 (4.10). X = H: orange solid; ^{1}H NMR (CDCl$_3$) δ (ppm) 8.63 (dd, 2 H, H$_2$ and H$_6$, J_{ortho} = 6.5 Hz; J_{meta} = 1.6 Hz), 7.92 (tt, 1 H, H$_4$, J_{ortho} = 7.8 Hz; J_{meta} = 1.6 Hz), 7.49 (m, 2 H, H$_3$ and H$_5$). Anal. Calcd (found): C 30.74 (31.01), H 1.84 (1.95), N 5.12 (5.38). X = CN: orange solid; ^{1}H NMR (CDCl$_3$) δ (ppm) 8.98 (d, 2 H, H$_2$ and H$_6$, J = 6.7 Hz), 7.75 (d, 2 H, H$_3$ and H$_5$, J = 6.7 Hz). Anal. Calcd (found): C 32.18 (32.30), H 1.34 (1.42), N 9.38 (9.51). X = 4′-*trans*-CH=CHC$_6$H$_4$NMe$_2$: yellow solid; ^{1}H NMR (CDCl$_3$) δ (ppm) 8.51 (d, 2 H, H$_2$ and H$_6$, J = 6.5 Hz), 7.45 (d, 2 H, H$_{2'}$ and H$_{6'}$, J = 8.9 Hz), 7.40 (d, 2 H, H$_3$ and H$_5$, J = 6.5 Hz), 7.34 (d, 1 H, *CH*Ph, J_{trans} = 15.9 Hz), 6.77 (d, 1 H, Py*CH*, J_{trans} = 15.9 Hz), 6.71 (d, 2 H, H$_{3'}$ and H$_{5'}$, J = 8.9 Hz), 3.04 (s, 6 H, NMe$_2$). Anal. Calcd (found): C 48.77 (48.70), H 3.85 (3.53), N 6.69 (6.66). X = 4′-*trans,trans*-(CH=CH)$_2$C$_6$H$_4$NMe$_2$: dark red solid; ^{1}H NMR (CDCl$_3$) δ (ppm) 8.51 (d, 2 H, H$_2$ and H$_6$, J = 6.6 Hz), 7.38 (broad "doublet" due to the overlap of two doublets, 4 H, H$_3$, H$_5$, H$_{2'}$ and H$_{6'}$), 7.31 (m, 1 H, PyCH=*CH*), 6.86 (d, 1 H, Py*CH*, J_{trans} = 14.7 Hz), 6.81 (m, 1 H, *CH*=CHPh), 6.69 (d, 2 H, H$_{3'}$ and H$_{5'}$, J = 8.7 Hz), 6.45 (d, 1 H, *CH*Ph, J_{trans} = 15.4 Hz), 3.02 (s, 6 H, NMe$_2$). Anal. Calcd (found): C 51.31 (51.26), H 4.05 (4.29), N 6.30 (6.43).

Preparation of [Rh(COD)Cl(4,4′-*trans*-NC$_5$H$_4$CH=CHC$_6$H$_4$NMe$_2$)]. In a two-necked flask [Rh(COD)Cl]$_2$[19] (0.201 g; 0.408 mmol) was dissolved in anhydrous dichloromethane (50 mL) under nitrogen, and then, 4,4′-*trans*-NC$_5$H$_4$CH=CHC$_6$H$_4$NMe$_2$ (0.183 g; 0.816 mmol) was added. After stirring at room temperature for ca. 7 h, the solution was evaporated to dryness, affording [Rh(COD)Cl(4,4′-*trans*-NC$_5$H$_4$CH=CHC$_6$H$_4$NMe$_2$)], which was stored in the dark under nitrogen: yellow

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[43] For 4,4′-*trans*-NC$_5$H$_4$CH=CHC$_6$H$_4$NMe$_2$, the reported assignments[9] of the ^{1}H NMR chemical shifts of CH=CH, H$_{3'}$, H$_{5'}$, H$_{2'}$, and H$_{6'}$ are different from ours (which have been assigned on the basis of the possible resonance structures), although the related ^{13}C NMR chemical shifts are the same. Therefore we used the heteronuclear multiple quantum correlation (HMQC) spectroscopy with bilinear rotation decoupling (BIRD) technique to determine which ^{1}H's of the molecule are bonded to which ^{13}C nuclei, confirming our assignments.

[44] McClellan, A. L. *Tables of experimental dipole moments*; W. H. Freeman and Co.: San Francisco, 1963.

solid; ^{1}H NMR (CDCl$_3$) δ (ppm) 8.57 (d, 2 H, H$_2$ and H$_6$, $J = 5.8$ Hz), 7.46 (d, 2 H, H$_{2'}$ and H$_{6'}$, $J = 8.4$ Hz), 7.35 (m, 3 H, H$_3$, H$_5$, and *CH*Ph), 6.76 (d, 1 H, Py*CH*, $J_{\text{trans}} = 17.2$ Hz), 6.72 (d, 2 H, H$_{3'}$ and H$_{5'}$, $J = 8.4$ Hz), 3.05 (s, 6 H, NMe$_2$), 4.17 (m, 4 H, olefinic H of COD), 2.52 (m, 4 H, aliphatic H of COD), 1.85 (m, 4 H, aliphatic H of COD). Anal. Calcd (found): C 58.61 (58.48), H 5.94 (6.06), N 5.94 (6.11).

General Procedure for the Preparation of *cis*-[Ir(CO)$_2$Cl(4-X-C$_5$H$_4$N)] Complexes. In a three-necked flask [Ir(COT)$_2$Cl]$_2$[17] (0.208 g; 0.232 mmol) was added to dehydrated CH$_3$CN (50 mL) under nitrogen. The suspension was stirred for 2 min, and then nitrogen was replaced by CO. A yellow solution was obtained immediately, due to the conversion of [Ir(COT)$_2$Cl]$_2$ in [Ir(CO)$_2$Cl]$_2$.[16] After 2 min under CO, the desired substituted 4-X-pyridine (0.464 mmol) was added. After ca. 5 min, all [Ir(CO)$_2$Cl]$_2$ had been converted in *cis*-[Ir(CO)$_2$Cl(4-X-C$_5$H$_4$N)], as shown by infrared spectroscopy. After 1 h, the solution was evaporated to dryness; the residue was dissolved in a minimum amount of dichloromethane, added with pentane, and cooled (0 °C). The resulting precipitate was filtered and dried under vacuum, affording pure *cis*-[Ir(CO)$_2$Cl(4-X-C$_5$H$_4$N)], which was stored in the dark under nitrogen.

X = NMe$_2$: yellow solid; ^{1}H NMR (CDCl$_3$) δ (ppm) 8.25 (d, 2 H, H$_2$ and H$_6$, $J = 6.5$ Hz), 6.53 (d, 2 H, H$_3$ and H$_5$, $J = 6.5$ Hz), 3.10 (s, 6 H, NMe$_2$); MS *m*/*e* 406 [M]$^+$. Anal. Calcd (found): C 26.18 (26.31), H 2.44 (2.16), N 6.79 (6.85). X = CMe$_3$: yellow solid; ^{1}H NMR (CDCl$_3$) δ (ppm) 8.66 (d, 2 H, H$_2$ and H$_6$, $J = 6.5$ Hz), 7.46 (d, 2 H, H$_3$ and H$_5$, $J = 6.5$ Hz), 1.34 (s, 9 H, CMe$_3$). Anal. Calcd (found): C 31.54 (31.45), H 3.13 (3.10), N 3.34 (3.28). X = CN: dark brown solid; ^{1}H NMR (CDCl$_3$) δ (ppm) 9.02 (d, 2 H, H$_2$ and H$_6$, $J = 6.4$ Hz), 7.75 (d, 2 H, H$_3$ and H$_5$, $J = 6.4$ Hz). Anal. Calcd (found): C 24.78 (24.80), H 1.04 (0.90), N 7.22 (7.12). X = 4′-*trans*-CH=CHC$_6$H$_4$-NMe$_2$: orange solid; ^{1}H NMR (CDCl$_3$) δ (ppm) 8.58 (d, 2 H, H$_2$ and H$_6$, $J = 5.9$ Hz), 7.49 (d, 2 H, H$_{2'}$ and H$_{6'}$, $J = 8.4$ Hz), 7.46 (d, 2 H, H$_3$ and H$_5$, $J = 5.9$ Hz), 7.40 (d, 1 H, *CH*Ph, $J_{\text{trans}} = 16.2$ Hz), 6.80 (d, 1 H, Py*CH*, $J_{\text{trans}} = 16.2$ Hz), 6.73 (d, 2 H, H$_{3'}$ and H$_{5'}$, $J = 8.4$ Hz), 3.04 (s, 6 H, NMe$_2$). Anal. Calcd (found): C 40.16 (40.46), H 3.15 (3.38), N 5.51 (5.40). X = 4′-*trans,trans*-(CH=CH)$_2$C$_6$H$_4$NMe$_2$: dark red solid; ^{1}H NMR (CDCl$_3$) δ (ppm) 8.56 (d, 2 H, H$_2$ and H$_6$, $J = 6.5$ Hz), 7.39 (broad "doublet" due to the overlap of two doublets, 4 H, H$_3$, H$_5$, H$_{2'}$ and H$_{6'}$), 7.33 (m, 1 H, PyCH=*CH*), 6.87 (d, 1 H, Py*CH*, $J_{\text{trans}} = 14.7$ Hz), 6.81 (m, 1 H, *CH*=CHPh), 6.70 (d, 2 H, H$_{3'}$ and H$_{5'}$, $J = 8.6$ Hz), 6.45 (d, 1 H, *CH*Ph, $J_{\text{trans}} = 15.3$ Hz), 3.03 (s, 6 H, NMe$_2$). Anal. Calcd (found): C 42.70 (42.88), H 3.40 (3.33), N 5.25 (5.27).

General Procedure for the Preparation of [Ir(COT)$_2$Cl(4,4′-*trans*- or *trans,trans*-NC$_5$H$_4$(CH=CH)$_n$C$_6$H$_4$NMe$_2$)] (*n* = 1 or 2) Complexes. In a three-necked flask [Ir(COT)$_2$Cl]$_2$[17] (0.208 g; 0.232 mmol) was dissolved in anhydrous dichloromethane (70 mL) under nitrogen, and then, the desired substituted 4-X-pyridine (X = 4′-*trans*-CH=CHC$_6$H$_4$NMe$_2$ or 4′-*trans,trans*-(CH=CH)$_2$C$_6$H$_4$NMe$_2$; 0.464 mmol) was added. After stirring at room temperature for ca. 4 h, the solution was evaporated to dryness; the residue was dissolved in a minimum amount of dichloromethane, added with pentane, and cooled (0 °C). The resulting precipitate was filtered and dried under vacuum, affording pure [Ir(COT)$_2$Cl(4,4′-*trans*- or *trans,trans*-NC$_5$H$_4$(CH=CH)$_n$C$_6$H$_4$NMe$_2$)] (*n* = 1 or 2), which was stored in the dark under nitrogen.

X = 4′-*trans*-CH=CHC$_6$H$_4$NMe$_2$; orange solid; ^{1}H NMR (CDCl$_3$) δ (ppm) 8.65 (2 H, H$_2$ and H$_6$), 7.43 (2 H, H$_{2'}$ and H$_{6'}$), 7.32 (3 H, H$_3$, H$_5$ and *CH*Ph), 6.70 (3 H, H$_{3'}$, H$_{5'}$, and Py*CH*), 3.03 (s, 6 H, NMe$_2$), 2.13 (4 H, olefinic H of COT), 1.61 (24 H, aliphatic H of COT); MS *m*/*e* 673 [M]$^+$. Anal. Calcd (found): C 55.40 (55.54), H 6.50 (6.38), N 4.20 (4.41). X = 4′-*trans,trans*-(CH=CH)$_2$C$_6$H$_4$NMe$_2$: dark orange solid; ^{1}H NMR (CDCl$_3$) δ (ppm) 8.63 (2 H, H$_2$ and H$_6$), 7.35 (5 H, H$_3$, H$_5$, H$_{2'}$, H$_{6'}$ and PyCH=*CH*), 6.70 (5 H, Py*CH*, *CH*=*CH*Ph, H$_{3'}$ and H$_{5'}$), 3.01 (s, 6 H, NMe$_2$), 2.13 (4 H, olefinic H of COT), 1.63 (24 H, aliphatic H of COT). Anal. Calcd (found): C 56.64 (56.81), H 6.58 (6.33), N 4.01 (4.11).

General Procedure for the Preparation of *fac*-[Os(CO)$_3$Cl$_2$(4-X-C$_5$H$_4$N)] Complexes. α-[Os(CO)$_3$Cl$_2$]$_2$[18b,20] (0.273 g; 0.395 mmol) was dissolved in 1,2-dichloroethane (180 mL), and then, the desired substituted 4-X-pyridine (0.790 mmol) was added. After stirring at room temperature for ca. 16 h, [Os(CO)$_3$Cl$_2$(4-X-C$_5$H$_4$N)] was obtained as a mixture of *mer* and *fac* isomers, as shown by infrared spectroscopy of the solution. The relative amount of the *fac* isomer, which was higher when the X substituent was a strong electron-acceptor group such as CN, could be increased by refluxing the reaction mixture for a few days. Evaporation of the solution to dryness followed by column chromatography (using silica gel 60 and dichloromethane as eluant) afforded pure *fac*-[Os(CO)$_3$Cl$_2$(4-X-C$_5$H$_4$N)] (isomer eluted first).

X = NMe$_2$: beige solid; ^{1}H NMR (CDCl$_3$) δ (ppm) 8.45 (d, 2 H, H$_2$ and H$_6$, $J = 7.5$ Hz), 6.53 (d, 2 H, H$_3$ and H$_5$, $J = 7.5$ Hz), 3.11 (s, 6 H, NMe$_2$). Anal. Calcd (found): C 25.70 (25.87), H 2.16 (2.26), N 5.99 (5.83). X = CMe$_3$: pale yellow solid; ^{1}H NMR (CDCl$_3$) δ (ppm) 8.92 (d, 2 H, H$_2$ and H$_6$, $J = 6.5$ Hz), 7.50 (d, 2 H, H$_3$ and H$_5$, $J = 6.5$ Hz), 1.36 (s, 9 H, CMe$_3$). Anal. Calcd (found): C 30.01 (30.25), H 2.73 (2.78), N 2.92 (2.90). X = H: pale yellow solid; ^{1}H NMR (CDCl$_3$) δ (ppm) 9.09 (dd, 2 H, H$_2$ and H$_6$, $J_{\text{ortho}} = 5.1$ Hz; $J_{\text{meta}} = 1.5$ Hz), 8.05 (tt, 1 H, H$_4$, $J_{\text{ortho}} = 7.6$ Hz; $J_{\text{meta}} = 1.5$ Hz), 7.55 (m, 2 H, H$_3$ and H$_5$). Anal. Calcd (found): C 22.65 (22.75), H 1.19 (1.05), N 3.30 (3.25). X = COMe: beige solid; ^{1}H NMR (CDCl$_3$) δ (ppm) 9.26 (d, 2 H, H$_2$ and H$_6$, $J = 6.3$ Hz), 7.95 (d, 2 H, H$_3$ and H$_5$, $J = 6.3$ Hz), 2.70 (s, 3 H, COMe). Anal. Calcd (found): C 25.75 (25.95), H 1.51 (1.69), N 3.00 (3.00). X = CN: beige solid; ^{1}H NMR (CDCl$_3$) δ (ppm) 9.30 (d, 2 H, H$_2$ and H$_6$, $J = 6.5$ Hz), 7.82 (d, 2 H, H$_3$ and H$_5$, $J = 6.5$ Hz). Anal. Calcd (found): C 24.06 (24.28), H 0.90 (0.97), N 6.23 (6.18). X = 4′-*trans*-CH=CHC$_6$H$_4$-NMe$_2$: orange solid; ^{1}H NMR (CDCl$_3$) δ (ppm) 8.80 (d, 2 H, H$_2$ and H$_6$, $J = 6.4$ Hz), 7.53 (d, 2 H, H$_{2'}$ and H$_{6'}$, $J = 9.0$ Hz), 7.48 (d, 2 H, H$_3$ and H$_5$, $J = 6.4$ Hz), 7.38 (d, 1 H, *CH*Ph, $J_{\text{trans}} = 15.7$ Hz), 6.79 (d, 1 H, Py*CH*, $J_{\text{trans}} = 15.7$ Hz), 6.73 (d, 2 H, H$_{3'}$ and H$_{5'}$, $J = 9.0$ Hz), 3.05 (s, 6 H, NMe$_2$). Anal. Calcd (found): C 37.97 (37.58), H 2.83 (2.63), N 4.91 (4.96). X = 4′-*trans,trans*-(CH=CH)$_2$C$_6$H$_4$NMe$_2$: red solid; ^{1}H NMR (CDCl$_3$) δ (ppm) 8.80 (d, 2 H, H$_2$ and H$_6$, $J = 6.3$ Hz), 7.38 (broad "doublet" due to the overlap of two doublets, 4 H, H$_3$, H$_5$, H$_{2'}$ and H$_{6'}$), 7.33 (m, 1 H, PyCH=*CH*), 6.88 (d, 1 H, Py*CH*, $J_{\text{trans}} = 14.7$ Hz), 6.82 (m, 1 H, *CH*=CHPh), 6.69 (d, 2 H, H$_{3'}$ and H$_{5'}$, $J = 8.7$ Hz), 6.46 (d, 1 H, *CH*Ph, $J_{\text{trans}} = 15.3$ Hz), 3.02 (s, 6 H, NMe$_2$). Anal. Calcd (found): C 40.33 (40.38), H 3.02 (3.13), N 4.70 (4.65).

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