5830 *Organometallics* **2002,** *21,* 5830−5840

Organometallic Counterparts of Push−Pull Aromatic Chromophores for Nonlinear Optics: Push−Pull Heteronuclear Bimetallic Complexes with Pyrazine and *trans*-1,2-Bis(4-pyridyl)ethylene as Linkers

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Received August 5, 2002

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on November 27, 2002 on http://pubs.acs.org | doi: 10.1021/om020633h

We report the synthesis, electronic properties, and second-order nonlinear optical (NLO) response of asymmetric heteronuclear push−pull bimetallic complexes with pyrazine (pyz) and *trans*-1,2-bis(4-pyridyl)ethylene (BPE) as polarizable linkers, connecting the "W(CO)$_5$" fragment (acting as donor group) and "*cis*-Rh(CO)$_2$Cl", "*cis*-Re(CO)$_4$Cl", and BF$_3$ fragments (acting as acceptor groups). The second-order NLO response was assessed by the EFISH technique (β_{vec}), working with a nonresonant incident wavelength of 1.907 μm and by solvatochromic studies (β_{CT}). These results are compared with the behavior of mononuclear [W(CO)$_5$L] complexes (L = pyridine or *trans*-stilbazole *para* substituted with acceptor groups) and of classical structurally related organic push−pull aromatic chromophores. The second-order NLO response of asymmetric chromophores with BPE as linker is comparable, with the exception of the sign, to classical push−pull stilbenic compounds. However when pyrazine is the linker, the response can be higher (BF$_3$ as acceptor group) or higher but with opposite sign ("*cis*-Rh(CO)$_2$Cl" as acceptor group) than the related push−pull benzenic chromophores. Only with a pyrazine linker and "*cis*-Re(CO)$_4$Cl" as acceptor does the second-order NLO response becomes irrelevant. The above results are interpreted assuming that the MLCT (W → π^*_L) transition, originating from the "W(CO)$_5$" moiety, dominates the second-order response of these push−pull heteronuclear dimeric chromophores.

Introduction

Bimetallic complexes, with reduced and oxidized metal centers in electronic communication through a polarizable bridge, first became of interest in the late 1960s with the synthesis of the Creuz−Taube complex containing pyrazine bridging Ru(II), Ru(III) centers.[1a] The relevant property of these bimetallic complexes is facile electron transfer through the pyrazine bridge, as confirmed by a metal-to-metal charge transfer absorption band (MMCT), absent in the electronic absorption spectrum of the individual fragments.[1b]

This usually intense charge transfer band, occurring at relatively low energy and with a large difference between the dipole moment of the ground and the excited state, could lead, in asymmetric bridged systems, to a significant NLO response, as predicted by the so-called two-level model.[2] In this approximation, the quadratic hyperpolarizability β_{CT} is expressed by the following equation:

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

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

The quadratic hyperpolarizability of various nitrogen donor π-delocalized ligands such as pyridines,[3,4,5a] stilbazoles,[4−6] bipyridines,[7] and terpyridines[8] can be greatly enhanced upon coordination to metals. These

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10.1021/om020633h CCC: $22.00 © 2002 American Chemical Society
Publication on Web 11/27/2002

Downloaded by CARLI CONSORTIUM on June 29, 2009 | doi: 10.1021/om020633h
Published on November 27, 2002 on http://pubs.acs.org | doi: 10.1021/om020633h

complexes, in excitation processes controlling the NLO response, can act as an electron donor or acceptor depending on electron configuration, oxidation state, and ligand environment and also on the donor or acceptor nature of the substituents in the pseudo-aromatic ring of the ligands.[4,5]

The second-order NLO properties of several heteronuclear bimetallic systems have been studied extensively,[9,10] but bimetallic complexes M−S−M′ (M, M′= metal carbonyl fragments; S = π-polarizable bridge such as pyrazine or a linear π-delocalized ligand with two nitrogen donor atoms at both ends) have never been investigated, although their redox properties and photophysical and photochemical behavior are well known.[11−13]

In these latter heteronuclear bimetallic systems, with a polarizable linker with two nitrogen donor atoms at both ends, the "$W(CO)_5$" moiety could act, in the excitation process, as a suitable electron donor when the opposite metal center is a stronger electron acceptor. This kind of molecular architecture with two metal fragments at both ends of this kind of pseudo-aromatic linker can be structurally considered as an organometallic counterpart of the well-known *para*-substituted benzenic push−pull chromophores.[14,15]

Homo- and heteronuclear complexes with pyrazine (pyz), 4,4′-bipyridine (bpy), or *trans*-1,2-bis(4-pyridyl)-ethylene (BPE) as bridges, such as $[(CO)_5W(pyz)M(CO)_5]$ (M = Cr, Mo, W),[13b] $[(CO)_5W(bpy)M(CO)_5]$ (M = Cr, Mo,W),[13c] or $[(CO)_5W(BPE)W(CO)_5]$,[13c,16] all show in their UV−visibile spectra a relatively strong metal-to-ligand charge transfer transition (MLCT; W → π^*_L where L = pyz, bpy, or BPE) shifted to lower energy with respect to the related mononuclear $[W(CO)_5L]$ complexes with pyrazine, bpy, or BPE acting only as η^1-monodentate ligands.[13b,c,16] Since a low-energy charge transfer process should favor, according to the two-level model[2] (eq 1), a significant second-order NLO response, we investigated the synthesis, electronic properties, and second-order NLO response of asymmetrical bimetallic heteronuclear complexes where pyrazine and BPE act as a polarizable linker between the "$W(CO)_5$" probe (acting as donor group)[4] and "*cis*-$Rh(CO)_2Cl$", "*cis*-$Re(CO)_4Cl$", and BF_3 fragments (acting as acceptor groups).[5,6,12] Their second-order NLO response is compared to that of related monomeric $[W(CO)_5L]$ complexes, where L is a pyridine or a *trans*-stilbazole *para*-substituted with strong organic acceptor groups,[3,4] and also to classical benzenic or *trans*-stilbenic *para*-substituted push−pull chromophores.[14,15]

Results and Discussion

Synthesis, Infrared, and ^1H NMR Characterization. The dimeric complexes were prepared under nitrogen atmosphere by room-temperature reaction of equimolar amounts of $[W(CO)_5pyz]$[13b,17] or $[W(CO)_5\text{-}BPE]$,[13c,16] freshly prepared by photochemical activation of $[W(CO)_6]$ in tetrahydrofuran (THF)[18] (see Experimental Section), with $BF_3{\cdot}OEt_2$ or the appropriate organometallic complex $[Rh(CO)_2Cl]_2$[19] or [*cis*-$Re(CO)_4Cl(THF)$] (obtained in situ from $[Re(CO)_4Cl]_2$):[20]

$$[W(CO)_5L] + BF_3{\cdot}OEt_2 \xrightarrow[25\ °C]{CHCl_3} [(CO)_5W(L)BF_3] + OEt_2$$

$$[W(CO)_5L] + [cis\text{-}Re(CO)_4Cl(THF)] \xrightarrow[0-5\ °C]{THF} [(CO)_5W(L)cis\text{-}Re(CO)_4Cl]$$

$$[W(CO)_5L] + 1/2[Rh(CO)_2Cl]_2 \xrightarrow[25\ °C]{CHCl_3} [(CO)_5W(L)cis\text{-}Rh(CO)_2Cl]$$

$$L = pyz,\ BPE$$

A different synthesis of $[(CO)_5W(pyz)$*cis*-$Re(CO)_4Cl]$, by reaction of [*cis*-$Re(CO)_4Clpyz$] with photochemically generated $[W(CO)_5(THF)]$, was reported.[12] However we were unable to obtain acceptable yields and purities using this method. Thus we followed, as shown above, the reverse pathway, which gives the pure dimeric complex in better yields.

All reactions take place rapidly, as evidenced by rapid color changes and the disappearance of ^1H NMR signals attributable to the $[W(CO)_5L]$ precursor.

All compounds were characterized by elemental analyses, IR (Table 1), and ^1H, ^{11}B, ^{19}F NMR spectroscopies (Table 2). They are quite stable in the solid state, when left under dry nitrogen. In solution, the compounds containing the BF_3 fragment are rather unstable and decompose in minutes, while the others, with the exception of $[(CO)_5W(pyz)$*cis*-$Re(CO)_4Cl]$, which is very stable in $CHCl_3$ at room temperature, very slowly rearranges to generate small amounts of both the

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Table 1. Carbonyl Stretching Frequencies in CH_2Cl_2 (Pyz = pyrazine; BPE = *trans*-1,2-bis(4-pyridyl)ethylene)

compound	ν_{CO} (cm^{-1})
$[W(CO)_5pyz]$	2074(m), 1934(vs), 1907(sh)
$[(CO)_5W(pyz)BF_3]$	2075(m), 1941(vs)
$[W(CO)_5BPE]$	2071(m), 1929(vs), 1896(sh)
$[(CO)_5W(BPE)BF_3]$	2071(m), 1930(vs), 1900(sh)
[*cis*-$Re(CO)_4Clpyz$][a]	2119(m), 2010(s), 1985(m), 1930(s)
$[(CO)_5W(pyz)$*cis*-$Re(CO)_4Cl]$	2118(w),2073(m), 2035(m), 2021(m), 2005(sh), 1940(vs)
$[(CO)_5W(BPE)$*cis*-$Re(CO)_4Cl]$	2136(w), 2071(w), 2013(m), 1996(m), 1931(vs), 1898(sh)
[*cis*-$Rh(CO)_2Clpyz$][b]	2086(s), 2012(s)
$[(CO)_5W(pyz)$*cis*-$Rh(CO)_2Cl]$	2107(w), 2095(m), 2074(m), 2034(w), 2023(m), 1937(vs)
[*cis*-$Rh(CO)_2ClBPE$][c]	2087(s), 2013(s)
$[(CO)_5W(BPE)$*cis*-$Rh(CO)_2Cl]$	2088(m), 2071(w), 2014(m), 1930(vs), 1898(sh)

[a] Reference 12. [b] In THF, ref 21. [c] In the presence of excess BPE.

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mononuclear species $[W(CO)_5L]$ and the symmetrical homonuclear species $[(CO)_5W(L)W(CO)_5]$, as evidenced by ^1H NMR spectroscopy. This rearrangement is slow enough to allow the correct determination of experimental dipole moments, second-order NLO response by EFISH, and UV–vis and fluorescence spectra (below), as confirmed by a ^1H NMR control after the measurements.

The IR spectrum in the carbonyl-stretching region of the asymmetric dimers is roughly the sum of the spectra of the two separate metal carbonyl fragments (Table 1). The stretching frequencies of the "$W(CO)_5$" moiety are unaltered when bridged by BPE, but experience a shift of 3–8 cm^{-1} to higher frequencies of the 1934 cm^{-1} band bridged by pyrazine. Equally, ν_{CO} of the "*cis*-$Re(CO)_4Cl$" and "*cis*-$Rh(CO)_2Cl$" fragments are unaltered by BPE bridges, while there is a shift of about 8–10 cm^{-1} to higher frequencies if pyrazine is used as a bridge. This suggests that, in the ground state, each inorganic fragment has a rather small pull effect on the other bridged fragment. This small perturbation is transmitted by pyrazine, but not by BPE, as expected, because of the greater distance between the two fragments.

The ^1H NMR spectra show the expected AA′BB′ pattern. The ^1H NMR spectra in $CDCl_3$ or CD_2Cl_2 of the mononuclear complexes and free pyrazine evidence a shift to low field of pyrazine protons close to the nitrogen atom coordinated to a metal carbonyl or BF_3 acceptor fragment, while the other protons do not shift significantly (Table 2). Since the observed low-field shift is associated with an σ inductive perturbation originating from electron donation to the acceptor center, we can assume, on the basis of the strength of this shift, that the acceptor properties decrease as follows: BF_3 > "*cis*-$Re(CO)_4Cl$" > "*cis*-$Rh(CO)_2Cl$" > "$W(CO)_5$" (Table 2).

A similar shift occurs when BPE is linked to "$W(CO)_5$" (in CD_2Cl_2 from 8.63 to 8.82 ppm) or to BF_3 (in CD_2Cl_2 from 8.63 to 8.78 ppm) (Table 2). For the monomeric species [*cis*-$Rh(CO)_2Cl(BPE)$], we could not obtain ^1H NMR spectra (see Experimental Section), due to its quick transformation in CD_2Cl_2 or $CDCl_3$ solution into the insoluble homonuclear dimer $[Cl(CO)_2$*cis*-$Rh(BPE)$-*cis*-$Rh(CO)_2Cl]$.[21]

These different acceptor properties of the various metal carbonyl fragments and of BF_3 should produce a significant electronic asymmetry in the ground state of the heteronuclear bimetallic complexes $[(CO)_5W(L)M']$ ($M' = BF_3$, *cis*-$Re(CO)_4Cl$, *cis*-$Rh(CO)_2Cl$; L = pyz, BPE), a requirement for second-order NLO responses.[2]

Such a significant asymmetry is confirmed by the ^1H NMR spectra of these heteronuclear bimetallic complexes with pyrazine bridges, which show two multiplets, typical of a very asymmetrical AA′BB′ system. When M′ is BF_3, there is a further shift to low field, as compared to the related monomeric species, of the protons close to the nitrogen coordinated to BF_3 (from 9.28 to 9.49 ppm), with in parallel a high-field shift of the protons close to the nitrogen atom coordinated to "$W(CO)_5$" (from 8.83 to 8.53 ppm). This latter value of 8.53 ppm is not far from that of free pyrazine (8.59 ppm), suggesting that, when coupled to a strong acceptor such as BF_3, the "$W(CO)_5$" moiety begins to behave even in the ground state as an electron donor as a consequence of the relevant pull effect of the acceptor center. A similar but less significant effect occurs when M′ = *cis*-$Rh(CO)_2Cl$, as expected for its poorer electron acceptor properties (Table 2).

However when M′ = *cis*-$Re(CO)_4Cl$, we see an opposite trend with a further small shift to lower fields of both pyrazine protons close to the nitrogen coordinated to "$W(CO)_5$" (from 9.10 to 9.27 ppm in deuterated acetone) and of those close to the nitrogen coordinated to "*cis*-$Re(CO)_4Cl$" (from 9.26 to 9.37 ppm in deuterated acetone) (Table 2). This is not in line with the comparable acceptor properties of "*cis*-$Rh(CO)_2Cl$" and "*cis*-$Re(CO)_4Cl$" (see above), suggesting that in our pyrazine-bridged heteronuclear bimetallic complexes the electronic asymmetry with two octahedral $5d^6$ metal fragments is not significant even with different oxidation states. The perturbation process probably involves both inductive σ effects and π back-donation. Obviously this latter process is more symmetrical when both metal centers have a $5d^6$ electron configuration with octahedral coordination.

When the bridging ligand is BPE, the ^1H NMR pattern is more complex, but similar trends are observed, with less relevant effects due to the increased distance between the donor and acceptor centers (Table 2).

The stronger pull effect generated by BF_3 coordination is confirmed by the expected shift to high field, compared to the related mononuclear complex, of the protons close to the nitrogen coordinated to "$W(CO)_5$", and also by two separate doublets due to the protons of the ethylene bridge, still in a *trans* arrangement, as a sign of a significant electronic asymmetry. When the other acceptor moiety is "*cis*-$Re(CO)_4Cl$" or "*cis*-Rh-

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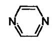
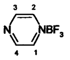
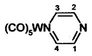
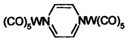
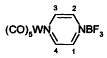
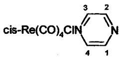
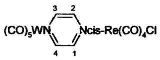
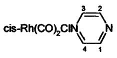
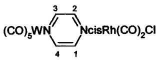
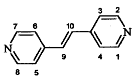
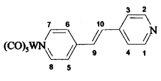
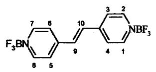
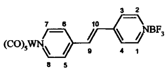
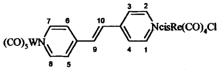
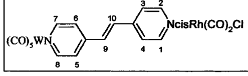
Table 2. ^{1}H, ^{11}B, and ^{19}F NMR Data (ppm)

Compound	δ (ppm)[(a)]	Solvent
	8.59(s) 8.62(s)	$CDCl_3$ d^6-acetone
(b) 	9.28(H_1H_2), 8.70(H_3H_4) ^{19}F −154.6(s)	CD_2Cl_2
	8.83(H_3H_4), 8.63(H_1H_2) 9.10(H_3H_4), 8.77(H_1H_2)	$CDCl_3$ d^6-acetone
	9.12(s)	d^6-acetone
(b) 	9.49(H_1H_2), 8.53(H_3H_4) ^{11}B 1.761(s); ^{19}F −156(s)	CD_2Cl_2
	9.26(H_3H_4), 8.96(H_1H_2)	d^6-acetone
	9.37(H_1H_2), 9.27(H_3H_4)	d^6-acetone
	8.90(H_3H_4), 8.75(H_1H_2)	$CDCl_3$ (-50°C)
	9.01(H_1H_2), 8.67(H_3H_4)	CD_2Cl_2
	8.63($H_1H_2H_7H_8$), 7.44($H_3H_4H_5H_6$), 7.28(s, H_9H_{10}) 8.60($H_1H_2H_7H_8$), 7.58($H_3H_4H_5H_6$), 7.51(s, H_9H_{10})	CD_2Cl_2 d^6-acetone
	8.82(H_7H_8), 8.67(H_1H_2), 7.46(H_5H_6), 7.40(H_3H_4), 7.33(d, H_9), 7.27(d, H_{10}) 9.01(H_7H_8), 8.63(H_1H_2), 7.73(H_5H_6), 7.67(d, H_9), 7.63(d, H_{10}),7.61(H_3H_4)	CD_2Cl_2 d^6-acetone
	8.78($H_1H_2H_7H_8$), 7.93($H_3H_4H_5H_6$), 7.57(s, H_9H_{10})	CD_2Cl_2
(b) 	8.94(H_1H_2), 8.75(H_7H_8), 8.10(H_3H_4), 7.57(d, H_9),7.50(H_5H_6), 7.45 (d, H_{10}) ^{11}B 0.879(s); ^{19}F −153.5(s)	CD_2Cl_2
	9.18(H_1H_2), 9.06(H_7H_8), 7.90(H_3H_4), 7.81(s, H_9H_{10}), 7.78(H_5H_6)	d^6-acetone
(c) 	8.82(H_1H_2), 8.70(H_7H_8), 7.58(H_3H_4), 7.38(H_5H_6), 7.30(s, H_9H_{10})	CD_2Cl_2

[a] The signals of pyz and BPE rings are multiplets of a AA′BB′ system. [b] For $BF_3 \cdot OEt_2$ in CD_2Cl_2: ^{19}F −155.6 ppm; ^{11}B 1.73 ppm. [c] At −80 °C the singlet at 7.30 ppm becomes two very close doublets.

(CO)$_2$Cl”, only a small shift is seen to low and high field, respectively, of the protons close to the nitrogen coordinated to the “W(CO)$_5$” moiety. In both cases, the ethylene bridge protons coalesce to a broad pseudo-singlet, suggesting a low electronic asymmetry (Table 2). When the acceptor center is “*cis*-Rh(CO)$_2$Cl”, this signal changes at −80°C in CD_2Cl_2 solution from a broad singlet into two close doublets.

UV Visibile and Emission Spectra. The UV−visible absorption spectrum of the monomeric complex [W(CO)$_5$pyz] shows a high-energy MLCT ($M \rightarrow \pi^*_{CO}$) transition and two other absorption bands that overlap at about 400 nm, due to a ligand field $^1A_1-^1E$ (LF) transition and to a MLCT transition ($W \rightarrow \pi^*_L$) where π^*_L are the acceptor orbitals of pyrazine (Table 3).[13c] In the complex [W(CO)$_5$BPE], the MLCT transition shifts as a shoulder to slightly lower energy (Table 3),[13c] as expected for the better acceptor properties of the π^*_L orbitals of the more π-conjugated BPE ligand. The complex [*cis*-Re(CO)$_4$Clpyz] is characterized by a similar spectrum, but with both transitions, $^1A_1-^1E$ (LF) and MLCT ($Re \rightarrow \pi^*_L$), at higher energy and not overlapping[12] (Table 3). The complexes [*cis*-Rh(CO)$_2$ClL] (L = pyz,[21] *para*-(dimethylamino)pyridine[5a]) show absorption bands only at high energy (250−340 nm). Probably the weak LF transitions are completely obscured by strong MLCT transitions (both $M \rightarrow \pi^*_{CO}$ and $M \rightarrow \pi^*_L$), as in many other Rh(I) dicarbonyl complexes with phosphines[22] or various pyridines[23] as ligands.

In symmetrical homonuclear dimeric complexes with pyrazine linking the “W(CO)$_5$” or “*cis*-Re(CO)$_4$Cl” moieties the MLCT ($M \rightarrow \pi^*_L$) transitions are shifted substantially to lower energy (Table 3);[12,13c] however in the homonuclear dimeric complex [*cis*-Rh(CO)$_2$Cl(pyz)-*cis*-Rh(CO)$_2$Cl], the absorption spectrum, which is similar to that of the mononuclear complex [*cis*-Rh(CO)$_2$Clpyz] (Table 3), does not result in a significant shift to lower energy of the MLCT ($Rh \rightarrow \pi^*_L$) transition.[21]

In our pyrazine asymmetric heteronuclear dimeric complexes, the MLCT ($W \rightarrow \pi^*_L$) transition of the “W(CO)$_5$pyz” moiety shows a significant red shift to 499 and 503 nm, respectively, when the acceptor metal carbonyl moiety is “*cis*-Rh(CO)$_2$Cl” or “*cis*-Re(CO)$_4$Cl”.[4] Such a trend is substantially the same as reported for the symmetrical dimeric [(CO)$_5$W(pyz)W(CO)$_5$] complex.[13c] On the other hand we find no evidence of a significant red shift of the MLCT ($Rh \rightarrow \pi^*_L$ or $Re \rightarrow \pi^*_L$) transitions of the acceptor metal carbonyl fragment. In the heteronuclear dimers [(CO)$_5$W(BPE)*cis*-Re(CO)$_4$Cl] and [(CO)$_5$W(BPE)*cis*-Rh(CO)$_2$Cl] the MLCT ($W \rightarrow \pi^*_L$) transition of the “W(CO)$_5$BPE” moiety shows a less significant red shift, while the MLCT transitions ($Re \rightarrow \pi^*_L$ or $Rh \rightarrow \pi^*_L$) of the acceptor metal carbonyl fragments do not show significant red shifts (Table 3).

When “W(CO)$_5$L” (L = pyz, BPE) is linked to the strong acceptor BF_3, either with pyrazine or BPE acting as linkers, a substantial red shift of its MLCT transition ($W \rightarrow \pi^*_L$) occurs, which is much more significant when L = pyz (528 nm compared to about 398 nm) than when L = BPE (449 nm compared to a shoulder at 440 nm) (Table 3).

In conclusion the significant red shift of the MLCT ($W \rightarrow \pi^*_L$) transition of the “W(CO)$_5$pyz” moiety, induced by linking through the free nitrogen of pyrazine, increases in the following order: BF_3 > “*cis*-Re(CO)$_4$Cl”

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Published on November 27, 2002 on http://pubs.acs.org | doi: 10.1021/om020633h

Table 3. UV–Visibile Absorption and Emission Spectra (Pyz = pyrazine; BPE = *trans*-1,2-bis(4-pyridyl)ethylene)

compound	absorption λ_{max} (nm) ($\log\epsilon$) LF(d → d)	MLCT(M → π^*_L)	emission λ_{max} (nm)	solvent
$[W(CO)_5pyz]$	398(3.84)[24b]	Under LF[24b]	656[24b]	$CHCl_3$
$[(CO)_5W(pyz)W(CO)_5]$	392(3.67)[24b]	537(4.03)[24b]	741[24b]	$CHCl_3$
$[(CO)_5W(pyz)BF_3]$	390(3.67)	536(3.80)	[a]	CH_2Cl_2
		528(3.70)		$CHCl_3$
$[W(CO)_5BPE]$	403(4.01)	441(sh)	549[13c]	$CHCl_3$
	402(3.93)[13c]	440(sh)[13c]		C_6H_6
$[(CO)_5W(BPE)W(CO)_5]$	404(4.24)	443(4.26)	560[13c]	$CHCl_3$
	404(4.17)[13c]	450(4.19)[13c]		C_6H_6
$[(CO)_5W(BPE)BF_3]$	403(3.76)	436(3.69)	[a]	CH_2Cl_2
		449(3.61)		$CHCl_3$
[*cis*-$Re(CO)_4Clpyz$]	323(3.08)[12]	371(sh)[12]	583[12]	CH_2Cl_2
[*cis*-$Rh(CO)_2Clpyz$]	under MLCT[21]	340(3.41)[21]	[a]	CH_2Cl_2
	M → π^*_{CO} and M → π^*_L	327(3.44)[21]		THF
[*cis*-$Rh(CO)_2Cl(pyz)$*cis*-$Rh(CO)_2Cl$]	under MLCT[21]	327(sh)[21]	[a]	THF
	M → π^*_{CO} and M → π^*_L			
[$(CO)_5W(pyz)$*cis*-$Re(CO)_4Cl$]	320(3.69),392(3.59)	503(4.02)	590[b]	CH_2Cl_2
[$(CO)_5W(BPE)$*cis*-$Re(CO)_4Cl$]	403(4.10)	437(sh)	535[c]	CH_2Cl_2
[$(CO)_5W(pyz)$*cis*-$Rh(CO)_2Cl$]	319(3.62),394(3.70)	499(3.44)	[a]	CH_2Cl_2
[$(CO)_5W(BPE)$*cis*-$Rh(CO)_2Cl$]	404(4.21)	435(4.19)	[a]	CH_2Cl_2
	405(3.77)	435(3.79)		$CHCl_3$

[a] Not fluorescent. [b] Exciting wavelength $\lambda = \lambda_{max}$ of MLCT (W → π^*_L). [c] Exciting wavelength $\lambda = 403$ nm.

≥ "*cis*-$Rh(CO)_2Cl$" (Table 3). For the "$W(CO)_5BPE$" moiety such a red shift is similar but less relevant. As in previous absorption studies on symmetrical dimeric complexes,[12,13c] we find no evidence of metal-to-metal charge transfer transitions (MMCT) here.

In homonuclear[13b] or pseudo-homonuclear[13a,c] dimeric complexes $[(CO)_5M(L)M'(CO)_5]$ (L = pyz, BPE; M = W; M′ =W, Cr, Mo) the red-shifted MLCT transition (W → π^*_L) is reported to be fluorescent. While we confirmed in our heteronuclear dimeric complexes such fluorescence behavior when "$W(CO)_5L$" is linked to "*cis*-$Re(CO)_4Cl$" (L = pyz,[12] BPE), with other acceptor fragments such as BF_3 or "*cis*-$Rh(CO)_2Cl$" no strong fluorescent emission was seen here (Table 3).

The red-shifted MLCT absorption bands (W → π^*_L) of our heteronuclear dimeric complexes are significantly solvatochromic as the related symmetrical $[(CO)_5W(L)W(CO)_5]$ (L = pyz, BPE)[16,24]or pseudo-symmetrical $[(CO)_5W(L)M(CO)_5]$ (L = pyz, M = Cr, Mo)[13b] or [$(CO)_5W(pyz)$*cis*-$Re(CO)_4Cl$][12] dimeric complexes. Only $[(CO)_5W(pyz)BF_3]$ shows a red shift with increasing solvent polarity, while for the related complexes with "*cis*-$Re(CO)_4Cl$" and "*cis*-$Rh(CO)_2Cl$" acting as electron acceptors blue shifts are observed with increases in solvent polarity. When BPE is the bridge, the solvatochromism is less significant and also $[(CO)_5W(BPE)BF_3]$ shows a blue shift. As expected[12,13b,24] the LF absorption band of the "$W(CO)_5L$" moiety is totally uninfluenced by solvent polarity in all our heteronuclear dimeric complexes. The emission band, originating from the MLCT transition (W → π^*_L), always shows the same solvatochromic trend.

Table 4. Experimental and Theoretical Dipole Moments

compound	μ_{exp} (D) ($CHCl_3$)	μ_{theor}[a] (D)[b]
$[pyzBF_3]$	n.d.	6.52 (6.71,[c] 7.36[d])
$[W(CO)_5pyz]$	2.7 (4)[e,f]	5.26
$[(BPE)BF_3]$	n.d.	9.01
$[W(CO)_5BPE]$	3.8[f]	7.40
$[(CO)_5W(pyz)BF_3]$	n.d.	3.34[g]
$[(CO)_5W(BPE)BF_3]$	n.d.	2.36[g]
[$(CO)_5W(pyz)$*cis*-$Re(CO)_4Cl$]	3.9	2.46
[$(CO)_5W(BPE)$*cis*-$Re(CO)_4Cl$]	4	2.52
[$(CO)_5W(pyz)$*cis*-$Rh(CO)_2Cl$]	3	3.32
[$(CO)_5W(BPE)$*cis*-$Rh(CO)_2Cl$]	3.6	3.67

[a] Reference 28. [b] Calculated with the density functional method (DFT) B3LYP, basis set LAN L2DZ unless otherwise stated (see Experimental Section and ref 28). [c] Calculated with the HF method.[28] [d] Calculated with the ZINDO method.[28] [e] In ref 3 experimental dipolar moment in chloroform was reported to be 4 D. [f] This complex in $CHCl_3$ solution slowly rearranges with formation of small amounts of the dimeric symmetrical species $[(CO)_5W(L)W(CO)_5]$. Therefore the experimental dipole moment can be underestimated. [g] In these complexes the sign of the total dipole moment is opposite that of the other monomeric or dimeric complexes. This means that the balance of electron distribution in the ground state produces an electron transfer to the BF_3 moiety.

Dipole Moments and Polarity of Bimetallic Heteronuclear Complexes. To evaluate the asymmetry of the ground state electronic distribution in our mononuclear and heteronuclear bimetallic complexes, we measured experimentally, when possible, or calculated the dipole moments. Experimental dipole moments were measured in $CHCl_3$ using the Guggenheim method.[25] However for the dimeric compounds containing the BF_3 fragment, reproducible values could not be obtained because they are not stable in $CHCl_3$ for the time necessary to carry out the experiments. For these latter, the dipole moments were only evaluated theoretically (see Experimental Section and Table 4).

For the $pyzBF_3$ adduct [reference], the dipole moment values were obtained using three different methods (ZINDO, HF, and DFT)[26,27] and are in satisfactory agreement (Table 4). Therefore dipole moments of monomeric and heteronuclear bimetallic complexes were

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computed using the DFT approach, considered the most reliable, especially for large systems including transition metals. Dipole moment calculations were carried out on DFT optimum molecular structures.[28]

The reliability of our computational approach can be judged on the basis of the agreement between experimental, when available, and calculated dipole moments values. The agreement is particularly good for the dimeric heteronuclear complexes, while experimental values for the monomeric complexes are noticeably lower than those calculated (Table 4). However, this disagreement can be due to the already observed (see ^{1}H NMR spectra discussion) very slow rearrangement of polar monomeric [W(CO)$_5$L] complexes (L = pyz, BPE) to generate small amounts of nonpolar symmetric dimeric complexes [(CO)$_5$W(L)W(CO)$_5$] (see Experimental Section), so that experimental values of the dipole moment are probably underestimated.

DFT calculations show that dipole moments decrease, as expected, going from mononuclear to binuclear complexes (Table 4) and that coordination of [W(CO)$_5$L] (L = pyz, BPE) to BF$_3$ leads to an inversion of the direction of the dipole moment. Calculated DFT values of the dipole moment of the monomeric fragments "pyzBF$_3$" and "W(CO)$_5$pyz" are 6.52 and 5.26 D, respectively, with an opposite polarity with respect to pyrazine. The DFT-calculated dipole moment of the heteronuclear dimer [(CO)$_5$W(pyz)BF$_3$] (3.34 D) agrees in sign but not in absolute value with a vectorial addition of the dipole moments of the single monomeric fragments.

Therefore, already in the ground state, coordination to BF$_3$ of the free nitrogen of the pyrazine or BPE ligand bound to the "W(CO)$_5$" fragment seems to produce a shift in the electronic charge from "W(CO)$_5$" to pyrazine, as suggested by the ^{1}H NMR investigation.

In agreement with this latter point, if only the local polarity is considered, DFT calculations show a decrease in the electron transfer in the ground state from pyrazine or BPE to W when the free nitrogen of L of [W(CO)$_5$L] (L = pyz, BPE) is interacting with BF$_3$, for instance from −0.65 to −0.53 electron when pyrazine is the bridge and from −0.71 to −0.67 electron when BPE is the bridge. In dimeric complexes containing BF$_3$, the component of the dipole moment along the MLCT (W → π^*_L) direction of the "W(CO)$_5$pyz" moiety is significant and quite coincident with the total dipole moment, while in heteronuclear dimeric complexes containing the "*cis*-Re(CO)$_4$Cl" and "*cis*-Rh(CO)$_2$Cl" fragments, the direction of the dipole moment vector is quite far from that of the MLCT (W → π^*_L) transition. In these latter complexes, the component of the dipole moment along the MLCT (W → π^*_L) direction is close to zero (0.07 D from W(pyz) to Re) or small (1.01 D from W(pyz) to Rh, 1.70 D from W(BPE) to Rh, and 0.66 D from W(BPE) to Re).[28] Of course, the transfer of electron density in the ground state is, by convention, opposite the dipole moment vector (Figure 1).

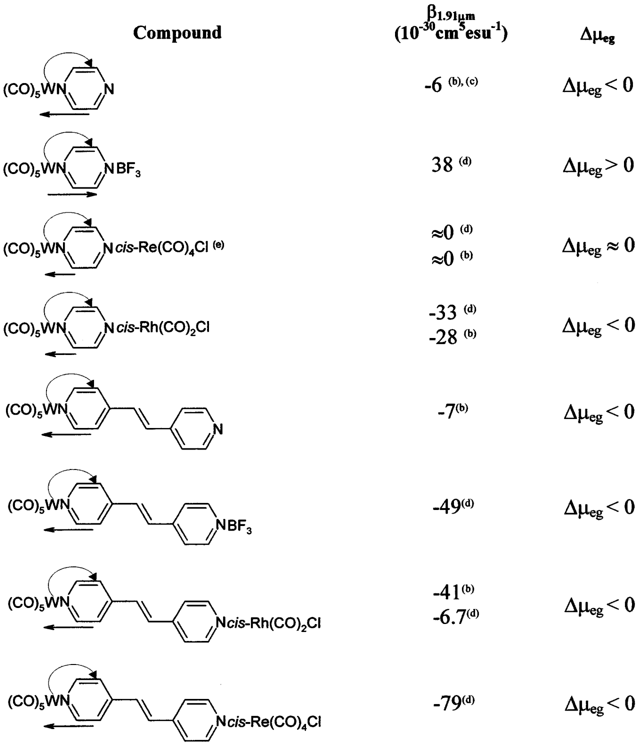

Figure 1. Electronic origin of the quadratic hyperpolarizability ($\beta_{1.91}$) of heteronuclear bimetallic complexes. (a) The straight arrows give the direction of the charge distribution in the ground state (by convention opposite the dipole moment vector). (b) Experimental values obtained by means of the EFISH technique, using CHCl$_3$ as solvent. (c) Reference 3. (d) Experimental values obtained by means of the solvatochromic methodology, with determination of the cavity radius *a* from structural data. (e) In agreement with the symmetrical complex [(CO)$_5$W(pyz)W(CO)$_5$] behavior, the strong solvatochromism observed for the MLCT (W → π^*_L) transition of this compound is due to metal−ligand polarity variations associated with specific interactions between solute−solvent induced dipoles.[24b,31b]

Second-Order NLO Properties by EFISH and Solvatochromic Investigations. The second-order NLO response was first measured by the EFISH technique (electric field second-harmonic generation; see Experimental Section),[29] which provides the intrinsic molecular NLO response γ_{EFISH} (see Experimental Section and eq 2):

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

where $\mu\beta_{vec}/5KT$ is the dipolar orientational contribution, while $\gamma_0(-2\omega;\omega,\omega,0)$, a third-order term in the rotary frequency ω of the incident wavelength, is the electronic contribution. The latter is usually considered negligible in similar organometallic push−pull molecules.[5] The β_{vec} term (Table 5) is the vectorial projection of the quadratic hyperpolarizability tensor β along the direction of the dipole moment vector μ. EFISH measurements were carried out working with a nonresonant incident wavelength of 1.907 μm. Unfortunately complexes containing the BF$_3$ moiety were not stable enough in CHCl$_3$, at the concentrations and for the times required by the EFISH experiments, to give reproducible measurements. Moreover, as already pointed out in the discussion of the experimental dipole moments, monomeric complexes [W(CO)$_5$L] (L = pyz, BPE)

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Table 5. EFISH β_{vec} and Solvatochromic β_{CT} Values (working with an incident 1.907 μm wavelength)

compound	$\beta_{CT}{}^{a}$ 10^{-30} (cm^5 esu^{-1})	$\beta_{vec}{}^{b}$ 10^{-30} (cm^5 esu^{-1})	$\beta_0{}^{c,d}$ 10^{-30} (cm^5 esu^{-1})	$\mu\beta_0$ 10^{-30} (D cm^5 esu^{-1})
$[W(CO)_5pyz]$	n.d.	-6^{e}	-4.7	-13^{f}
$[(CO)_5W(pyz)BF_3]$	38	n.d.	24^{g}	80^{h}
$[(CO)_5W(pyz)$*cis*-$Re(CO)_4Cl]$	*k*	*k*	*k*	*k*
$[(CO)_5W(pyz)$*cis*-$Rh(CO)_2Cl]$	-33	-28	-19	-57^{f}
$[W(CO)_5BPE]$	n.d.	-7	-5.2	-20^{f}
$[(CO)_5W(BPE)BF_3]$	-49	n.d.[i]	-36^{g}	-86^{h}
$[(CO)_5W(BPE)$*cis*-$Re(CO)_4Cl]$	-79	-52^{l}	-39	-156^{f}
$[(CO)_5W(BPE)$*cis*-$Rh(CO)_2Cl]$	-6.7	-41	-31	-111^{f}
$[W(CO)_5L]^{m}$	n.d.	-5.7		
$[W(CO)_5L_1]^{n}$	n.d.	-20		

[a] Obtained using structural data for the determination of the cavity radius *a*. [b] The main error is about ±20% unless otherwise stated. [c] Calculated with the two-level model where $\beta_0 = \beta_\lambda(1 - (2\lambda_{max}/\lambda)^2)(1 - (\lambda_{max}/\lambda)^2)$; ref 2. [d] From β_{vec}. [e] A similar value was reported in ref 3. [f] By using experimental dipole moment. [g] From β_{CT}. [h] By using the theorethical value of the dipole moment. [k] The experimental value is close to zero for both β_{CT} and β_{vec} (and therefore β_0 and $\mu\beta_0$). [i] EFISH measurements were not enough reproducible, but in any case the value of β_{vec} was always negative. [l] Measured at 1.34 μm incident wavelength and calculated at 1.907 μm with the two-level model, ref 2. [m] L = *trans*-stilbazole (ref 3). [n] L_1 = *para*-nitro-substituted *trans*-stilbazole (ref 3).

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rearrange slowly in $CHCl_3$ solution to give some amount of homonuclear dimeric complexes $[(CO)_5W(L)W(CO)_5]$, which, being symmetrical, are characterized by a β_{vec} value close to zero. It follows that experimental β_{vec} values of these mononuclear complexes (Table 5) are probably slightly underestimated, although both their order of magnitude and sign were always consistent and reproducible in a large series of experiments carried out working quickly and at different concentrations. In particular both the negative sign and the absolute value of β_{vec} of $[W(CO)_5pyz]$ (Table 5) are in agreement with what was previously reported for this compound.[3] In addition β_{vec} values of -6×10^{-30} and -7×10^{-30} cm^5 esu^{-1} for monomeric complexes $[W(CO)_5L]$ (L = pyz, BPE) (Table 5) are consistent with the sign and absolute values of β_{vec} of related complexes $[W(CO)_5L]$, stable in $CHCl_3$, where L is a series of *para*-substituted pyridines.[3,4]

To get some semiquantitative information on the second-order NLO response of the unstable heteronuclear dimeric complexes containing the BF_3 moiety and in parallel to confirm the trend and order of magnitude of β_{vec}, obtained by EFISH measurements, of the stable heteronuclear dimeric complexes (Table 5), we carried out a solvatochromic investigation, assuming that the quadratic hyperpolarizability (β_{CT}, see eq 1) originates mainly from the MLCT ($W \rightarrow \pi^*_L$) transition[2] (see Experimental Section for details of the methodology). β_{CT} and β_{vec} can be compared mainly when the axis of the major charge transfer process is quite parallel to the dipole moment direction.[30,31] As pointed out above, only in dimeric heteronuclear complexes carrying the BF_3 fragment is the MLCT transition ($W \rightarrow \pi^*_L$) axis coincident with the dipole moment vector.

The solvatochromic investigation, when carried out on both the absorption and emission bands, using the McRae[32] and Liptay[33] equations, allows the direct determination, less subject to significant errors, of the radius of the solvent cavity *a* (see Experimental Section and ref 30). Unfortunately, as already pointed out, contrary to various $[W(CO)_5L]$ complexes (L = substituted pyridines,[34] pyrazine,[18a] or BPE[16]) or to the dimers $[(CO)_5W(L)W(CO)_5]$ (L = pyz,[13a,b] BPE[13c]), the majority of our heteronuclear dimeric complexes, with the exception of those with the "*cis*-$Re(CO)_4Cl$" fragment, are not characterized by a fluorescent MLCT ($W \rightarrow \pi^*_L$) transition (Table 3). Thus for the heteronuclear bimetallic complexes carrying the BF_3 moiety or the "*cis*-$Rh(CO)_2Cl$" fragment, the value of the cavity radius, *a*, was deduced from known structures of related complexes such as [*cis*-$Rh(CO)_2ClL$] (L = pyrazole[35a] or N-substituted imidazole[35b]), $[W(CO)_5L]$ (L = various pyridines),[10a] [*cis*-$Re(CO)_3L_2Br$] (L = conjugated pyridine),[35c] BF_3, or $B(C_6F_5)_3$ adducts of various pyridines[6] and of azastilbenes,[35d] after correction of the van der Waals repulsion (see Experimental Section), as the best way to limit some large errors originated by the traditional empirical calculation based on the molecular weight and on the assumption of a spherical cavity (see Experimental Section and ref 30).

The validity of our choice was confirmed, for the complex $[(CO)_5W(pyz)$*cis*-$Re(CO)_4Cl]$, by the good agreement of the value of radius *a* obtained directly by absorption and emission solvatochromic studies[30] and those deduced empirically from structural data of known related structures[10a,35c] (Table 6).

The quite satisfactory agreement of β_{vec} and β_{CT}, in both sign and absolute value, for complexes $[(CO)_5W(pyz)$*cis*-$Re(CO)_4Cl]$ and $[(CO)_5W(pyz)$*cis*-$Rh(CO)_2Cl]$ (Table 5), despite the lack of good coincidence of the charge transfer and dipole moment directions,[28] supports our assumption that the solvatochromic quadratic hyperpolarizability β_{CT} of the dimeric pyrazine complex containing the BF_3 group (Table 5) is an acceptable indication of the second-order NLO response. In addition it is experimental evidence that the second-order NLO response of our heteronuclear dimeric complexes is dominated by the MLCT ($W \rightarrow \pi^*_L$) transition.

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Table 6. Solvatochromic Determination of β_{CT} at 1.907 μm

compound	λ_{max} (nm)	f[a]	a (nm)	$\Delta\mu_{eg}$ (D)	β_{CT} 10^{-30} (cm^5 esu^{-1})
[(CO)$_5$W(pyz)BF$_3$]	536[b]	0.11	6.2[d]	11.8	25
			7.1[e]	17.8	38
[(CO)$_5$W(BPE)BF$_3$]	436[b]	0.21	6.6[d]	−2.4	−13
			9.4[e]	−9.6	−49
[(CO)$_5$W(pyz)*cis*-Re(CO)$_4$Cl]	519[c]	0.17	7.1[d]	0.06	0.2
			8.3[e]	0.10	0.3
			8.9[f]		
[(CO)$_5$W(BPE)*cis*-Re(CO)$_4$Cl]	437[b]	0.11	7.4[d]	−11.8	−27
			10.6[e]	−32.7	−79
[(CO)$_5$W(pyz)*cis*-Rh(CO)$_2$Cl]	511[c]	0.04	6.7[d]	−26	−15
			8.7[e]	−58	−33
[(CO)$_5$W(BPE)*cis*-Rh(CO)$_2$Cl]	435[c]	0.09	7.0[d]	−1	−2
			10.5[e]	−3.3	−6.7

[a] f is the transition oscillator strength, obtained from the experimental integrated absorption coefficient in CHCl$_3$ (ref 30a). [b] In CH$_2$Cl$_2$. [c] In CHCl$_3$. [d] Value obtained by molecular weight determination of the cavity radius a. [e] Value obtained by using structural data for the determination of the cavity radius a. [f] Value obtained by using both absorption and emission data for the determination of the cavity radius a.

The same conclusions can be reached from the satisfactory agreement between β_{vec} and β_{CT} in sign and values of heteronuclear bimetallic complexes with BPE as bridge (Table 5).

The trend of the second-order NLO response of both monomeric and heteronuclear dimeric complexes with BPE bridges gives additional evidence that also in these complexes the response is dominated by the MLCT (W → π^*_L) transition of the "W(CO)$_5$BPE" moiety. The negative value of β_{vec} of the monomeric complex [W(CO)$_5$BPE] originates, as in [W(CO)$_5$pyz][3,4] (Figure 1), from the opposite sign of the electron transfer process of this transition (from W to BPE) with respect to the local electron transfer (from BPE to W).[4]

Also in heteronuclear dimeric complexes, with BPE as bridge, both β_{CT} and β_{vec} remain negative, as expected if their NLO response is still controlled by the electron transfer of the W → π^*_L process. The absolute value of the quadratic hyperpolarizability of the [W(CO)$_5$BPE] complex increases, in the dimeric complexes, in agreement with the increased acceptor properties of the π^*_L orbitals (Table 5), as a consequence of the relevant electron-withdrawing effect due to the coordination to BF$_3$, "*cis*-Rh(CO)$_2$Cl", and "*cis*-Re(CO)$_4$Cl" of the free nitrogen donor atom of [W(CO)$_5$BPE]. These assumptions are confirmed for instance by the negative $\Delta\mu_{eg}$ value of the MLCT (W → π^*_L) transition of [(CO)$_5$W(BPE)BF$_3$] (Table 6) and by its red shift from 440 (as a shoulder) to 449 nm with respect to the monomer [W(CO)$_5$(BPE)] (Table 3) and supported by the conclusions of the ZINDO-SOS investigation of Marks, Ratner, et al.[4] on the π^*_L levels of complexes [W(CO)$_5$L] where L are *trans*-stilbazoles, structurally very similar to BPE, carrying an electron-withdrawing group.

The role of "*cis*-Rh(CO)$_2$Cl" or "*cis*-Re(CO)$_4$Cl" fragments as significant electron-withdrawing groups in our dimeric complexes with BPE as bridge is confirmed by the evidence that the introduction of an acceptor nitro group in the *para* position of *trans*-stilbazole in [W(CO)$_5$L] complexes (L = *trans*-stilbazole or *para*-nitro *trans*-stilbazole) produces a shift of β_{vec} from −5.7 to −20 × 10^{-30} cm^5 esu^{-1},[3] comparable to or even lower than the shift of β_{vec} from −7 to about −41 × 10^{-30} cm^5 esu^{-1} or to about −52 × 10^{-30} cm^5 esu^{-1} induced by coordination of "*cis*-Rh(CO)$_2$Cl" or "*cis*-Re(CO)$_4$Cl" respectively to the free nitrogen of [W(CO)$_5$BPE] (Table 5).

Coordination of [W(CO)$_5$BPE] to BF$_3$ produces, according to DFT calculations,[28] an inversion of the sign of the total dipole moment with respect to [W(CO)$_5$BPE] (Table 4), which has not be reported to occur by substitution of *trans*-stilbazole with *para*-nitro *trans*-stilbazole in [W(CO)$_5$L] complexes.[3] However, the β_{CT} remains negative: the substantial negative $\Delta\mu_{eg}$ of its MLCT (W → π^*_L) transition (Table 6) suggests that what is relevant for the sign of the second-order NLO response is the local ground state polarity (Figure 1) of the N−W bond between the "W(CO)$_5$" fragment and the pyridine ring of BPE (electron transfer from this ring to "W(CO)$_5$").[28]

This suggestion is in agreement with the above cited ZINDO-SOS studies of Marks, Ratner, et al.[4] on [W(CO)$_5$L] complexes (L = various *para*-substituted *trans*-stilbazoles). According to their conclusions, mainly the pyridine ring adjacent to the "W(CO)$_5$" moiety serves as the primary acceptor of the electronic density of the MLCT (W → π^*_L) transition.

The trends of the second-order NLO response of heteronuclear bimetallic complexes with pyrazine as bridge are less straightforward to be interpreted. Coordination of "W(CO)$_5$pyz" to an acceptor fragment probably does not produce only a perturbation in the levels of π^*_L or LUMO orbitals of the pseudo-aromatic ring adjacent to the "W(CO)$_5$" fragment, as it occurs in the "W(CO)$_5$BPE". According to Marks, Ratner, et al.,[4] the effect of the *para* substitution with electron-withdrawing groups on the LUMO orbitals is much more relevant in pyridine than in *trans*-stilbazole complexes with "W(CO)$_5$". In addition they suggest that when the effect of the substitution of the pyridine ring with an electron-withdrawing group is very strong, the HOMO orbitals of the organometallic fragment are also influenced significantly.

Therefore it is not unexpected that in the complex [(CO)$_5$W(pyz)BF$_3$] coordination of BF$_3$ strongly perturbs the electron density to generate an inversion, with respect to [W(CO)$_5$pyz], of the sign of the total dipole moment (Table 4).

As a consequence, the local ground state electron distribution for the chromophore [(CO)$_5$W(pyz)BF$_3$] not only is parallel in direction but also has the same sign as the electron transfer process of the MLCT transition (W → π^*_L) of the "W(CO)$_5$pyz" moiety (Figure 1), as supported by its positive and significant $\Delta\mu_{eg}$ value (Table 6).

Therefore on the basis of the two-level model of eq 1, the β_{CT} value of [(CO)$_5$W(pyz)BF$_3$] is positive and with a significant absolute value (Table 5), in agreement with the red-shifted solvatochromism due to the positive $\Delta\mu_{eg}$ and the large red shift of the MLCT transition (W → π^*_L) (Table 6).

In contrast, when the "W(CO)$_5$pyz" moiety is coordinated to the acceptor fragment "*cis*-Rh(CO)$_2$Cl", both β_{CT} and β_{vec} remain negative (Table 5). DFT calculations indicate that in the latter case the total dipole moment does not change its sign with respect to [W(CO)$_5$pyz], although its component along the charge transfer axis is only 1.01 D (with electron transfer still from Rh to

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W). The increase in the absolute value of the quadratic hyperpolarizability is comparable to or even higher than that reported to occur in [W(CO)$_5$L] complexes (L = various *para*-substituted pyridines) by introducing electron-withdrawing groups.[3] A MLCT (W → π^*_L) transition in the opposite direction to the ground state charge transfer from N to W (Figure 1) is suggested by the blue-shifted solvatochromism and confirmed by the negative $\Delta\mu_{eg}$, while the increase of the absolute value of both β_{CT} and β_{vec} (Table 5) is in agreement with both a significant red shift of the MLCT transition from about 400 nm to 499 nm (Table 3) and an increase of the absolute value of $\Delta\mu_{eg}$ (Table 6).

Quite unexpected is a second-order NLO response close to zero (either as β_{CT} or β_{vec}) (Table 5) when the "W(CO)$_5$pyz " moiety interacts with a 5d^6 acceptor fragment such as "*cis*-Re(CO)$_4$Cl", electronically quite similar to the 5d^6 "W(CO)$_5$" fragment. We have already described the anomalous ^{1}H NMR shift of the hydrogens close to the nitrogen coordinated to "W(CO)$_5$".

Due to the similarity of the two 5d^6 electronic systems of the W(0) and Re(I) metal carbonyl centers, the ground state dipole moment is relatively low; DFT calculations indicate a very small component of only 0.07 D along the charge transfer axis (with total electron transfer still from Re to W). For the complex [(CO)$_5$W(pyz)*cis*-Re(CO)$_4$Cl] we confirmed the previously reported[12] significant and strongly solvatochromic MLCT (W → π^*_L) transition (Table 3). It seems that a fundamentally pseudo-symmetrical electronic distribution along the charge transfer axis linking W to Re is maintained in the MLCT process because its $\Delta\mu_{eg}$ is very small (Table 6). A similar significant red shift of the MLCT transition and its blue shift with increasing solvent polarity were reported also for the symmetrical homonuclear dimeric complex [(CO)$_5$W(pyz)W(CO)$_5$].[13c] As in this latter case, the solvatochromism of the MLCT (W → π^*_L) transition of [(CO)$_5$W(pyz)*cis*-Re(CO)$_4$Cl] is not due to a significant negative $\Delta\mu_{eg}$, which is positive and very small, but principally to specific solute−solvent interactions, with induced strong dipolar and polarizability contributions in the ground and excited states,[24] so that β_{CT} becomes irrelevant (Table 6) despite the significant red shift of the MLCT (W → π^*_L) transition.

Conclusions

The asymmetrical heteronuclear bimetallic complexes investigated in this work can be considered as organometallic counterparts of classical push−pull aromatic chromophores for second-order nonlinear optical responses,[14,15] with the electronically well-studied "W(CO)$_5$" fragment acting as a push organometallic group which donates electrons by an excitation process to a pseudo-aromatic polarizable bridge such as pyrazine and BPE ligands (L) acting as linker toward acceptor inorganic (BF$_3$) or organometallic centers.

The push properties of the "W(CO)$_5$" fragment are well studied;[4] they originate from a MLCT (W → π^*_L)[3] transition known to be sensitive to the energy of the interaction of the linker L with another organometallic center, like "M(CO)$_5$" (M = W, Mo, Cr), acting as a weak acceptor.[13c]

We find that this transition is red-shifted by coordination of the bifunctional linker to acceptor centers such as "*cis*-Rh(CO)$_2$Cl", "*cis*-Re(CO)$_4$Cl", or BF$_3$, acting as pull groups in these heteronuclear bimetallic push−pull chromophores. In the chromophores described here this effect is characterized by a strong absorption ($\epsilon \cong 10^4$) at relatively low energy (λ_{max} between 440 and 540 nm), with a solvatochromic effect dependent on the nature of the organometallic or inorganic pull center and upon the nature of the polarizable linker. With the exception of the fundamentally symmetrical complex [(CO)$_5$W(pyz)*cis*-Re(CO)$_4$Cl], it is the origin of a significant second-order NLO response.

When compared to structurally related push−pull aromatic chromophores, there are some significant electronic differences. The MLCT process (W → π^*_L), which according to our solvatochromic studies is the major origin of the second-order NLO response, remains localized on the part of the polarizable linker L close to the push "W(CO)$_5$" organometallic center, although strongly perturbed in energy and slightly also in intensity and $\Delta\mu_{eg}$ value. In other words, in our heteronuclear bimetallic chromophores, the relevant MLCT process never assumes a MMCT character directly involving, in the charge transfer process, both the push and pull organometallic or inorganic centers as it occurs for the acceptor and donor groups in classical push−pull aromatic chromophores.[15]

In our organometallic push−pull chromophores, when the distance between the push and pull groups is relevant enough, such as when BPE is the linker, the trend in the second-order NLO response is quite similar to that of structurally related classical organic push−pull chromophores. In the latter the second-order NLO response increases by introducing an unsaturation between two aromatic rings carrying the push and pull group, respectively.[15]

The only difference is the sign of the response, which in our organometallic push−pull chromophores becomes negative due to a localized charge transfer process from metal to linker. The absolute values of the quadratic hyperpolarizability when various inorganic (BF$_3$) and organometallic ("*cis*-Rh(CO)$_2$Cl", "*cis*-Re(CO)$_4$Cl") pull groups are involved are comparable to or slightly lower than those of related push−pull organic chromophores (compare for instance $\beta_{CT} = -49 \times 10^{-30}$ and $\beta_{vec} = -41 \times 10^{-30}$ and -52×10^{-30} cm^5 esu^{-1} when BF$_3$, "*cis*-Rh(CO)$_2$Cl", and "*cis*-Re(CO)$_4$Cl", respectively, are acting as pull groups with $\beta_{vec} = 73 \times 10^{-30}$ cm^5 esu^{-1} of the structurally related *trans*-4-dimethylamino, 4′-nitrostilbene).[15] The behavior of these organometallic push−pull chromophores is quite different when the distance between the organometallic "W(CO)$_5$" push group and the organometallic or inorganic pull group is small, such as when pyrazine is the linker. In this case, the perturbation of the pull groups can be so strong as to change the sign of the quadratic hyperpolarizability, e.g., when BF$_3$ is the pull group. In this instance its absolute value, originating from a low-energy and strong MLCT (W → π^*_L) and not from a higher energy and less strong $\pi \to \pi^*$ or n → π^* transition, is higher than that of structurally related classical *para*-substituted push−pull benzenic chromophores.[14,15]

Compare for instance $\beta_{CT} = 38 \times 10^{-30}$ or $\beta_{vec} = -28 \times 10^{-30}$ cm^5 esu^{-1} when BF$_3$ or "*cis*-Rh(CO)$_2$Cl" is acting

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as pull group with $\beta_{vec} = 12 \times 10^{-30}$ cm^5 esu^{-1} of *para*-nitrodimethylaniline.[15]

While the trends for the second-order NLO response of classical benzene-based push−pull chromophores are easily predicted on the basis of the energy of the π system, those of our organometallic push−pull chromophores with pyrazine as linker cannot be predicted easily. This is due to the strong and different electronic perturbations that the various inorganic or organometallic pull groups may exert on the π^*_L levels of pyrazine, which control the second-order response.

The different behavior of the pull group "*cis*-Re(CO)$_4$Cl" when pyrazine or BPE is acting as linker is a clear example of such variability. According to our ^{1}H NMR investigation, "*cis*-Re(CO)$_4$Cl" may be considered an acceptor center with acceptor properties between those of BF$_3$ and "*cis*-Rh(CO)$_2$Cl".

The NLO responses of our organometallic chromophores with BPE as linker agree well with this classification. However when pyrazine is the linker, "*cis*-Re(CO)$_4$Cl" does not show any significant acceptor properties either in the ground state (dipole moment along the transfer axis close to zero) or in the excited state (both β_{CT} and β_{vec} with values close to zero).

This anomalous behavior is probably due to the similar electronic 5d^6 structures of "*cis*-Re(CO)$_4$Cl" and "W(CO)$_5$" which generate a simple and opposite compensation between the push and pull properties in both the ground and excited state.[28]

In conclusion the organometallic counterparts with BPE as linker when compared to stilbenic aromatic chromophores show second-order NLO responses quite similar, with the exception of the sign, to those of the organic chromophores.

When the linker is pyrazine, the second-order NLO response may be higher than that of the related classical benzenic push−pull chromophore, but it is strongly dependent as sign and absolute value on the electronic structure of the pull inorganic and in particular organometallic group.

Experimental Section

[W(CO)$_5$pyz],[18a] [W(CO)$_5$BPE],[16] [*cis*-Re(CO)$_4$Clpyz],[12] [Re(CO)$_4$Cl]$_2$,[20] [Rh(CO)$_2$Cl]$_2$,[19] and [*cis*-Rh(CO)$_2$Clpyz][21] were prepared as reported in the literature, whereas the ligands pyrazine (pyz) and *trans*-1,2-bis(4-pyridyl)ethylene (BPE) were purchased from Aldrich Chemicals Co. and used without further purification. [Re(CO)$_4$Cl(THF)] was prepared in situ from the dimer [Re(CO)$_4$Cl]$_2$ dissolved in THF. All solvents were dried over 4 Å molecular sieves, and all reactions were carried out under nitrogen atmosphere. Infrared spectra were collected using a Jasco FT-IR 420 spectrometer. UV−vis spectra were recorded with a UVIKON 943 spectrometer. ^{1}H, ^{11}B, and ^{19}F NMR spectra were recorded using a Bruker Advance DRX 300 spectrometer. Elemental analyses were carried out in the Dipartimento di Chimica Inorganica, Metallorganica e Analitica (Milan University). Dipole moments were obtained with the Guggenheim method[25] by using a WTW-DM01 dipolmeter coupled with a Pulfrich Zeiss PR2 refractometer, to measure respectively the dielectric constant and the refractive index of solutions in CHCl$_3$.

DFT calculations have been carried out adopting a basis set of type LAN L2DZ[36] for all atoms, except H atoms, for which a basis of split valence type was adopted.

The exchange−correlation potential used is that proposed by Becke[37] and Lee, Yang, and Parr,[38] B3LYP. Geometry optimizations have been carried out using standard gradient driven algorithms. The details of DFT calculations of dipole moments and second-order NLO properties will be reported in a separate paper.[28]

Determination of the Quadratic Hyperpolarizabilities. (i) EFISH Tecnique.[29] EFISH measurements of β_{vec} were carried in the Dipartimento di Chimica Inorganica, Metallorganica e Analitica (Milan University), in CHCl$_3$ solutions of different concentrations working with a fundamental incident wavelength of 1.907 μm, using a Q-switched, mode-locked Nd^{3+}:YAG laser with pulse durations of 15 or 90 ns at a 10 Hz repetition rate. All our experimental EFISH β_{vec} values (Table 5) are calculated according to the "phenomenological" convention.[31]

(ii) Solvatochromic Measurements. The solvatochromic effect of the MLCT (W → π^*_L) transition was investigated by means of both absorption and emission spectra, when possible, using a JASCO V-570 UV−visibile spectrophotometer and a JASCO FP-777 spectrofluorimeter. The investigation of solvatochromism by both absorption and emission spectra allows a direct evaluation of the radius of the cavity *a* occupied by the solute in the solvent, which when calculated empirically, is the origin of major discrepancies.[30] However in the majority of compounds investigated the MLCT (W → π^*_L) transition did not show a significant fluorescent emission (Table 3); therefore the cavity *a* was evaluated from known structures of related compounds.[8,13a,35]

The solvent-induced shift of the absorption and emission frequencies (ν_a and ν_e) can be expressed by the McRae[32] and Liptay[33] equations, respectively:

$$\nu_a = \nu_a{}^g + A\frac{2(n^2-1)}{a^3(2n^2+1)} + B\left(\frac{\epsilon-1}{\epsilon+2} - \frac{n^2-1}{n^2+2}\right) \qquad (3)$$

$$B = \frac{-2\mu_g(\mu_e-\mu_g)}{hca^3}$$

$$\nu_a - \nu_e = C + D\left(\frac{\epsilon-1}{\epsilon+2} - \frac{n^2-1}{n^2+2}\right) \qquad (4)$$

$$D = \frac{2(\mu_e-\mu_g)^2}{hca^3}$$

where ν_a, ν_e, and $\nu_a{}^g$ are, respectively, the frequencies (cm^{-1}) of the absorption and emission maxima in a given solvent and of the same absorption in the gaseous phase; ϵ and n are the solvent dielectric constant and refractive index; μ_g and μ_e are respectively the molecular ground and excited state dipole moments; and *a* is the radius (cm) of the cavity occupied by the solute in the solvent. Since *A* and *C*, like *B* and *D*, are constant for a specific absorption transition of a given molecule, taking $\mu_e - \mu_g$ as a constant, a suitable fitting of experimental data to linear eqs 3 and 4 yields values of both *B* and *D*, allowing an estimate of $\Delta\mu_{eg} = \mu_e - \mu_g$ by a two-equation system. In this way an empirical evaluation of *a*, which is usually the source of large errors, is not required.[30] The element of the β tensor along the charge transfer direction (β_{CT}) is derived from the two-level Oudar equation[2] (eq 1), where $\Delta\mu_{eg}$ and *f* values are obtained from solvatochromic measurements, assuming the MLCT (W → π^*_L) as the major origin of the second-order NLO response (Table 6).

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Published on November 27, 2002 on http://pubs.acs.org | doi: 10.1021/om020633h

As all the EFISH β_{vec} values were measured in chloroform, the integrated absorption coefficient *f* was obtained from four solutions of known concentration in chloroform.

The following solvents with increasing polarity have been used: benzene, toluene, $CHCl_3$, chlorobenzene, CH_2Cl_2, α,α,α-trifluorotoluene, 1,2-dichloroethane (compounds [W(CO)$_5$(pyz)-BF$_3$] and [W(CO)$_5$(BPE)BF$_3$]); toluene, $CHCl_3$, ethyl acetate, THF, CH_2Cl_2, 1,2-dichloroethane, acetone, acetonitrile (compound [(CO)$_5$W(pyz)*cis*-Re(CO)$_4$Cl]); cyclohexane, benzene, CCl_4, toluene, $CHCl_3$, chlorobenzene, CH_2Cl_2, trifluorotoluene, 1,2-dichloroethane (compound [(CO)$_5$W(pyz)*cis*-Rh(CO)$_2$Cl]); toluene, $CHCl_3$, ethyl acetate, THF, 1,2-dichloroethane, acetone, DMF (compound [(CO)$_5$W(BPE)*cis*-Rh(CO)$_2$Cl]); and toluene, anisole, $CHCl_3$, CH_2Cl_2, ethyl acetate, 1,2-dichloroethane, acetonitrile (compound [(CO)$_5$W(BPE)*cis*-Re(CO)$_4$Cl]).

Synthesis of [Rh(CO)$_2$Cl(BPE)]. To a solution of BPE (880 mg, 4.80 mmol) in anhydrous CH_2Cl_2 (20 mL) was added a solution of [Rh(CO)$_2$Cl]$_2$ (62.5 mg, 0.16 mmol) in CH_2Cl_2 (20 mL). After 2 h, a beige precipitate was obtained by adding *n*-hexane (20 mL); it was filtered off and dried in vacuo (yield 48%). Additional precipitate can be obtained by adding some more *n*-hexane; however some orange dimer [Cl(CO)$_2$*cis*-Rh-(BPE)*cis*-Rh(CO)$_2$Cl] can coprecipitate if excess *n*-hexane is used. The monomeric compound is unstable, and it transforms quickly in solution into the insoluble orange dimer. Therefore reliable ^{1}H NMR and UV−vis spectra could not be recorded. Anal. Found (Calcd): C 44.22 (44.61), H 2.87 (2.66), N 7.51 (7.44). IR (CH_2Cl_2, in the presence of excess BPE): ν_{CO} 2087(s), 2013(s) cm^{-1}.

Synthesis of [(CO)$_5$W(L)M′Ln] (L = pyz, BPE; M′Ln = BF$_3$, *cis*-Re(CO)$_4$Cl, *cis*-Rh(CO)$_2$Cl). These complexes were obtained by reacting under nitrogen equimolar amounts of [W(CO)$_5$L] (L = pyz, BPE) and $BF_3 \cdot OEt_2$ or [Rh(CO)$_2$Cl]$_2$ in CH_2Cl_2 solution or [*cis*-Re(CO)$_4$Cl(THF)] in THF solution. For the assignment of ^{1}H NMR signals see Table 2.

[(CO)$_5$W(pyz)BF$_3$]. To a solution of [W(CO)$_5$pyz] (160 mg, 0.40 mmol) in anhydrous CH_2Cl_2 (20 mL) was dropped 60 μL of 7.9 M $BF_3 \cdot OEt_2$ (0.48 mmol) through a rubber cap. The solution turned immediately from red-orange to violet. After 10 min, anhydrous *n*-hexane (4 mL) was added, and the violet precipitate was filtered off under dry nitrogen atmosphere and dried under a dry nitrogen stream. Additional precipitate can be obtained by adding some more *n*-hexane; however some dimer [(CO)$_5$W(pyz)W(CO)$_5$] can coprecipitate if excess *n*-hexane is used. The compound must be stored under nitrogen and kept in a dry atmosphere (yield 45%). Anal. Found (Calcd): C 22.82 (22.91), H 0.81 (0.85), N 5.88 (5.94). IR (Nujol mull): ν_{CO} 2081(w), 1935(s) cm^{-1} ν_{B-F} 1071(m), 1031(m) cm^{-1}. UV (CH_2Cl_2): λ_{max} (nm) (log ϵ) 390(3.67), 536(3.80). ^{1}H NMR (CD_2Cl_2): δ (ppm) 9.49 (2H, H_1H_2), 8.53 (2H, H_3H_4). ^{11}B NMR (CD_2Cl_2): δ (ppm) 1.761(s) (ref $BF_3 \cdot OEt_2$). ^{19}F NMR (CD_2Cl_2): δ (ppm) −156(s); δ ($BF_3 \cdot OEt_2$) −131(s) ppm (ref $CFCl_3$).

[(CO)$_5$W(BPE)BF$_3$]. The procedure of the synthesis is similar to that of the corresponding pyrazine complex (see above).The solution turned from yellow to red by addition of $BF_3 \cdot OEt_2$ (30 μL, 0.23 mmol) to [W(CO)$_5$BPE] (92 mg, 0.19 mmol) dissolved in CH_2Cl_2 (10 mL). The compound must be stored under nitrogen and kept in a dry atmosphere (yield 63%). Anal. Found (Calcd): C 35.71 (35.58), H 1.87 (1.76), N 4.80 (4.88). IR (Nujol mull): ν_{CO} 2071(m), 1981(m), 1894(vs), 1843(s), ν_{B-F} 1099(m), 1051(m) cm^{-1}. UV (CH_2Cl_2): λ_{max} (nm) (log ϵ) 403(3.76), 436(3.69). ^{1}H NMR (CD_2Cl_2): δ (ppm) 8.94 (2H, H_1H_2), 8.75 (2H, H_7H_8), 8.10 (2H, H_3H_4), 7.57 (d, H_9) 7.50 (2H, H_5H_6), 7.45 (d,H_{10}). ^{11}B NMR (CD_2Cl_2): δ (ppm) 0.879(s) (ref $BF_3 \cdot OEt_2$). ^{19}F NMR (CD_2Cl_2): δ (ppm) −153.5(s); δ (BF_3-OEt_2) −131(s) ppm (ref $CFCl_3$).

[(CO)$_5$W(pyz)*cis*-Re(CO)$_4$Cl]. [Re(CO)$_4$Cl]$_2$ (116 mg, 0.174 mmol) was added to THF (40 mL) and stirred until a clear solution evidenced the formation of [*cis*-Re(CO)$_4$Cl(THF)], as confirmed by infrared spectroscopy. Then a solution of [W(CO)$_5$pyz] (136 mg, 0.337 mmol) in THF (30 mL) was slowly dropped into the solution of [*cis*-Re(CO)$_4$Cl(THF)] cooled with an ice bath. After few minutes, the solution was concentrated and *n*-hexane was added, affording a red-orange precipitate, which, after filtration, was chromatographed on a silica gel column eluting with CH_2Cl_2. After elimination of [(CO)$_5$W-(pyz)W(CO)$_5$], the red-orange compound, which eluted last, was obtained in 49% yield. Anal. Found (Calcd): C 21.07 (21.16), H 0.61 (0.55), N 3.71 (3.80). IR (CH_2Cl_2): ν_{CO} 2118(w), 2073(m), 2035(m), 2021(m), 2005(sh), 1940(vs) cm^{-1}. UV (CH_2Cl_2): λ_{max} (nm) (log ϵ) 320(3.69), 392(3.59), 503(4.02). ^{1}H NMR (acetone-d_6): δ (ppm) 9.37 (2H, H_1H_2), 9.27 (2H, H_3H_4).

[(CO)$_5$W(BPE)*cis*-Re(CO)$_4$Cl]. [Re(CO)$_4$Cl]$_2$ (100 mg, 0.15 mmol) was added to THF (40 mL) and stirred until a clear solution evidenced the formation of [*cis*-Re(CO)$_4$Cl(THF)], as confirmed by infrared spectroscopy. A solution of [(CO)$_5$WBPE] (144 mg, 0.28 mmol) in THF (30 mL) was slowly dropped into the solution of [*cis*-Re(CO)$_4$Cl(THF)] cooled in an ice bath. After 45 min the solution was evaporated to dryness and the residue was chromatographed on a silica gel column eluting with CH_2Cl_2/hexane (9:1). A yellow compound was eluted (80% yield) after elimination of traces of [(CO)$_5$W(BPE)W(CO)$_5$]. Anal. Found (Calcd): C 29.98 (30.03), H 1.23 (1.20), N 3.41 (3.34). IR (CH_2Cl_2): ν_{CO} 2136(w), 2071(w), 2013(m), 1996(m), 1931-(vs), 1898(sh) cm^{-1}. UV (CH_2Cl_2): λ_{max} (nm) (log ϵ) 403(4.1), 437(sh). ^{1}H NMR (acetone-d_6): δ (ppm) 9.18 (2H, H_1H_2), 9.06 (2H, H_7H_8), 7.90 (2H, H_3H_4), 7.81 (s, 2H, H_9H_{10}), 7.78 (2H, H_5H_6).

[(CO)$_5$W(pyz)*cis*-Rh(CO)$_2$Cl]. To a solution of [W(CO)$_5$pyz] (174 mg, 0.43 mmol) in anhydrous CH_2Cl_2 (30 mL) was added [Rh(CO)$_2$Cl]$_2$ (83.4 mg, 0.215 mmol) dissolved in CH_2Cl_2. The solution turned from yellow to dark red. After 15 min, by adding *n*-hexane, a red powder precipitated, which was separated and washed with *n*-hexane (yield 50%). In the mother liquor the major products left were the symmetrical binuclear compounds [(CO)$_5$W(pyz)W(CO)$_5$] and [(CO)$_2$ClRh-*cis*(pyz)*cis*-Rh(CO)$_2$Cl], as evidenced by ^{1}H NMR spectroscopy. Anal. Found (Calcd): C 21.95 (22.05), H 0.73 (0.67), N 4.78 (4.67). IR (CH_2Cl_2): ν_{CO} 2107(w), 2095(m), 2074(m), 2034(w), 2023(m), 1937(vs) cm^{-1}. UV (CH_2Cl_2): λ_{max} (nm) (log ϵ) 319(3.62), 394(3.70), 499(3.44). ^{1}H NMR (CD_2Cl_2): δ (ppm) 9.01 (2H, H_1H_2), 8.67 (2H, H_3H_4).

[(CO)$_5$W(BPE)*cis*-Rh(CO)$_2$Cl]. To a solution of [W(CO)$_5$-BPE] (100 mg, 0.198 mmol) in CH_2Cl_2 (20 mL) maintained at 0 °C (ice bath) was added [Rh(CO)$_2$Cl]$_2$ (38.2 mg, 0.099 mmol) dissolved in CH_2Cl_2. The solution turned from orange to dark orange. After 15 min an orange powder precipitated by adding *n*-hexane and reducing the volume in turns more times. It was separated and washed with *n*-hexane (yield 55%). Anal. Found (Calcd): C 32.46 (32.58), H 1.33 (1.44), N 4.12 (4.00). IR (CH_2Cl_2): ν_{CO} 2088(m), 2071(w), 2014(m), 1930(vs), 1898(sh) cm^{-1}. UV (CH_2Cl_2): λ_{max} (nm) 404(4.21) 435(4.19). ^{1}H NMR (CD_2Cl_2): δ (ppm) 8.82 (2H, H_1H_2), 8.70 (2H, H_7H_8), 7.58 (2H, H_3H_4), 7.38 (2H, H_5H_6), 7.30 (s, 2H, H_9H_{10}; at −80 °C the broad singlet becomes two very close doublets).

Acknowledgment. This work was supported by the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (Programma di ricerca MURST di tipo interuniversitario, nell'area delle scienze chimiche, ex 40%, 1999, Research Title: Molecole per materiali funzionali nanostrutturati: Composti organometallici con proprietà ottiche non lineari (NLO) per materiali nanostrutturati) and by the Consiglio Nazionale delle Ricerche. We thank Dr. Elena Cariati and Dr. Francesca Tessore for EFISH measurements, Dr. Claudia Dragonetti for some experimental help, and Mr. Pasquale Illiano for NMR measurements.

OM020633H