Synthesis and Nonlinear Optical Properties of Carbonylrhenium Bromide Complexes with Conjugated Pyridines

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Dedicated to Professor Klaus-Jürgen Range on the occasion of his 60th birthday

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Carbonylrhenium bromide complexes *fac*-$Br(OC)_3ReL_2$ (**3a**,**b**, **4a**,**b**) and *cis*-$Br(OC)_4ReL$ (**5a**,**b**) with conjugated pyridines L = Fc–CH=CH–*p*-C_5H_4N (**1a**), Fc–CH=CHC-(CH_3)=CHCH=CHCH=C(CH_3)CH=CH–*p*-C_5H_4N (**1b**), 1,1′-Fc(–CH=CH–*p*-$C_5H_4N)_2$ (**1c**), *p*-Me_2N–C_6H_4–CH=CHCH= CH–*p*-C_5H_4N (**2a**), and *p*-Me_2N–C_6H_4–CH=CHC(CH_3)= CHCH=CHCH=C(CH_3)–CH=CH–*p*-C_5H_4N (**2b**) have been synthesized. The structures of **4a** and **5a** have been determined by X-ray diffraction analysis. Compound **4a** exhibits a remarkable quadratic hyperpolarizability.

1. Introduction

Following the discovery of a marked first hyperpolarizability of *cis*-[1-ferrocenyl-2-(4-nitrophenyl)ethylene] by Green et al.[1] in 1987, organometallic materials with nonlinear optical properties have attracted increasing attention. Compared to organic substances, metal complexes have some definitive advantages such as tunability of the polarizability by changing the oxidation state of the metal atom or by variation of the ligands.[2a] In a recent article by Whittall et al.,[2b] the scope of various nonlinear optical organometallic complexes was reviewed.

Kanis et al.[3] have performed ZINDO-SOS calculations for substituted pyridine complexes of the type (py)ML_5 (py = substituted pyridine derivative; ML_5 = d-metal fragment) in order to determine their hyperpolarizabilities β. They found that the metal fragments in complexes bearing donor-substituted pyridines as ligands contribute as inductive acceptors to the β response of the materials. A series of conjugated pyridine-containing nonlinear optical (NLO) metal complexes have been reported.[3–5] Furthermore, some carbonylrhenium compounds $X(OC)_3ReL_2$ incorporating aromatic N-donors have been studied as NLO materials.[6] Carbonylrhenium compounds,[7] including those of the type $X(OC)_3ReL_2$[8] and $[(OC)_3ReL_2L']^+$, have frequently been used in investigations of other photophysical or electron-transfer processes.

In continuation of our studies of metal complexes with polyene-containing ligands,[9] we have used new pyridine-containing ligands with an olefinic backbone and electron-donating organic or organometallic substituents to construct and investigate complexes of the type $(R-py)_nRe(CO)_{5-n}Br$ (n = 1, 2). We chose to prepare complexes of this type because of their stability and ease of handling.

As the molecular structures of our complexes fulfilled the basic requirements for NLO active materials, HRS measurements were performed.

Complexes of the type *cis*/*trans*-$LRe(CO)_4X$ have been investigated by several research groups, with L being some kind of phosphane.[10] To the best of our knowledge, only one complex of this type has been reported with an N-donor.[11] We have obtained new stable complexes of the type $(R-py)Re(CO)_4Br$ by reaction of $Re(CO)_5Br$ with pyridyl ligands.

2. Results and Discussion

2.1 Synthesis

Pyridine derivatives bearing extended conjugated olefinic substituents **1a–c**, **2a**,**b** in all-*trans* configuration were obtained by Wittig–Horner reaction of aldehydes with diphenyl(4-picolyl)phosphane oxide in yields of up to 70% according to the procedure of Effenberger et al.[12] We used formylferrocene, 1,1′-diformylferrocene, 9-ferrocenyl-2,7-dimethylnonatetraenal,[13] *p*-(dimethylamino)cinnamaldehyde, and 9-(*p*-dimethylaminophenyl)-2,7-dimethylnonatetraenal[13] as aldehyde components. The new compounds were purified by column chromatography on grade-III Al_2O_3 using dichloromethane as eluent. The ligand **1a** has previously been synthesized by other routes[5] and complexes $[(\mathbf{1a})M(CO)_5]$ (M = Cr, W, Mn^+, Re^+) have been prepared as NLO materials.

By reaction of $Re(CO)_5Br$ with two equivalents of the pyridine-containing ligands **1a**,**b** and **2a**,**b** in boiling tolu-

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[+] X-ray structure analysis.
[++] NLO measurements.

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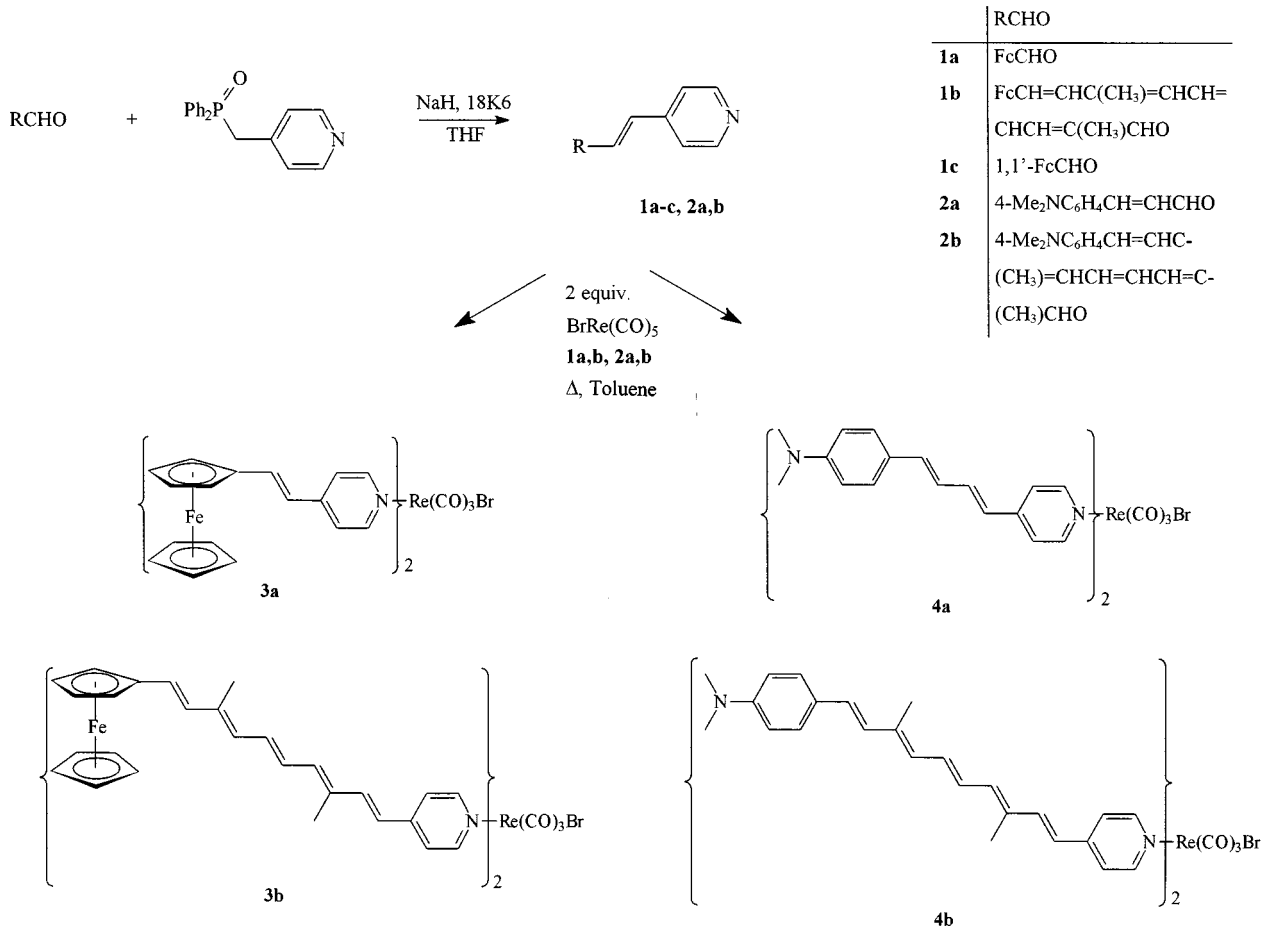


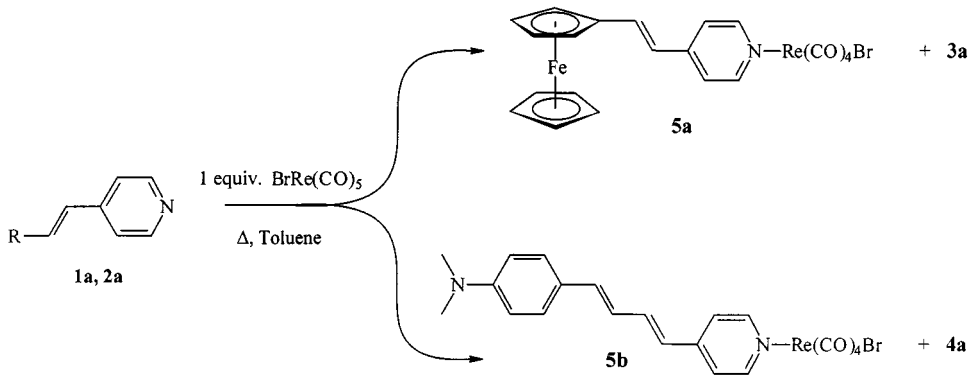
	RCHO
1a	FcCHO
1b	FcCH=CHC(CH_3)=CHCH=CHCH=C(CH_3)CHO
1c	1,1'-FcCHO
2a	4-$Me_2NC_6H_4$CH=CHCHO
2b	4-$Me_2NC_6H_4$CH=CHC(CH_3)=CHCH=CHCH=C(CH_3)CHO

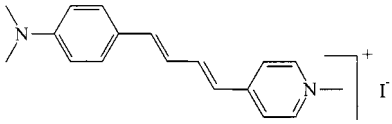
ene, two carbonyl ligands were substituted to give the *fac*-tricarbonylrhenium complexes **3a**,**b** and **4a**,**b**. These complexes were isolated by column chromatography of the crude reaction mixtures on silica gel using dichloromethane as eluent. Upon reaction of **1c** with $Re(CO)_5Br$, a red powder was obtained, presumably of the polymeric structure $[Re(CO)_3BrL]_n$.

Reaction of only one equivalent of the pyridine derivatives **1a** and **2a** with $Re(CO)_5Br$ led to the formation of a mixture of monosubstituted *cis*-(R−py)$Re(CO)_4Br$ (**5a**,**b**) and disubstituted complexes (R−py)$_2Re(CO)_3Br$ (**3a**, **4a**), which could be separated by column chromatography.

2.2 Characterization

For the complexes **3a**−**c** and **4a**,**b**, three CO absorptions of similar intensity are observed in the IR spectra, which is typical for *fac*-$L_2Re(CO)_3X$ complexes.[10] The CO band at the highest frequency is the one most sensitive to the nature of the ligand L. This absorption appears at lower energies compared with existing data for similar substituted pyridyl complexes.[6,10c] This indicates that the π-donor strength of our pyridine ligands is larger. For the complexes (R−py)Re(CO)$_4$Br (**5a** and **5b**), four CO absorptions are detected, in accordance with their *cis* configuration.





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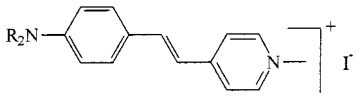
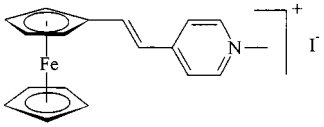


7a : R= CH_3; **7b**: R= $C_{16}H_{33}$



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In agreement with the results of McCleverty et al.,[5b] the pyridyl protons H^2 and H^6 as well as H^3 and H^5 in **3**−**5** are equivalent and thus each pair gives rise to just one signal in the room-temperature ^{1}H-NMR spectra. This implies rapid rotation of the pyridyl rings in relation to the vinyl group to which they are attached; if the pyridyl ring were coplanar with the rest of the conjugated system, it could not have two-fold symmetry.

Several intense absorption bands are seen in the UV/Vis spectra in CH_2Cl_2. For the ferrocene-containing compounds, the following transitions are expected: two ferrocene-based MLCT absorptions between 350 and 500 nm and an intense π→π* absorption around 300 nm.[5a] Furthermore, π→π* or intense ILCT absorptions for the olefinic backbones, as well as MLCT bands of d(Re)→π* (py−R) around 340 nm are observed. The intense π→π* absorption of **1a**[5a] (313 nm) is red-shifted upon complexation (**3a**: 342 nm) and becomes superimposed by the expected MLCT band. A further weaker absorption appears at 501 nm. The principal absorption band of compound **3b** is a π→π* absorption of the olefinic backbone at 443 nm. Weaker absorptions of **3b** give bands at 334 nm and as a shoulder at 521 nm. Compounds **4a** (438 nm) and **5b** (444 nm) show strong and broad ILCT absorptions, which cover the MLCT [d(Re)→π*(py−R)] absorptions.

For compound **2a**, an emission spectrum is observed. The fluorescence band may be attributed to a long-distance intramolecular charge transfer (ICT).[14] This emission band is red-shifted in complexes **4a** and **5b**, in accordance with the inductive electron-accepting effect of the complex fragment.[3] For the other compounds, no fluorescence could be observed at $\lambda_{em} \leq 630$ nm with excitation between 350 and 450 nm.

Table 1. UV/Vis data for compounds **1a**,**b**, **2a**,**b**, **3a**,**b**, **4a**,**b** and **5a**,**b** in CH_2Cl_2

	λ_{max} [nm] (lg ε)
1a	313 (4.47), 374 (3.67), 464 (3.47)
1b	417 (4.99), 493 sh (4.35)
2a	394 (4.58)
2b	448 (4.85)
3a	343 (4.72), 501 (3.99)
3b	443 (4.98), 521 sh (4.69)
4a	438 (5.11)
4b	328 (4.49), 484 (5.01)
5a	341 (4.66), 508 (3.89)
5b	307 (4.59), 444 (5.00)

2.3 X-ray Crystallography

X-ray quality crystals of **4a** and **5a** were obtained by diffusion of *n*-pentane into solutions of the complexes in CH_2Cl_2. The structures are essentially as expected and confirm the expected structures of the complexes. Crystal parameters are given in Table 2.[15]

Both compounds crystallize in centrosymmetric space groups (**4a** in *C*2/*c* and **5a** in *R*−3). Both crystal structures contain relatively large channels, which extend along the C_2 (in **4a**) or C_3 axes (in **5a**), and which constitute 17% and 5.4% of the respective cell volumes. The cavities in **4a** are surrounded by bromine atoms with distances of 3.89 Å, while in **5a** they are surrounded by the oxygen atoms of two carbonyl ligands with distances of 3.68 Å (O1) and 3.20 Å

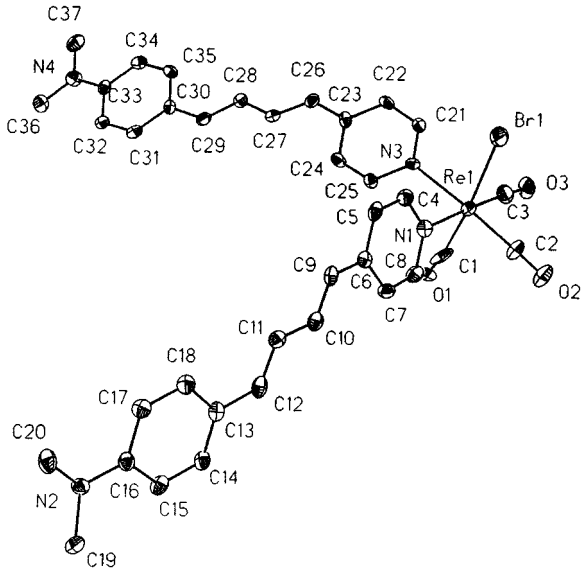

Figure 1. Molecular structure of complex **4a** × $(CH_2Cl_2)_{1.5}$; selected bond lengths [Å] and angles [°]: Re(1)−C(2) 1.89(1), Re(1)−C(3) 1.90(2), Re(1)−C(1) 1.8900(1), Re(1)−N(3) 2.21(1), Re(1)−N(1) 2.21(1), Re(1)−Br(1) 2.614(2), O(1)−C(1) 1.1701(2), O(2)−C(2) 1.18(1), O(3)−C(3) 1.17(2), C(6)−C(9) 1.46(2), C(9)−C(10) 1.31(2), C(10)−C(11) 1.44(2), C(11)−C(12) 1.36(2), C(12)−C(13) 1.47(2), C(23)−C(26) 1.45(2), C(26)−C(27) 1.33(2), C(27)−C(28) 1.42(2), C(28)−C(29) 1.33(2), C(29)−C(30) 1.45(2); C(10)−C(9)−C(6) 125(1), C(9)−C(10)−C(11) 126(1), C(12)−C(11)−C(10) 122(1), C(11)−C(12)−C(13) 129(1), C(27)−C(26)−C(23) 126(1), C(26)−C(27)−C(28) 129(1), C(29)−C(28)−C(27) 124(1), C(28)−C(29)−C(30) 130(1)

(O2).[16] In compound **4a**, a molecule of CH_2Cl_2 was found to be localized in the "void channel" and could be refined (besides a further CH_2Cl_2 molecule in a general position). No solvent molecules were found in the crystal structure of **5a**, which might in part be due to the incompatibility of

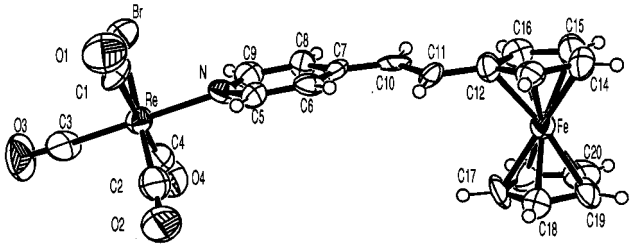

Figure 2. Molecular structure of complex **5a**; selected bond lengths [Å] and angles [°]: Re−C(2) 1.89(2), Re−C(3) 1.97(2), Re−C(4) 2.01(2), Re−C(1) 2.06(2), Re−N 2.187(13), Re−Br 2.595(2), O(1)−C(1) 1.00(2), O(2)−C(2) 1.17(2), O(3)−C(3) 1.11(2), O(4)−C(4) 1.10(2), C(7)−C(10) 1.46(2), C(10)−C(11) 1.29(2), C(11)−C(12) 1.43(2); C(4)−Re−C(1) 75.8(7), C(1)−Re−Br 85.7(5), N−Re−Br 86.4(3), C(11)−C(10)−C(7) 127(2), C(10)−C(11)−C(12) 127(2)

CH_2Cl_2 symmetry with the trigonal symmetry of the void.

In both compounds, the rhenium atoms are very close to ideal octahedral geometry, with Re−Br and Re−N distances in the expected ranges.[6c]

In **4a**, the pyridine ligands are mutually *cis* oriented, with an interplanar angle of 72°. In both compounds, the pyridine ligands are in a staggered orientation with respect to the $Re(CO)_2BrN$ fragments: The interplanar angles are 38° and 50° in **4a**, and 49° in **5a**. This indicates that minimization of steric interactions prevails over electronic π-delocalization.[5b]

The π-system in compound **5a** is less twisted than that in compound **4a**. The angle between the cp ligand and the pyridyl ring is only 4°, which results from two mutually cancelling torsions at the double bond (C6−C7−C10−C11 −9.3°/C10−C11−C12−C13 −170.3°). In **4a**, however, the torsions are additive and lead to interplanar angles of 17° between the terminal planes containing N1, and of 7° between the termini in the second pyridyl ligand (C5−C6−C9−C10 −174.8°/C9−C10−C11−C12 −173.0° and C22−C23−C26−C27 −178.4°/C26−C27−C28−C29 −177.8°).

The small twist in the ferrocenyl derivative **5a** permits additional intermolecular interactions between a cyclopentadienyl ring and a pyridine ring of a neighbouring molecule. The distance between the ring centroids is 3.68 Å, and with a vertical plane distance of 3.42 Å; this leads to a β angle of 18°, indicative of effective π-stacking of the molecules.[16]

2.4 NLO Properties of 3a and 4a

The first hyperpolarizabilities of **3a** and **4a** were determined by hyper Rayleigh scattering (HRS)[17] To circum-

Table 2. Crystallographic data for complexes **4a** and **5a**

	4a	**5a**
Empirical Formula	$C_{38.50}H_{37}BrC_{13}N_4O_3Re$	$C_{21}H_{15}BrFeNO_4Re$
Molecular mass	976.18	667.30
Crystal color, habit	orange plate	redbrown needles
Crystal dimensions [mm]	0.20 × 0.15 × 0.05	0.20 × 0.175 × 0.075
Crystal system	monoclinic	rhombohedral
Space group	*C*2/*c*	*R*−3
a [Å]	18.3826(1)	30.357(4)
b [Å]	15.1048(1)	30.357(4)
c [Å]	28.5866(1)	12.398(2)
β [°]	92.848(1)	90
V [Å^3]	7927.71(7)	9895(2)
Z	8	18
$D_{calcd.}$ [gcm^{-3}]	1.636	2.016
Absorption coefficient [mm^{-1}]	4.317	8.003
F(000)	3848	5688
θ range for data collection	2.86−58.46° (2θ)	2.26−24.96°
Index ranges	$-23 \le h \le 23$, $-18 \le k \le 18$, $-35 \le l \le 35$	$-2 \le h \le 27$, $-30 \le k \le 29$, $-13 \le l \le 12$
Reflections collected	18304	3679
Independent reflections	7804 [*R*(int) = 0.0728]	2930 [*R*(int) = 0.0715]
Absorption correction	semi-empirical	ψ scan
Max. and min. transmission	0.492 and 0.598	0.177 and 0.130
Refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2
Data/restraints/parameters	7804/9/480	2929/0/262
Goodness-of-fit on F^2	1.216	1.036
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0726$, $wR^2 = 0.1723$	$R1 = 0.0578$, $wR^2 = 0.1048$
R indices (all data)	$R1 = 0.1044$, $wR^2 = 0.1964$	$R1 = 0.1250$, $wR^2 = 0.1302$
Structure solution program	*SHELXS-97* (G. M. Sheldrick, **1997**)	*SHELXS-93* (G. M. Sheldrick, **1993**)
Refinement details:		
Program used	*SHELXL-97* (G. M. Sheldrick, **1997**)	*SHELXL-97* (G. M. Sheldrick, **1997**)
	Distances Re1−C1 and C1−O1 were fixed. In free refinement the C1−O1 distance was too short (0.9 Å) and the Re1−C1 distance too long (1.98 Å).	
CifRtf version used	2.0	

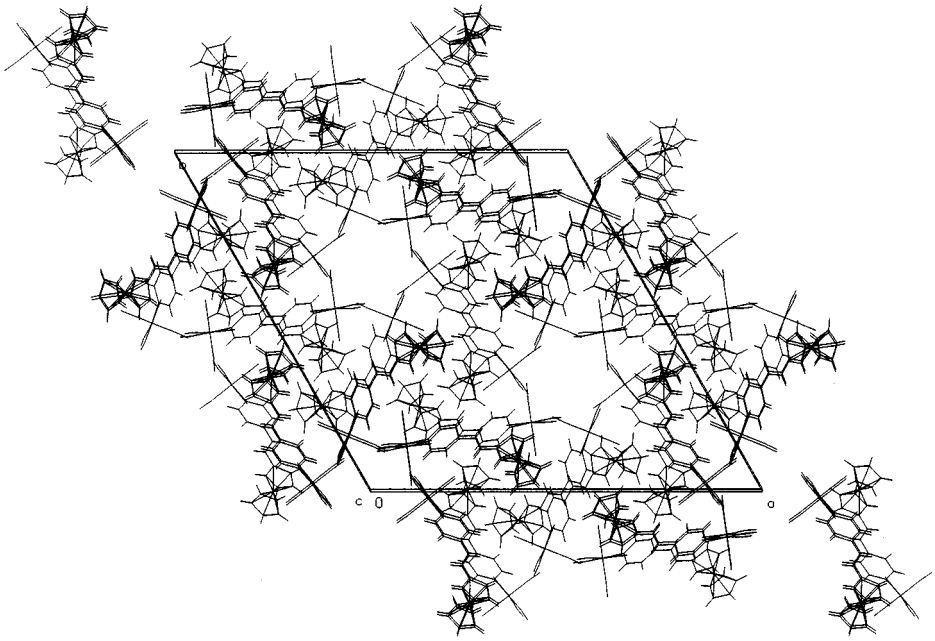

Figure 3. Crystal structure of complex **5a** view down the *c* axis

vent problems associated with reabsorption of the second harmonic and enhancement of β by multiphoton-induced fluorescence,[18] the measurements were carried out at fundamental wavelengths of 1300 nm (**3a**) and 1500 nm (**4a**), respectively. Descriptions of the HRS apparatus and of the method of data analysis have been given previously,[19,20] thus we describe here in brief only the key features. As an external standard, *p*-dimethylaminocinnamaldehyde (DMAZ) was used ($\beta_{zzz} = 41 \times 10^{-30}$ esu at 1300 nm, and 35×10^{-30} esu at 1500 nm in $CHCl_3$).[21] A plot of $I(2\omega)$, the intensity of the measured second harmonic, versus the number density for both sample and reference leads to the ratio $<\beta_{HRS}^2>_{sample}/<\beta_{HRS}^2>_{reference}$, from which specific components of the β tensor may be determined. Depending on the molecular symmetry, only some tensor elements contribute to $\langle\beta_{HRS}^2\rangle$. For 1D molecules such as DMAZ:

$$\langle\beta_{HRS}^2\rangle = \frac{6}{35}\beta_{zzz}^2 \qquad (1)$$

3a and **4a** have approximate C_2 symmetry, therefore:

$$\langle\beta_{HRS}^2\rangle = \frac{6}{35}\beta_{zzz}^2 + \frac{4}{7}\beta_{xyz}^2 + \frac{38}{105}\left(\beta_{xxz}^2 + \beta_{yyz}^2\right) + \frac{16}{105}\left(\beta_{xxz}\beta_{yyz} + \beta_{xxz}\beta_{zzz} + \beta_{yyz}\beta_{zzz}\right) \qquad (2)$$

Since it is not possible to deduce β_{xxz}, β_{xyz}, β_{yyz} and β_{zzz} of **3a** and **4a** from the measured $<\beta_{HRS}^2>$ value, a theoretical ratio $\beta_{xxz}/\beta_{xyz}/\beta_{yyz}/\beta_{zzz}$ was calculated by tensor addition.[20,22] For the sake of simplicity, **3a** and **4a** were assumed to consist of two non-interacting 1D subunits. From X-ray crystallography measurements on **4a**, a 90° angle between the subunits was derived. For **3a**, the same angle was assumed. Electron transitions within the Re complex were neglected. As a result, β_{xyz} and β_{yyz} vanish, and β_{xxz} and β_{zzz} were found to be equal. Together with Eq. 2, this yields:

$$\langle\beta_{HRS}^2\rangle = \frac{24}{35}\beta_{zzz}^2; \quad \beta_{zzz} = \beta_{xxz} \qquad (3)$$

The results of the HRS measurements and the β values of the subchromophores **6** and **8** given in the literature are summarized in Table 2. The modulus

$$\|\beta\| = \sqrt{\sum_{ijk}\beta_{ijk}^2}$$

was used to compare the hyperpolarizabilities of molecules with different specific components of the β tensor.

Table 3. First hyperpolarizabilities of **3a**, **4a**, **6**−**8**; hyperpolarizabilities are given in 10^{-30} esu; 1×10^{-30} esu = 3.713×10^{-51} Cm^3V^{-2}; the HRS measurements were carried out in $CHCl_3$

	λ_{max} [nm]	β_{xxz}	β_{zzz}	$\|\beta\|$	fundamental wavelength [nm]
3a	501[e]	12	12	24	1300
4a	438[e]	104	104	208	1500
6	526[a]		343[a]	343	1910
7a	509[e]/479[a]		178[a]	178	1910
7b	515[d]		140[b]	140	1910
8	521[c]		68[c]	68	1910

[a] ZINDO-derived value, ref.[23] – [b] HRS measurement at 1500 nm,[25] converted to 1910 nm by the two-level model.[26] – [c] ZINDO-derived value, ref.[24] – [d] In $CHCl_3$. – [e] In CH_2Cl_2.

Taking the β values of the 1D molecules **6** and **8** as starting points, the theoretical moduli $\|\beta\|$ of angled clusters consisting of two equal 1D subchromophores were calculated by tensor addition. For a 90° angle, this yielded $\|\beta\| = 96 \times 10^{-30}$ esu (subchromophore **8**) and $\|\beta\| = 485 \times 10^{-30}$ esu (subchromophore **6**), respectively, at 1910 nm. Although comparison of the calculated and experimental data for **7a** and **7b** indicates an overestimation of the β values by ZINDO, the hyperpolarizabilities of the complexes **3a** and **4a** are much smaller than those calculated for the angled clusters consisting of the corresponding subchromophores **6** and **8**, respectively. Therefore, replacement of the methyl

moiety by the Re complex leads to a noticeable reduction of the acceptor properties of the pyridinium moiety. Nevertheless, **4a** shows a remarkably high first hyperpolarizability. Even higher quadratic hyperpolarizabilities have recently been reported for the complexes $[(\mathbf{1a})M(CO)_5]^+$ (M = Mn, Re).[5d]

Experimental Section

All operations were carried out under nitrogen using the Schlenk technique. $Re(CO)_5Br$ was synthesized according to a literature procedure.[27] Solvents were dried by distillation from sodium/benzophenone, $LiAlH_4$, or CaH_2 as appropriate. − NMR spectra were recorded with a Jeol GSX 270 (^1H: 270.17 MHz; ^{13}C: 67.94 MHz; ^{31}P: 109.38 MHz) or a Jeol EX 400 spectrometer (^1H: 399.78 MHz; ^{13}C: 100.53 MHz). − IR: Perkin−Elmer 841, Nicolet 520 FT-IR. − UV/Vis: Philips PU 8710. − Luminescence: Perkin−Elmer Luminescence Spectrometer LS 50B.

Ligands 1a−c, 2a,b: Essentially the same procedures were followed to synthesize **1a−c** and **2a**,**b**. Thus, only the preparation of **1a** is described here in detail.

***trans*-Fc−CH=CH−C_5H_4N (1a):** A mixture of 275 mg (0.94 mmol) of diphenyl(4-picolyl)phosphane oxide, 200 mg (0.94 mmol) of ferrocene aldehyde, 250 mg (0.96 mmol) of 18-crown-6, and 55 mg (1.2 mmol; 55% in paraffin; washed twice with pentane) of NaH was stirred in 40 mL of THF at room temperature for 3 h. At the beginning of the reaction, 25 μL of H_2O was added to activate the NaH. The resulting red suspension was then filtered through a G3 glass funnel. The solvent was removed from the filtrate in vacuo, and the crude product was chromatographed on grade-III Al_2O_3. The first fraction (R_f = 0.5) was identified as the product, and furnished a red powder upon evaporation of the solvent. Yield 136 mg (50%). − IR (KBr): ṽ(C=C, C=N) = 1632 (s), 1594 cm^{-1} (vs). − ^1H NMR (270 MHz, $CDCl_3$): δ = 8.53 (d, 2 H, ^3J = 6.2 Hz, NC*H*), 7.28 (d, 2 H, ^3J = 6.0 Hz, NCHC*H*), 7.13 (d, 1 H, ^3J = 15.7 Hz, H_{ol}), 6.60 (d, 1 H, ^3J = 16.1 Hz, H_{ol}), 4.51 (t, 2 H, ^3J = 1.9 Hz, C_5H_4), 4.36 (t, 2 H, ^3J = 2.2 Hz, C_5H_4), 4.16 (s, 5 H, C_5H_5). − UV/Vis (CH_2Cl_2) (lg ε): λ_{max} = 313 (4.47), 374 (3.67), 464 nm (3.47). − $C_{17}H_{15}FeN$ (289.1): calcd. C 70.61, H 5.22, N 4.84; found C 69.31, H 5.30, N 4.48.

all-*trans*-(C_5H_5)Fe(C_5H_4)CH=CHC(CH_3)=CHCH=CHCH=C(CH_3)CH=CHC_5H_4N (1b): Dark-red powder, yield 150 mg (37%). − IR (KBr): ṽ(C=C, C=N) = 1618 (m), 1598 (s), 1588 (s), 1556 cm^{-1} (vs). − ^1H NMR (270 MHz, $CDCl_3$): δ = 8.53 (d, 2 H, ^3J = 5.9 Hz, NC*H*), 7.28 (d, 2 H, ^3J = 6.0 Hz, NCHC*H*), 7.07 (d, 1 H, ^3J = 15.6 Hz, H_{ol}), 6.74−6.24 (m, 6 H, H_{ol}), 6.48 (d, 1 H, ^3J = 15.9 Hz, H_{ol}), 4.42 (t, 2 H, ^3J = 1.9 Hz, C_5H_4), 4.29 (t, 2 H, ^3J = 1.8 Hz, C_5H_4), 4.12 (s, 5 H, C_5H_5), 2.02 (s, 6 H, CH_3). − UV/Vis (CH_2Cl_2) (lg ε): λ_{max} = 417 (4.99), 493 nm (sh, 4.35). − $C_{27}H_{27}FeN$ (421.2): calcd. C 76.93, H 6.46, N 3.32; found C 76.30, H 6.46, N 3.29.

***trans*-Fe[(C_5H_4)CH=CHC_5H_4N]$_2$ (1c):** Red powder, yield 263 mg (70%). − IR (KBr): ṽ(C=C, C=N) = 1629 (s), 1593 cm^{-1} (vs). − ^1H NMR (270 MHz, $CDCl_3$): δ = 8.44 (d, 4 H, ^3J = 6.3 Hz, NC*H*), 7.08 (d, 4 H, ^3J = 6.5 Hz, NCHC*H*), 6.93 (d, 2 H, ^3J = 16.1 Hz, H_{ol}), 6.47 (d, 2 H, ^3J = 16.1 Hz, H_{ol}), 4.48 (t, 4 H, ^3J = 2.0 Hz, C_5H_4), 4.35 (t, 4 H, ^3J = 2.1 Hz, C_5H_4). − $C_{24}H_{20}N_2Fe$ (392.1): calcd. C 73.49, H 5.14, N 7.14; found C 72.48, H 5.06, N 6.95.

all-*trans*-($H_3C)_2N(C_6H_4$)CH=CHCH=CHC_5H_4N (2a): Bright-yellow needles, yield 140 mg (57%). − IR (KBr): ṽ(C=C, C=N) = 1601 (s), 1588 cm^{-1} (s). − ^1H NMR (270 MHz, $CDCl_3$): δ = 8.51 (d, 2 H, ^3J = 6.1 Hz, NC*H*), 7.36 (d, 2 H, ^3J = 8.7 Hz, C_6H_4), 7.26 (d, 2 H, ^3J = 6.0 Hz, NCHC*H*), 7.07 (dd, 1 H, ^3J = 15.3, ^3J = 9.7 Hz, H_{ol}), 6.82−6.73 (m, 2 H, H_{ol}), 6.69 (d, 2 H, ^3J = 9.0 Hz, C_6H_4), 6.46 (d, 1 H, ^3J = 15.3 Hz, H_{ol}), 3.00 [s, 6 H, ($H_3C)_2N$]. − UV/Vis (CH_2Cl_2) (lg ε): λ_{max} = 394 nm (4.58). − Emission spectrum (CH_2Cl_2, λ_{ex} = 350 nm): $\lambda_{em,max}$ = 511 nm. − $C_{17}H_{18}N_2$ (250.1): calcd. C 81.55, H 7.25, N 11.20; found C 79.26, H 6.70, N 10.80.

($H_3C)_2N(C_6H_4$)CH=CHC(CH_3)=CHCH=CHCH=C(CH_3)CH=CHC_5H_4N (2b): Orange powder, yield 120 mg (35%). − IR (KBr): ṽ(C=C, C=N) = 1609 (vs, sh), 1604 (s), 1597 cm^{-1} (vs). − ^1H NMR (400 MHz, $CDCl_3$): δ = 8.52 (d, 2 H, ^3J = 5.8 Hz, NC*H*), 7.35 (d, 2 H, ^3J = 8.6 Hz, C_6H_4), 7.27 (d, 1 H, NCHC*H*), 7.07 (d, 1 H, ^3J = 15.9 Hz, H_{ol}), 6.83−6.30 (m, 7 H, H_{ol}), 6.70 (d, 2 H, ^3J = 9.0 Hz, C_6H_4), 2.98 [s, 6 H, ($H_3C)_2N$], 2.05/2.03 (each s, each 3 H, CH_3). − UV/Vis (CH_2Cl_2) (lg ε): λ_{max} = 448 nm (4.85). − $C_{25}H_{28}N_2$ (356.2): calcd. C 84.22, H 7.92, N 7.86; found C 83.82, H 7.71, N 7.79.

Complexes 3a−c, 4a,b, 5a,b: All the compounds were found to be moderately stable as solids and did not decompose significantly upon exposure to air for several days. Essentially the same procedures were followed to synthesize **3a−c** and **4a**,**b**, thus only the preparation of **4a** is described here in detail.

[all-*trans*-($H_3C)_2N(C_6H_4$)CH=CHCH=CHC_5H_4N]$_2$Re(CO)$_3$Br (4a): 100 mg (0.4 mmol) of **2a** and 80 mg (0.2 mmol) of $Re(CO)_5Br$ were allowed to react in refluxing toluene for 1 h. The solvent was then evaporated from the resulting orange solution. The crude product was chromatographed on silica gel using CH_2Cl_2 as eluent. The first fraction was found to contain the product. Bright-orange powder, yield 85 mg (77%). − IR (KBr): ṽ(C=O) = 2019 (vs), 1919 (vs), 1878 cm^{-1} (vs). − ^1H NMR (270 MHz, $CDCl_3$): δ = 8.63 (d, 4 H, ^3J = 6.9 Hz, NC*H*), 7.37 (d, 4 H, ^3J = 9.2 Hz, C_6H_4), 7.21 (d, 4 H, ^3J = 6.9 Hz, NCHC*H*), 7.16 (m, 2 H, H_{ol}), 6.79−6.77 (m, 4 H, H_{ol}), 6.69 (d, 4 H, ^3J = 9.0 Hz, C_6H_4), 6.42 (d, 2 H, ^3J = 15.3 Hz, H_{ol}), 3.00 [s, 12 H, ($H_3C)_2N$]. − ^{13}C NMR (68 MHz, $CDCl_3$): δ = 195.39/192.20 (CO), 154.04, 147.59, 138.95, 137.85, 130.67, 129.11, 128.51, 124.96, 121.73, 112.30 (C_{ar}, C_{ol}), 40.31 [$N(CH_3)_2$]. − UV/Vis (CH_2Cl_2) (lg ε): λ_{max} = 438 nm (5.11). − Emission spectrum (CH_2Cl_2, λ_{ex} = 350 nm): $\lambda_{em,max}$ = 564 nm. − $C_{37}H_{36}BrN_4O_3Re$ (850.7): calcd. C 52.23, H 4.27, N 6.59; found C 51.85, H 3.92, N 6.45.

(*trans*-Fc−CH=CH−$C_5H_4N)_2$Re(CO)$_3$Br (3a): Red powder, yield 60 mg (67%). − IR (KBr): ṽ(C=O) = 2021 (vs), 1914 (vs), 1884 cm^{-1} (vs). − ^1H NMR (270 MHz, $CDCl_3$): δ = 8.66 (d, 4 H, ^3J = 6.6 Hz, NC*H*), 7.30 (m, 2 H, H_{ol}), 7.22 (d, 4 H, ^3J = 8.2 Hz, C_6H_4), 7.21 (d, 4 H, ^3J = 6.9 Hz, NCHC*H*), 6.56 (d, 2 H, ^3J = 15.6 Hz, H_{ol}), 4.53 (t, 4 H, ^3J = 1.9 Hz, C_5H_4), 4.43 (t, 4 H, ^3J = 1.9 Hz, C_5H_4), 4.16 (s, 10 H, C_5H_5). − UV/Vis (CH_2Cl_2) (lg ε): λ_{max} = 343 (4.72), 501 nm (3.99). − $C_{37}H_{30}BrFe_2N_2O_3Re$ (928.0): calcd. C 47.85, H 3.26, N 3.02; found C 47.80, H 3.43, N 2.87.

[(C_5H_5)Fe(C_5H_4)CH=CHC(CH_3)=CHCH=CHCH=C(CH_3)-CH=CHC_5H_4N]$_2$Re(CO)$_3$Br (3b): Dark-red powder, yield 80 mg (67%). − IR (KBr): ṽ(C=O) = 2021 (vs), 1916 (vs), 1882 cm^{-1} (vs). − ^1H NMR (270 MHz, $CDCl_3$): δ = 8.64 (d, 4 H, ^3J = 6.4 Hz, NC*H*), 7.23 (d, 4 H, ^3J = 6.8 Hz, NCHC*H*), 7.11 (d, 2 H, ^3J = 15.8 Hz, H_{ol}), 6.86−6.25 (m, 12 H, H_{ol}), 6.43 (d, 2 H, ^3J = 16.3 Hz, H_{ol}), 4.46 (t, 4 H, ^3J = 1.8 Hz, C_5H_4), 4.30 (t, 4 H, ^3J = 1.9 Hz, C_5H_4), 4.12 (s, 10 H, C_5H_5), 2.02/2.01 (each s, each 6 H, CH_3). − UV/Vis (CH_2Cl_2) (lg ε): λ_{max} = 443 (4.98), 521 nm (sh, 4.69). − $C_{57}H_{54}BrFe_2N_2O_3Re$ (1192.2): calcd. C 57.37, H 4.57, N 2.35; found C 57.51, H 4.39, N 2.19.

{trans-Fe[(C_5H_4)CH=CHC_5H_4N]$_2$Re(CO)$_3$Br}$_n$ (3c): Dark-red powder, washing with CH_2Cl_2 furnished the product; yield 30 mg (23%). − IR (KBr): $\tilde{\nu}$(C=O) = 2020 (vs), 1912 (vs), 1884 cm^{-1} (vs). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 8.70−8.60 (m, 4 H, NC*H*), 7.37−7.15 (m, 6 H, NCHC*H*, H_{ol}), 6.58−6.42 (m, 2 H, H_{ol}), 4.55−4.35 (m, 8 H, C_5H_4). − ($C_{27}H_{20}BrFeN_2O_3Re)_n$ (1/*n* M = 741.96): calcd. C 43.67, H 2.72, N 3.77; found C 42.79, H 2.89, N 3.65.

[($H_3C)_2$N(C_6H_4)CH=CHC(CH_3)=CHCH=CHCH=C(CH_3)CH=CHC_5H_4N]$_2$Re(CO)$_3$Br (4b): Dark-red powder, yield 40 mg (67%). − IR (KBr): $\tilde{\nu}$(C=O) = 2019 (vs), 1915 (vs), 1880 cm^{-1} (vs). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 8.65 (d, 4 H, ^3J = 6.7 Hz, NC*H*), 7.37 (d, 4 H, ^3J = 8.7 Hz, C_6H_4), 7.23 (d, 4 H, ^3J = 6.5 Hz, NCHC*H*), 7.12 (d, 1 H, ^3J = 15.8 Hz, H_{ol}), 6.88−6.32 (m, 14 H, H_{ol}), 6.71 (d, 4 H, ^3J = 8.6 Hz, C_6H_4), 3.00−2.99 [m, 12 H, ($H_3C)_2$N], 2.05/2.02 (each s, each 6 H, CH_3). − UV/Vis (CH_2Cl_2) (lg ε): λ_{max} = 328 (4.49), 485 nm (5.01). − $C_{53}H_{56}BrN_4O_3Re$ (1062.3): calcd. C 59.87, H 5.31, N 5.27; found C 59.53, H 5.81, N 5.63.

***trans*-Fc−CH=CH−C_6H_4N−*cis*-Re(CO)$_4$Br (5a):** 58 mg (0.2 mmol) of *trans*-Fc−CH=CH−C_6H_4N was added to 81 mg (0.2 mmol) of $Re(CO)_5Br$ in toluene and the mixture was heated until a solution was obtained. The solvent was then evaporated and the residue was subjected to column chromatography on silica gel using CH_2Cl_2 as eluent. Two main fractions were collected, the first containing **5a** (32 mg, 25%) and the second **4a** (52 mg, 28%). Dark-red powder. − IR (KBr): $\tilde{\nu}$(C=O) = 2105 (m), 2002 (vs), 1988 (vs), 1946 cm^{-1} (vs). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 8.84 (d, 2 H, ^3J = 7.0 Hz, NC*H*), 7.39 (d, 2 H, ^3J = 8.9 Hz, C_6H_4), 7.30 (d, 2 H, ^3J = 6.8 Hz, NCHC*H*), 7.26−7.20 (m, 1 H, H_{ol}), 6.83 (m, 2 H, H_{ol}), 6.70 (d, 2 H, ^3J = 8.7 Hz, C_6H_4), 6.45 (d, 1 H, ^3J = 15.6 Hz, H_{ol}), 3.03 [s, 6 H, ($H_3C)_2$N]. − ^{13}C NMR (109 MHz, $CDCl_3$): δ = 195.47, 192.17 (CO), 154.07, 147.27, 136.73 (C_{ar}), 121.44/120.92 (C_{ol}), 80.47, 70.64, 69.55, 67.93 (Fc). − UV/Vis (CH_2Cl_2) (lg ε): λ_{max} = 341 (4.66), 508 nm (3.89). − $C_{21}H_{15}BrFeNO_4Re$ (666.9): calcd. C 37.79, H 2.27, N 2.10; found C 38.15, H 2.49, N 2.13.

[all-*trans*-($H_3C)_2$N(C_6H_4)CH=CHCH=CHC_5H_4N]−*cis*-Re(CO)$_4$-Br (5b): Orange powder, yield 55 mg (22%). − IR (KBr): $\tilde{\nu}$(C=O) = 2108 (m), 2024 (vs), 1990 (vs), 1938 cm^{-1} (vs). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 8.87 (d, 2 H, ^3J = 6.8 Hz, NC*H*), 7.34 (d, 2 H, ^3J = 6.9 Hz, NCHC*H*), 7.30 (d, 1 H, ^3J = 16.1 Hz, H_{ol}), 6.59 (d, 1 H, ^3J = 16.1 Hz, H_{ol}), 4.56 (t, 2 H, ^3J = 1.8 Hz, C_5H_4), 4.46 (t, 2 H, ^3J = 1.9 Hz, C_5H_4), 4.18 (s, 5 H, C_5H_5). − UV/Vis (CH_2Cl_2) (lg ε): λ_{max} = 307 (4.59), 444 nm (5.00). − Emission spectrum (CH_2Cl_2, λ_{ex} = 350 nm): $\lambda_{emi,max}$ = 573 nm. − $C_{21}H_{18}BrN_2O_4Re$ (628.0): calcd. C 40.13, H 2.89, N 4.46; found C 39.53, H 2.90, N 4.27.

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[1] M. L. H. Green, S. R. Marder, M. E. Thompson, J. A. Bandy, D. Bloor, P. V. Kolinsky, R. J. Jones, *Nature* **1987**, *330*, 360−362.

[2] [2a] N. J. Long, *Angew. Chem.* **1995**, *107*, 37−56; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 21. − [2b] I. R. Whittall, A. M. McDonagh, M. G. Humphrey, M. Samoc, *Adv. Organomet. Chem.* **1998**, *42*, 291−362.

[3] D. R. Kanis, P. G. Lacroix, M. A. Ratner, T. J. Marks, *J. Am. Chem. Soc.* **1994**, *116*, 10089−10102.

[4] [4a] B. J. Coe, J. A. Harris, L. J. Harrington, J. C. Jeffery, L. H. Rees, S. Houbrechts, A. Persoons, *Inorg. Chem.* **1998**, *37*, 3391−3399. − [4b] R. H. Naulty, A. M. McDonagh, I. R. Whittall, M. P. Cifuentes, M. G. Humphrey, S. Houbrechts, J. Maes, A. Persoons, G. A. Heath, D. C. R. Hockless, *J. Organomet. Chem.* **1998**, *563*, 137−146. − [4c] S. L. W. McWhinnie, J. A. Thomas, T. A. Hamor, C. J. Jones, J. A. McCleverty, D. Collison, F. E. Mabbs, C. J. Harding, L. J. Yellowlees, M. G. Hutchings, *Inorg. Chem.* **1996**, *35*, 760−774. − [4d] S. Houbrechts, K. Clays, A. Persoons, V. Cadierno, M. P. Gamasa, J. Gimeno, *Organometallics* **1996**, *15*, 5266−5268. − [4e] D. W. Bruce, A. Thornton, B. Chaudret, S. Sabo-Etienne, T. L. Axon, G. H. Cross, *Polyhedron* **1995**, *13−14*, 1765−1770. − [4f] W.-Y. Wong, W.-T. Wong, K.-K. Cheung, *J. Chem. Soc., Dalton Trans.* **1995**, 1379−1387. − [4g] B. J. Coe, J. P. Essex-Lopresti, J. A. Harris, S. Houbrechts, A. Persoons, *J. Chem. Soc., Chem. Commun.* **1997**, 1645−1646. − [4h] J. T. Lin, J. J. Wu, C.-S. Li, Y. S. Wen, K.-J. Lin, *Organometallics* **1996**, *15*, 5028−5034.

[5] [5a] M. M. Bhadhade, A. Das, J. C. Jeffery, J. A. McCleverty, J. A. Navas Badiola, M. D. Ward, *J. Chem. Soc., Dalton Trans.* **1995**, 2769−2777. − [5b] S. Sakanishi, D. A. Bardwell, S. Couchman, J. C. Jeffery, J. A. McCleverty, M. D. Ward, *J. Organomet. Chem.* **1997**, *528*, 35−45. − [5c] J. Mata, S. Uriel, E. Peris, R. Llusar, S. Houbrechts, A. Persoons, *J. Organomet. Chem.* **1998**, *562*, 197−202. − [5d] I. S. Lee, S. S. Lee, Y. K. Chung, D. Kim, N. W. Song, *Inorg. Chim. Acta* **1998**, *279*, 243−248.

[6] [6a] V. W.-W. Yam, K.-Z. Wang, C.-R. Wang, Y. Yang, K.-K. Cheung, *Organometallics* **1998**, *17*, 2440−2446. − [6b] V. W.-W. Yam, V. C.-Y. Lau, K.-Z. Wang, K.-K. Cheung, C.-H. Huang, *J. Mater. Chem.* **1998**, *8*, 89−97. − [6c] J. T. Lin, S.-S. Sun, J. J. Wu, Y.-C. Liaw, K.-J. Lin, *J. Organomet. Chem.* **1996**, *517*, 217−226. − [6d] J. C. Calabrese, W. Tam, *Chem. Phys. Lett.* **1987**, *133*, 244−245. − [6e] M. Bourgault, K. Baum, H. Le Bozec, G. Pucetti, I. Ledoux, J. Zyss, *New. J. Chem.* **1998**, 517−522.

[7] [7a] B. D. Rossenaar, E. Lindsay, D. J. Stufkens, A. Vlcek, Jr., *Inorg. Chim. Acta* **1996**, *250*, 5−14. − [7b] E. Schutte, J. B. Helms, S. M. Woessner, J. Bowen, B. P. Sullivan, *Inorg. Chem.* **1998**, *37*, 2618−2619. − [7c] G. F. Strouse, J. R. Schoonover, R. Duesing, T. J. Meyer, *Inorg. Chem.* **1995**, *34*, 2725−2734. − [7d] A. P. Zipp, L. Sacksteder, J. Streich, A. Cook, J. N. Demas, B. A. DeGraff, *Inorg. Chem.* **1993**, *32*, 5629−5632. − [7e] L. Wallace, D. P. Rillema, *Inorg. Chem.* **1993**, *32*, 3836−3843. − [7f] L. Sacksteder, M. Lee, J. N. Demas, B. A. DeGraff, *J. Am. Chem. Soc.* **1993**, *115*, 8230−8238.

[8] [8a] A. I. Baba, J. R. Shaw, J. A. Simon, R. P. Thummel, R. H. Schmehl, *Coord. Chem. Rev.* **1998**, *171*, 43−59. − [8b] B. D. Rossenaar, D. J. Stufkens, A. Vlcek, *Inorg. Chem.* **1996**, *35*, 2902−2909. − [8c] R. Ziessel, A. Juris, M. Venturi, *J. Chem. Soc., Chem. Commun.* **1997**, 1593−1594. − [8d] H. Hori, F. P. A. Johnson, K. Koike, K. Takeuchi, T. Ibusuki, O. Ishitani, *J. Chem. Soc., Dalton Trans.* **1997**, 1019−1023. − [8e] F. P. A. Johnson, M. W. George, F. Hartl, J. J. Turner, *Organometallics* **1996**, *15*, 3374−3387. − [8f] M. Wrighton, D. L. Morse, *J. Am. Chem. Soc.* **1974**, *96*, 998−1003; P. J. Giordano, S. M. Fredericks, M. S. Wrighton, D. L. Morse, *J. Am. Chem Soc.* **1978**, *100*, 2257−2259; C.-F. Shu, M. S. Wrighton, *Inorg. Chem.* **1988**, *27*, 4326−4329.

[9] A. Fehn, O. Briel, W. Beck, *Chem. Ber.* **1997**, *130*, 1467−1473; O. Briel, A. Fehn, K. Polborn, W. Beck, *Polyhedron*, in press; O. Briel, A. Fehn, W. Beck, *J. Organomet. Chem.*, in press.

[10] [10a] P. W. Jolly, F. G. A. Stone, *J. Chem. Soc.* **1965**, 5259−5261. − [10b] P. Braunstein, L. Douce, F. Balegroune, D. Grandjean, D. Bayeul, Y. Dusausoy, P. Zanello, *New J. Chem.* **1992**, *16*, 925−929. − [10c] T. M. Miller, K. J. Ahmed, M. S. Wrighton, *Inorg. Chem.* **1989**, *28*, 2347−2355. − [10d] P. J. Giordano, M. S. Wrighton, *J. Am. Chem. Soc.* **1979**, *101*, 2888−2997. − [10e] F. Zingales, U. Sartorelli, F. Canziani, M. Raveglia, *Inorg. Chem.* **1966**, *6*, 154−157; M. Schweiger, W. Beck, *Z. Anorg. Allg. Chem.* **1991**, *595*, 203−210.

[11] W. Hieber, L. Schuster, *Z. Anorg. Allg. Chem.* **1956**, *287*, 214−222.

[12] F. Effenberger, C.-P. Niesert, *Synthesis* **1992**, 1137−1144.

[13] F. Effenberger, H. Schlosser, *Synthesis* **1990**, 1085−1094.

[14] A. Salma-Schwok, M. Blanchard-Desce, J.-M. Lehn, *J. Phys. Chem.* **1990**, *94*, 3894−3902.

[15] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-112120 (**4a**) and -111966 (**5a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336033; E-mail: deposit@ccdc.cam.ac.uk].
[16] *PLATON 98* (ver. 170698, by A. Spek, L. Farrugia).
[17] K. Clays, A. Persoons, *Phys. Rev. Lett.* **1991**, *66*, 2980−2987.
[18] [18a] S. Stadler, G. Bourhill, C. Bräuchle, *J. Phys. Chem.* **1996**, *100*, 6927−6934. − [18b] M. C. Flipse, R. de Jonge, R. H. Woudenberg, A. W. Marsman, C. A. von Walree, L. W. Jenneskens, *Chem. Phys. Lett.* **1995**, *245*, 297−303.
[19] S. Stadler, R. Dietrich, G. Bourhill, C. Bräuchle, *Opt. Lett.* **1996**, *21*, 251.
[20] C. Lambert, E. Schmälzlin, K. Meerholz, C. Bräuchle, *Chem. Eur. J.* **1998**, *4*, 512−521.
[21] E. Schmälzlin, K. Meerholz, S. Stadler, C. Bräuchle, H. Patzelt, D. Oesterhelt, *Chem. Phys. Lett.* **1997**, *280*, 551−555.
[22] [22a] J. L. Oudar, J. Zyss, *Phys. Rev.* **1982**, *A26*, 2016. − [22b] J. Zyss, J. L. Oudar, *Phys. Rev.* **1982**, *A26*, 2028.
[23] D. R. Kanis, M. A. Ratner, T. J. Marks, *Chem. Rev.* **1994**, *94*, 195−242.
[24] D. R. Kanis, M. A. Ratner, T. J. Marks, *J. Am. Chem. Soc.* **1992**, *114*, 10338−10357.
[25] [25a] S. Stadler, G. Bourhill, C. Bräuchle, *Proc. SPIE* **1996**, *2852*, 142. − [25b] S. Stadler, Ph. D. Thesis, Ludwig-Maximilians-Universität München, **1996**.
[26] J. L. Oudar, D. S. Chemla, *J. Chem. Phys.* **1977**, *66*, 2664−2668.
[27] W. P. Fehlhammer, W. A. Herrmann, K. Öfele, *Handbuch der präparativen Anorganischen Chemie* (Ed.: G. Brauer), 3rd. ed., Enke-Verlag, Stuttgart, **1981**.

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