DOI: 10.1002/ejic.200500955

Dipolar Organoiron Pyranylideneacetaldehyde Hydrazone Complexes: Synthesis, Characterization, Crystal Structure, Linear and Nonlinear Optical Properties

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Keywords: Donor–acceptor systems / Iron / Pyranylideneacetaldehyde / Nonlinear optics / Sandwich complexes

New cationic organoiron(II) pyranylideneacetaldehyde hydrazone complexes were prepared in high yields through condensation reactions of the organometallic hydrazine precursor $[CpFe(\eta^6\text{-}p\text{-}MeC_6H_4NHNH_2)]^+PF_6^-$ with differently substituted α- and γ-pyranylideneacetaldehydes. The mononuclear hydrazones were stereoselectively obtained as their (*E*) isomers about the N=C double bond. All the new compounds were thoroughly characterized by a combination of elemental analysis and spectroscopic techniques (^1H and ^{13}C NMR, IR, and UV/Vis), and by a single-crystal X-ray diffraction analysis of the 2-*t*Bu-chromene derivative **5**. The spectroscopic data suggest that these complexes have a partial pyrylium character due to the electron-accepting ability of the cationic organometallic fragment and to the electron-releasing properties of the methylenepyran-based donor. The crystal structure of **5** shows that the η^6-coordinated tolyl ring and the pyran ring are coplanar (dihedral angle 3.2°), a favorable situation that allows conjugation between the intracyclic oxygen atom and the cationic iron center through the entire hydrazone backbone. Compounds **4**–**6** are strongly polarized D–π–A systems that exhibit solvatochromic properties, low-lying intramolecular charge-transfer bands in their electronic absorption spectra, and enhanced second-order NLO properties ($\mu\beta$), as measured by the EFISH technique at 1.907 μm.

Introduction

The electron-donating and -accepting capabilities of organoligand–metal fragments have been successfully applied in the design and development of highly efficient dipolar chromophores in order to achieve high second-order nonlinear optical (NLO) responses.[1] This has led to a growing development of organometallic push–pull rod-shaped oligomers, mainly ferrocene-based donor–acceptor materials,[2] and, in particular, those incorporating a cationic acceptor subunit have demonstrated good second-harmonic generation (SHG) efficiency.[3,4] The potentially attractive NLO properties of ferrocene-based complexes are coupled with good thermal and photochemical stability,[5] excellent donor capability,[6] and redox-switching abilities.[7] On the other hand, the cationic isolobal electron-acceptor counterparts of ferrocene, namely the robust mixed-sandwich derivatives $[CpFe(\eta^6\text{-arene})]^+$,[8] have also been the subject of intense investigations within the domains of arene functionalization,[9] electron transfer and redox processes,[10] photochemistry,[11] and, in one case, as an organometallic chromophore to achieve second-order NLO responses.[12] Along this line, some of us have thoroughly investigated organometallic dipolar chromophores in which the electron-withdrawing cationic organometallic fragment $[CpFe(\eta^6\text{-arene})]^+$ (A) is connected to a potent donating organic[13] or ferrocenyl[14] subunit (D) by an asymmetric –NR–N=CR– (R = H, Me) hydrazone conjugated bridge (π), and have shown that in such D–π–A-type systems an effective electron delocalization or electronic interaction between the electron-donating and -accepting termini takes place through the entire hydrazone skeleton. Others of us have recently reported on donor–acceptor pentacarbonylmetal methylenepyran Fischer-type methoxycarbene complexes (metal = Cr, W).[15]

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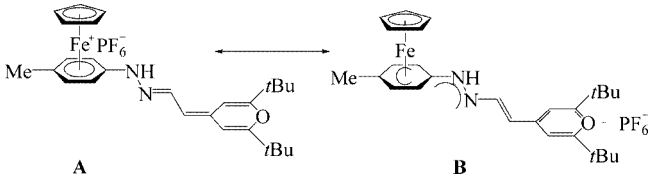
These complexes, which have a pyrylium character owing to the π-electron-accepting ability of the carbene fragment and to the electron-releasing properties of the methylenepyran core, exhibit a large first hyperpolarisability $\mu\beta$, as measured by the electric-field-induced-second-harmonic (EFISH) generation technique.[16] These facts, and the results of a recent theoretical study, which focused attention on the importance of pyrylium–methylenepyran duality for NLO purposes,[17] prompted us to investigate new push–pull structures that combine an ionic iron acceptor with a methylenepyran group, which should act as electron donors because of the aromaticity gain upon electron delocalization of the heterocyclic oxygen lone-pair (Scheme 1).



Scheme 1. Resonance forms for the methylenepyran–pyrylium mesomers.

For this purpose, we have chosen three archetypal pyranylideneacetaldehyde-type structures where the pyranyl ring is substituted at positions 2,6 (**1**) and 4,6 (**3**), or fused with a six-membered ring (**2**), as depicted in Figure 1. The present contribution reports on the preparation and full spectroscopic characterization (IR, UV/Vis, ^{1}H, and ^{13}C NMR) of

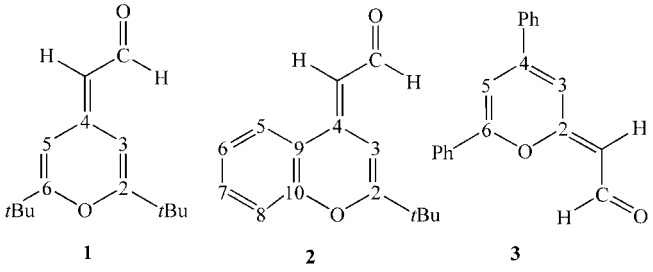
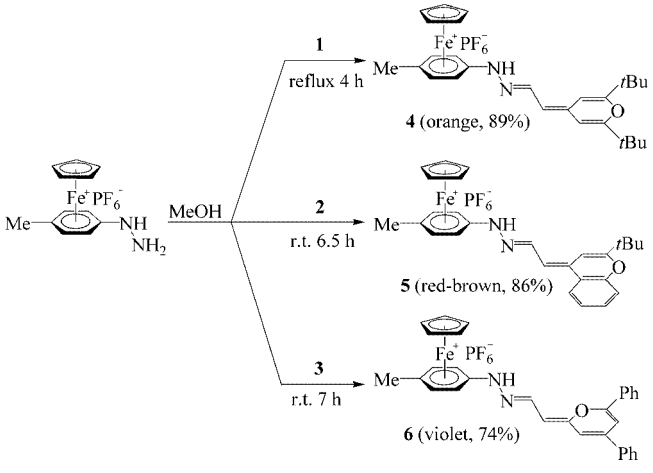


Figure 1. Substituted α- and γ-pyranylideneacetaldehydes used in this work and their labelling scheme.



Scheme 2. Preparation of complexes **4**–**6**.

the resulting new mononuclear complexes **4**–**6**, in which a substituted α- or γ-methylenepyran fragment is attached to a [CpFe(η^6-*p*-tolylhydrazone)]$^+$ moiety (the structural formulae of complexes **4**–**6** are given in Scheme 2), the crystal and molecular structures of the benzopyran derivative **5** to gain insight into influence of the electron-withdrawing organometallic group on the geometry of D–π–A systems, and finally the second-order NLO properties of these three compounds by measuring the second-harmonic generation efficiency, $\mu\beta$, by the EFISH generation technique.

Results and Discussion

Syntheses and Spectroscopic Characterization

The new mononuclear chromophores **4**–**6** were successfully prepared by a condensation reaction of the ionic organometallic hydrazine precursor [CpFe(η^6-*p*-MeC$_6$H$_4$-NHNH$_2$)]$^+$PF$_6^-$ with the γ-pyranylideneacetaldehydes **1** and **2**, and the α-pyranylideneacetaldehyde **3** (see Figure 1), respectively, in ethanol solution (Scheme 2). The three complexes were isolated as orange (**4**), reddish-brown (**5**), and dark-violet (**6**) microcrystalline solids, in excellent yields of between 74 and 89% after recrystallization from a dichloromethane/diethyl ether mixture. All three mononuclear species display good thermal stability in air. Compound **6** has the same intense dark color as the methylenepyran Fischer-type carbene derivatives.[15a] Complexes **4**–**6** exhibit a good solubility in common polar organic solvents, but are insoluble in diethyl ether, hydrocarbons, and water. Their structures were inferred from satisfactory elemental analysis, ^{1}H and ^{13}C NMR, IR, and UV/Vis spectroscopy, and additionally, in the case of complex **5**, by an X-ray diffraction analysis (vide infra).

The solid-state IR spectra of compounds **4**–**6** exhibit the three typical features we have previously observed for related mononuclear organometallic hydrazones.[13] These are: (i) a weak to medium ν(N–H) stretching vibration at about 3320 cm^{-1}, (ii) a sharp intense band at about 1565 cm^{-1} attributed to the asymmetric ν(C=N) stretching vibration, and (iii) a splitting of the very strong ν(PF$_6$) band at about 845 and 828 cm^{-1} and a sharp and strong δ(P–F) band at around 557 cm^{-1}. In addition, the IR spectra show weak bands in the 1640–1590 cm^{-1} region assigned to the ν(C=C) stretching mode of the methylenepyran fragment.[18]

Interestingly, the organoiron hydrazones **4**–**6** are formed stereoselectively as the sterically less hindered (*E*) isomer (about the N=C double bond), as indicated by the unique set of signals in their ^{1}H and ^{13}C NMR spectra (see Exp. Sect.), and definitively assigned from the structural analysis of complex **5** (see below). In the ^{1}H NMR spectra of all the compounds, the sandwich moiety [CpFe(η^6-*p*-MeC$_6$H$_4$–)]$^+$ is clearly identified by the characteristic sharp singlets of the Cp and *p*-methyl tolyl proton resonances observed at $\delta \approx 5.00$ and 2.48 ppm, respectively. In addition, the upfield-shifted signals of the aromatic protons of the coordinated C$_6$ ring ($\delta \approx 6.20$ ppm), the doublet (δ = 8.15–8.37, $^3J_{H,H}$

≈ 10 Hz) assigned to the deshielded imine proton, and the low-field position (δ = 9.21–9.48 ppm) of the acidic benzylic N–H signal appear in their expected regions.[13,14] On the other hand, the vinylic 3-H resonance of the methylenepyran core (see Figure 1 for labelling scheme), which is common to the three compounds under investigation, appears as a doublet ($^4J_{H,H}$ = 2.0 Hz) for **4** and as a singlet for **5** and **6**, at δ = 6.24, 6.38, and 6.85, respectively. Like the 3-H signal, 5-H also appears as a singlet, which strongly indicates that compound **6** is isolated as a single isomer about the C-2=C(exocyclic) double bond, even though the starting pyranic aldehyde **3** is a mixture of (*Z*) and (*E*) isomers.[19] However, the formation of a minor isomer, the population of which is too low to be detected by 300 MHz NMR spectroscopy, cannot be ruled out. It should be noted that the ^{1}H NMR spectrum was recorded after recrystallization of the compound and that both isomers have indeed been spectroscopically characterized for a related Fischer-type carbene complex derived from the same mixture of aldehydes.[20]

Consistent with the proposed structure, the ^{13}C NMR spectra of complexes **4**–**6** exhibit the expected characteristic sharp resonances for the C_5 ring and the *p*-Me substituent of the sandwich fragments at $\delta \approx$ 76 and 19 ppm, respectively. The two carbon atoms linked to a nitrogen atom appear as broad signals at lower field, with the imine carbon signal at $\delta \approx$ 143 ppm and the coordinated C_{ipso} signal at $\delta \approx$ 120 ppm. This latter value suggests a partial C–N multiple-bond character, in agreement with the findings of the crystallographic study (see below). The carbon signals of the coordinated C_6 ring are shifted upfield relative to those of the free benzo and phenyl rings of compounds **5** and **6**, respectively. In addition, the three types of methylenepyran frameworks exhibit five resonances assigned to five types of skeletal carbon atoms. Molecule **4**, for example, shows the quaternary C-2, C-4, and C-6 carbon atoms as peaks at δ = 164.67, 134.86, and 163.91 ppm, respectively, with the vinylic C-3 and C-5 signals at δ = 98.04 and 104.35 ppm, respectively, and the exocyclic carbon signal at δ = 106.45 ppm. Moreover, the *tert*-butyl carbon atoms show up as two sets of two closely spaced singlets at δ = 27.09 and 27.13 and 35.16 and 35.47 ppm for the methyl and the quaternary carbon atoms, respectively.

The ^{1}H NMR chemical shift of the 3-H proton has previously been taken as a criterion for the degree of pyrylium character.[21] In general, as the contribution of the pyrylium resonance form contributes more to the ground-state structure of a compound, the chemical shift of the signal of the hydrogen atom in the 3-position tends to shift downfield. Thus, from comparison of the observed 3-H chemical-shift values of compounds **4**–**6** with those, more deshielded (see Exp. Sect. and Tables S1 and S2), of unsaturated Fischer-type carbene complexes bearing an α- and γ-methylenepyran or γ-methylenebenzopyran group, namely [$(OC)_5$-W=C(OMe)$(CH=CH)_n$CH=(pyran)] (n = 0–2),[15,20] it seems that the sandwich molecules **4**–**6** have a lower pyrylium or benzopyrylium character. This trend is also confirmed by the ^{13}C NMR spectroscopic data (Tables S1 and S2). This would suggest that the [CpFe(η^6-*p*-tolyl)]$^+$ moieties have a lower electron-withdrawing ability than the [$(OC)_5$W=C(OMe)] carbene fragment. However, a decrease of the electronic transmission between the ends of the molecule through the NH–N=CH spacer should also be considered.

X-ray Crystal Structure

The molecular structure of the cationic organometallic moiety **5**$^+$, along with the atom-labelling scheme, is presented in Figure 2. Selected bond lengths and angles are listed in Table 1, and details of data collection and refinement are provided in the Exp. Sect. Compound **5** crystallizes in the monoclinic space group $P2_1/n$ with four molecules in the unit cell. In the mixed-sandwich fragment, the iron atom is coordinated to the cyclopentadienyl ring at a ring centroid–iron distance of 1.654 Å, and to the tolyl ring at a ring centroid–iron distance of 1.554 Å. The carbocyclic rings coordinated to the iron center are essentially parallel to one another (deviation of 4.10°), which gives rise to a ring centroid–iron–ring centroid angle of 177.2°. These metrical parameters, together with those listed in Table 1, are similar to those we have already reported for related mononuclear hydrazone complexes,[13] and are typical of an η^5-Fe^{II}-η^6 metallocene-type coordination.[22] More interestingly, the coordinated tolyl ring and the pyran ring, as well as the two six-membered rings of the benzopyran subunit, are coplanar (dihedral angles 3.2° and 1.4°, respectively), a situation which allows conjugation between the intracyclic oxygen atom and the cationic iron center through the entire hydrazone backbone.

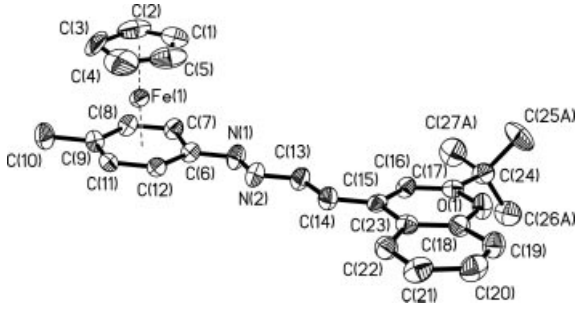


Figure 2. Molecular structure and atom-numbering scheme for **5**·CH_2Cl_2. Hydrogen atoms, the PF_6^- counteranion, one of the disordered positions of the *tert*-butyl substituent, and the solvent molecule have been omitted for clarity. Displacement ellipsoids are at the 30% probability level.

A close inspection of Table 1 reveals characteristic structural features provoked by the electron-withdrawing CpFe$^+$ moiety on the η^6-coordinated arylhydrazone ligand. Thus, the Fe(1)–C(6) bond [2.198(6) Å] is longer than the mean value of the other five Fe(1)–C(C_6 ring) bonds (2.048 Å). This elongation (0.15 Å) is a consequence of a partial delocalization of the benzylic nitrogen electron lone-pair toward the cationic mixed-sandwich moiety, and is reflected by (i) a depyramidalization of the N(1) atom, with idealized bond angles at this sp^2-hybridized nitrogen atom [C(6)–N(1)–

Table 1. Selected bond lengths [Å] and angles [°] for **5**·CH_2Cl_2.

Fe(1)–C(6)	2.198(6)	C(6)–N(1)	1.342(7)
Fe(1)–C(7)	2.087(6)	N(1)–N(2)	1.357(7)
Fe(1)–C(8)	2.044(6)	N(2)–C(13)	1.280(7)
Fe(1)–C(9)	2.065(6)	C(13)–C(14)	1.425(8)
Fe(1)–C(11)	2.040(6)	C(14)–C(15)	1.354(8)
Fe(1)–C(12)	2.083(6)	C(15)–C(16)	1.446(8)
Fe(1)–C(1–5)av.	2.061	C(15)–C(23)	1.455(8)
O(1)–C(17)	1.372(7)	C(16)–C(17)	1.309(8)
O(1)–C(18)	1.383(7)	C(18)–C(23)	1.381(8)
C(6)–C(7)	1.410(8)	C(6)–C(12)	1.410(8)
C(7)–C(8)	1.398(8)	C(8)-C(9)	1.366(8)
C(9)–C(11)	1.395(8)	C(11)–C(12)	1.389(8)
C(6)–N(1)–N(2)	120.7(5)	N(1)–N(2)–C(13)	115.7(6)
N(2)–C(13)–C(14)	121.9(6)	C(13)–C(14)–C(15)	126.2(6)
C(14)–C(15)–C(16)	122.7(6)	C(14)–C(15)–C(23)	123.3(6)
O(1)–C(17)–C(16)	122.4(6)	O(1)–C(18)–C(23)	122.0(5)
C(17)–O(1)–C(18)	118.3(5)		

N(2) = 120.7(5)°], (ii) a C(6)–N(1) bond length of 1.342(7) Å, which is intermediate between a single and a double carbon–nitrogen bond,[22] and (iii) a very weak cyclohexadienyl character of the coordinated phenyl ring, with a folding dihedral angle of 3.3° about the C(7)–C(12) axis. Moreover, this cyclohexadienyl character is exemplified by two long C(6)–C(7) and C(6)–C(12) distances of 1.410(8) Å, while the remaining four other C–C bonds are significantly shorter and fall in the interval 1.366(8)–1.398(8) Å (Table 1), thus emphasizing the weight of the iminocyclohexadienyl mesomeric form (Scheme 1).[8a,13a] On the benzomethylenepyran side, we observe that the exocyclic bond C(14)–C(15) is 1.354(8) Å long, which suggests a weak benzopyrylium character. In fact, for comparison, the exocyclic bond lengths 1.393(8),[15c] 1.389(10),[23] and 1.40(1) Å[15a] measured for γ-methylenepyran Fischer-type carbene complexes have more single-bond character, in accordance with a large conjugation between the intracyclic oxygen lone-pair and the strongly electron-withdrawing carbene fragment. It is worth remarking that these findings fully corroborate the observed NMR spectroscopic data (see above). In addition, it should be noted that NMR studies have shown that the presence of a fused benzene ring decreases the electron-donating ability of the pyran heterocycle.[16]

Linear and Nonlinear Optical Properties

The UV/Vis spectra of the three complexes under study are similar in that the spectra consist of two intense and broad absorption bands in the visible region. As expected from its dark-violet color, the low-energy absorption band of compound **6** is red-shifted relative to those of **4** and **5**. The origin of the high-energy absorption band in the range 300–380 nm is assumed to be an intra-ligand charge-transfer (ILCT) transition, and the low-energy absorption band in the region 380–550 nm is assigned to a metal-to-ligand charge-transfer (MLCT) transition.[12,13b,24] Deconvolution of the spectra with Gaussian curves gives rise to three or four absorption bands for these two CT transitions (Figure 3 and Table 2). The data of Table 2 indicate that the linear-optical properties (i.e. the energies and intensities of the absorption bands corresponding to the above-mentioned CT transitions) of **4**–**6** are in agreement with those reported for other D–π–A systems having the same $[CpFe(\eta^6\text{-arene})]^+$ fragment as electron acceptor linked to an organic electron-donating group.[12,13b] The broadening of the low-energy band is probably the result of the overlap of broad d–d visible bands of the $[CpFe(\eta^6\text{-arene})]^+$ fragment.[10a,11,25] For compounds **4** and **6**, the two characteristic CT bands exhibit bathochromic shifts when the solvent polarity is increased, thus indicating increased polarity in the excited state. The solvatochromism is much larger for **4** than for **6**, whereas the solvent influence is negligible for compound **5**. Nevertheless, solvatochromic effects can hint at the magnitude of the expected nonlinear optical properties, since they reflect the polarizability of a chromophore.[26]

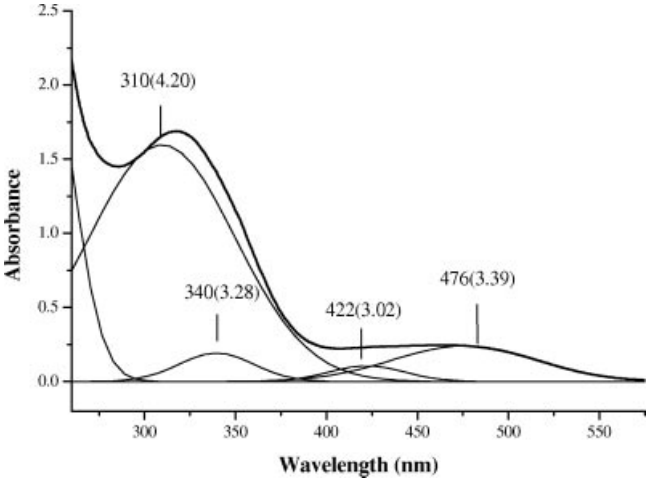


Figure 3. Deconvoluted UV/Vis spectrum of compound **5** recorded in CH_2Cl_2. The first number is the wavelength (λ) and the value in parentheses is logε (see Table 2).

Table 2. Electronic absorption and EFISH data.

Compound	λ [nm] (logε) CH_2Cl_2	λ [nm] (logε) DMSO	$\Delta\lambda$ [nm]	$\mu\beta$ ($\times 10^{-48}$) [esu] CH_2Cl_2
4	369 (4.48)	382 (4.55)	+23	154 ± 20
	396 (3.80)	452(3.27)	+56	
	451 (4.07)	486 (3.69)	+35	
5	310 (4.20)	309 (4.11)	–1	149 ± 10
	340 (3.28)	348 (3.66)	+8	
	422 (3.02)	415 (2.92)	–7	
	476 (3.39)	469 (3.34)	–7	
6	369 (4.17)	374 (4.05)	+5	83 ± 40
	453 (3.86)	483 (3.65)	+30	
	486 (3.62)	498 (2.94)	+12	
	523 (4.05)	531 (3.75)	+8	

The second-order NLO properties of compounds **4**–**6** were investigated using the electric-field-induced second-harmonic (EFISH) generation technique, which provides information about the scalar product, $\mu\beta$, of the vectorial part of the first hyperpolarisability tensor, β, and the dipole

moment vector, μ.[27] Compounds **4**–**6** exhibit reasonable $\mu\beta$ values (Table 2), although they remain significantly weaker than those reported for organic hydrazone molecules ($\mu\beta$ = $100–640 \times 10^{-48}$ esu).[28] However, these compounds contain a longer conjugated moiety containing two phenyl rings and are substituted with a very strong acceptor group (NO_2) and a good alkoxy donor substituent. The $\mu\beta$ values reported in the present work are comparable to the values of 74×10^{-48} and 310×10^{-48} esu determined for two Fischer-type methoxycarbene complexes bearing an identical methylenepyran donor fragment to that in **4** and **5** (Table S3).[20] This clearly indicates that the hydrazone and the methylenepyran fragments act as a good π-conjugated spacer and electron donor, respectively, and that the $[CpFe(\eta^6\text{-arene})]^+$ group, which can be functionalized by easy, $CpFe^+$-induced transformations at the coordinated arene ring,[9] could be used as a strong electron-acceptor substituent in molecular engineering for quadratic NLO.[29] Finally, it is interesting to note that the $\mu\beta$ values of **4** and **5** are practically identical, whereas that of **6** is only half as large. This behavior can be attributed to the fact that the spacer is located at the α-position of the electron-donating pyran ring in compound **6**, whereas in **4** and **5** it is located at the γ-position. As a consequence, the internal charge transfer responsible for the β value should be smaller and the $\mu\beta$ scalar product is also reduced by the fact that μ and β are probably not parallel to one another.

Concluding Remarks

In summary, three new organometallic π-conjugated push-pull chromophores have been prepared in high yields by condensation reactions of cyclopentadienyliron(II)-complexed *p*-tolylhydrazines with differently substituted archetypal pyranylideneacetaldehydes. Their original design combines an organometallic acceptor group, namely the cationic mixed-sandwich fragment $[CpFe(\eta^6\text{-}p\text{-}MeC_6H_4)]^+$, associated with an α- and γ-methylenepyran donor through the asymmetric hydrazone spacer NH–N=CH. Single-crystal X-ray diffraction analysis of compound **5** has shown a favorable electronic structure resulting from the coplanarity of the coordinated tolyl ring and the pyran ring, as well as the two six-membered rings of the benzopyran subunit, thus allowing conjugation between the intracyclic oxygen atom and the cationic iron center through the entire hydrazone backbone. As such, the organometallic hydrazones described in this work can be defined as type-I non-rod-shaped dipolar chromophores,[30] and have been proven to favor electronic delocalization along the conjugated chain. Finally, compounds **4**–**6** are strongly polarized D–π–A systems that exhibit solvatochromic properties and have low-lying intramolecular charge-transfer bands in their electronic absorption spectra and enhanced second-order NLO properties ($\mu\beta$). Theoretical computations are obviously required before discussing the electronic structures of the complexes and the electronic transitions giving rise to the NLO properties in more detail; these are currently underway and will be published in due course.

Experimental Section

General Procedures: Unless otherwise noted, all reactions and manipulations were performed at room temperature under dinitrogen using standard Schlenk-line techniques. Solid IR spectra were obtained from KBr disks with a Perkin–Elmer Model Spectrum One FT IR spectrophotometer. Electronic spectra were collected with a Spectronic Genesys 2 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded with a Bruker Advance DPX 300, 400 Digital or a DPX 500 spectrometer, as noted within the text. All NMR spectra are reported in ppm (δ) relative to tetramethylsilane, with the residual solvent proton resonance and carbon resonances used as internal standards. Coupling constants are reported in Hz. ^1H and ^{13}C NMR chemical shift assignments are supported by data obtained from ^1H-^1H COSY, ^1H-^{13}C HMQC, and ^1H-^{13}C HMBC NMR experiments, and are given according to the numbering scheme of Figure 1. Melting points were determined in evacuated capillaries and are not corrected. Microanalytical data were obtained by the Institut de Chimie de Rennes Microanalysis Service with a Thermo-FINNIGAN Flash EA 1112 CHNS/O analyzer.

Materials: Solvents were dried and distilled under dinitrogen by standard methods prior to use. Reagents were purchased from commercial suppliers and used without further purification. The organometallic hydrazine precursor $[CpFe(\eta^6\text{-}p\text{-}CH_3C_6H_4NHNH_2)]^+\text{-}PF_6^-$ was synthesized as described previously,[13e] and the γ-pyranylideneacetaldehydes **1**–**3** (see Figure 1) were also prepared according to published procedures.[19,31]

(η^5-Cyclopentadienyl)[(2,6-di-*tert*-butyl-4*H*-pyran-4-ylidene)acetaldehyde (η^6-*p*-tolyl)hydrazone]iron Hexafluorophosphate (4): A Schlenk tube was charged with a magnetic stirring bar, $[CpFe(\eta^6\text{-}p\text{-}CH_3C_6H_4NHNH_2)]^+PF_6^-$ (105 mg, 0.271 mmol), (2,6-di-*tert*-butyl-4*H*-pyran-4-ylidene)acetaldehyde (**1**; 63.0 mg, 0.269 mmol), and ethanol (15 mL). The reaction mixture was refluxed for 4 h, then cooled to room temperature and stored at –30 °C overnight. The orange precipitate was filtered off, washed with diethyl ether (2×5 mL), and dried under vacuum. It was then dissolved in a minimum amount of CH_2Cl_2 and the solution was layered with an equivalent volume of diethyl ether. Compound **4** was isolated as an orange, microcrystalline solid. Yield: 145 mg (89%). M.p. 212 °C (dec.). $C_{27}H_{35}F_6FeN_2OP$ (604.39): calcd. C 53.66, H 5.84, N 4.64; found C 53.53, H 6.02, N 4.85. IR (KBr pellet): $\tilde{\nu}$ = 3319 (m) ν(N–H); 3109 (vw), 3080 (vw), 2964 (m), 2928 (w), 2904 (w), 2870 (w) ν(C–H); 1668 (s), 1609 (m), 1588 (s) ν(C=C); 1570 (s) ν(C=N); 1501 (m) ν(C–O); 840 (vs), 826 (vs) ν(PF_6); 555 (s) δ(P–F) cm^{-1}. ^1H NMR (400 MHz, CD_3COCD_3, 25 °C): δ = 1.24, 1.26 [2 × s, 2 × 9 H, $C(CH_3)_3$], 2.47 (s, 3 H, $CH_3C_6H_4$), 4.97 (s, 5 H, Cp), 5.54 (d, $^3J_{H,H}$ = 10.4 Hz, 1 H, N=CH–C*H*=), 5.90 (d, $^4J_{H,H}$ = 2.0 Hz, 1 H, 5-H), 6.14 (d, $^3J_{H,H}$ = 6.8 Hz, 2 H, C_6H_4), 6.18 (d, $^3J_{H,H}$ = 6.8 Hz, 2 H, C_6H_4), 6.24 (d, $^4J_{H,H}$ = 2.0 Hz, 1 H, 3-H), 8.15 (d, $^3J_{H,H}$ = 10.4 Hz, 1 H, N=C*H*–CH=), 9.21 (s, 1 H, NH) ppm. ^{13}C NMR (125 MHz, CD_3COCD_3, 25 °C): δ = 19.06 ($CH_3C_6H_4$); 27.09, 27.13 [$C(CH_3)_3$]; 35.16, 35.47 [$C(CH_3)_3$]; 67.73 (*o*-C_6H_4); 76.09 (Cp); 86.14 (*m*-C_6H_4); 96.73 (*p*-C_6H_4); 98.04 (C-3); 104.35 (C-5); 106.45 (N=CH–*C*H=); 120.07, 120.19 (C_{ipso} C_6H_4); 134.86 (C-4); 144.28 (N=*C*H–CH=); 163.91 (C-6); 164.67 (C-2) ppm.

[(2-*tert*-Butyl-4*H*-chromen-4-ylidene)acetaldehyde (η^6-*p*-tolyl)hydrazone](η^5-cyclopentadienyl)iron Hexafluorophosphate (5): A Schlenk tube was charged with a magnetic stirring bar, $[CpFe(\eta^6\text{-}p\text{-}CH_3C_6H_4NHNH_2)]^+PF_6^-$ (150 mg, 0.387 mmol), [(4*E*)-2-*tert*-butyl-4*H*-chromen-4-ylidene]acetaldehyde (**2**; 88.0 mg, 0.387 mmol), and ethanol (10 mL). The reaction mixture was stirred at room temperature for 6.5 h and was then stored at –30 °C overnight. Workup as described above yielded 200 mg (86%) of **5** as reddish-

brown crystals. A crystal from this crop was used for an X-ray structure determination. M.p. 239 °C (dec.). $C_{27}H_{29}F_6FeN_2OP$ (598.35): calcd. C 54.20, H 4.89, N 4.68; found C 54.35, H 4.92, N 4.76. IR (KBr pellet): $\tilde{\nu}$ = 3319 (w) ν(N–H); 3116 (vw), 2969 (w), 2920 (w), 2848 (vw) ν(C–H); 1648 (m), 1592 (m) ν(C=C); 1568 (m) ν(C=N); 1501 (m) ν(C–O); 847 (vs), 829 (vs) ν(PF_6); 558 (m) δ(P–F) cm^{-1}. ^1H NMR (400 MHz, CD_3COCD_3, 25 °C): δ = 1.31 [s, 9 H, $C(CH_3)_3$], 2.49 (s, 3 H, $CH_3C_6H_4$), 5.01 (s, 5 H, Cp), 6.25 (s, 4 H, C_6H_4), 6.38 (s, 1 H, 3-H), 6.47 (d, $^3J_{H,H}$ = 10.0 Hz, 1 H, N=CH–CH=), 7.23–7.33 (m, 2 H, 6-H, 8-H), 7.47 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, 5-H), 7.87 (d, $^3J_{H,H}$ = 7.7 Hz, 1 H, 7-H), 8.37 (d, $^3J_{H,H}$ = 10.0 Hz, 1 H, N=CH–CH=), 9.48 (s, 1 H, NH) ppm. ^{13}C NMR (125 MHz, CD_3COCD_3, 25 °C): δ = 19.10 ($CH_3C_6H_4$), 27.15 [$C(CH_3)_3$], 35.38 [$C(CH_3)_3$], 68.28 (*o*-C_6H_4), 76.29 (Cp), 86.26 (*m*-C_6H_4), 96.69 (C-3) 97.14 (*p*-C_6H_4), 107.38 (N=CH–CH=), 117.62 (C-8), 119.56 (C_{ipso} C_6H_4), 120.88 (C-4), 122.82 (C-5), 124.63 (C-6), 130.36 (C-7), 132.38 (C-10), 143.50 (N=CH–CH=), 151.97 (C-9), 162.61 (C-2) ppm.

(η⁵-Cyclopentadienyl)[(4,6-diphenyl-2*H*-pyran-2-ylidene)acetaldehyde (η⁶-*p*-tolyl)hydrazone]iron Hexafluorophosphate (6): A Schlenk tube was charged with a magnetic stirring bar, $[CpFe(\eta^6\text{-}p\text{-}CH_3C_6H_4NHNH_2)]^+PF_6^-$ (131 mg, 0.338 mmol), (2*Z*)-(4,6-diphenyl-2*H*-pyran-2-ylidene)acetaldehyde (**3**; 92.0 mg, 0.335 mmol), and ethanol (10 mL). The reaction mixture was stirred at room temperature for 7 h, and then stored at –30 °C overnight. Workup as above yielded 160 mg (74%) of **6** as a dark-violet powder. M.p. 254 °C (dec.). $C_{31}H_{27}F_6FeN_2OP$ (644.38): calcd. C 57.78, H 4.22, N 4.35; found C 57.63, H 4.41, N 4.08. IR (KBr pellet): $\tilde{\nu}$ = 3322 (w) ν(NH); 3058 (vw), 2964 (vw), 2920 (vw), 2848 (vw) ν(CH); 1639 (w), 1593 (w) ν(C=C); 1557 (m) ν(C=N); 1494 (m) ν(C–O); 842 (vs), 830 (vs) ν(PF_6); 558 (m) δ(P–F) cm^{-1}. ^1H NMR (300.08 MHz, CD_3COCD_3, 25 °C): δ = 2.46 (s, 3 H, $CH_3C_6H_4$), 4.98 (s, 5 H, Cp), 5.63 (d, $^3J_{H,H}$ = 10.0 Hz, 1 H, N=CH–CH=), 6.18 (s, 4 H, C_6H_4), 6.85 (s, 1 H, 3-H), 6.90 (s, 1 H, 5-H), 7.50 (m, 6 H, *m*- and *p*-H Ph at C-4 and C-6), 7.79 (d, $^3J_{H,H}$ = 7.0 Hz, 2 H, *o*-H Ph at C-4), 7.97 (d, $^3J_{H,H}$ = 7.9 Hz, 2 H, *o*-H Ph at C-6), 8.35 (d, $^3J_{H,H}$ = 10.0 Hz, 1 H, N=CH–CH=), 9.37 (s, 1 H, NH) ppm. ^{13}C NMR (75.46 MHz, CD_3COCD_3, 25 °C): δ = 19.07 ($CH_3C_6H_4$); 67.91 (*o*-C_6H_4); 76.20 (Cp); 86.18 (*m*-C_6H_4); 96.86 (*p*-C_6H_4); 99.35 (N=CH–CH=); 100.42 (C-5); 116.56 (C-3); 119.94 (C_{ipso} C_6H_4); 124.96 (*o*-C Ph at C-6); 125.65 (*o*-C Ph at C-4); 128.84, 128.95 (*m*-C Ph at C-4 and C-6); 129.18, 130.00 (*p*-C Ph at C-4 and C-6); 132.35 (C_{ipso} Ph at C-6); 136.20 (C_{ipso} Ph at C-4); 137.94 (C-4); 141.93 (N=CH–CH=); 155.34 (C-6); 156.36 (C-2) ppm.

X-ray Crystal-Structure Determination for 5·CH_2Cl_2: A red-orange plate of complex **5** with dimensions 0.18 × 0.11 × 0.10 mm was mounted on a glass fiber in a random orientation. Data collection was performed at room temperature with a Bruker Smart Apex diffractometer equipped with a two-dimensional CCD detector and a graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) source, with a nominal crystal-to-detector distance of 6.3 cm. A hemisphere of data was collected on the basis of four ω-scans runs (starting ω = 28°) at φ values of 0°, 120°, 240°, and 0°, with the detector at 2θ = 28°. In each of these runs, frames (600, 600, 600, and 50, respectively) were collected at 0.3° intervals and for 10 s per frame. The diffraction frames were integrated using the SAINT package,[32] and corrected for absorption with SADABS.[33] The positions of the heavy atoms were determined by direct methods, and successive difference electron density maps were produced with the SHEXTL 6.14 software package[34] to locate the remaining atoms. Refinement was performed by the full-matrix least-squares method based on F^2. The *tert*-butyl group was disordered over two positions, with an occupation multiplicity, μ, of 0.71/0.29. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in their calculated positions, assigned fixed isotropic thermal parameters, and allowed to ride on their respective parent atoms. $C_{27}H_{29}F_6FeN_2OP{\cdot}CH_2Cl_2$, M_r = 683.27, *a* = 10.1473(10), *b* = 18.7529(19), *c* = 16.2043(16) Å, β = 95.395(2)°, *V* = 3069.9(5) $Å^3$, monoclinic, $P2_1/n$, *Z* = 4, $D_{calcd.}$ = 1.478 $g cm^{-3}$, μ = 0.779 mm^{-1}, SADABS absorption correction applied, *F*(000) = 1400, *T* = 299(2) K, $2\theta_{max}$ = 28.08°, reflections collected/unique 25343/6916 [$I > 2\sigma(I)$], data/restraints/parameters 6916/126/459, R/R_{w2} [$I > 2\sigma(I)$] = 0.0923/0.1923, R/R_{w2} (all data) = 0.2394/0.2485, GOF = 0.962, $[\Delta\rho]_{min}/[\Delta\rho]_{max}$ = –0.346/0.476. CCDC-272776 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

EFISH Measurements: The principle of the EFISH technique has been described elsewhere.[35,36] In order to avoid reabsorption of the generated second harmonics, the data were recorded using 1.907-μm, 10-ns incident laser pulses produced by a hydrogen Raman shifter pumped by an Nd:YAG laser at 1.06 μm at a repetition rate of 10 Hz. The centrosymmetry of the solution was broken by dipolar orientation of the chromophores with a high-voltage pulse (8 kV applied on 3 mm during 1 μs) synchronized with the laser pulse. The compounds were dissolved in dichloromethane at various concentrations (10^{-3} to 10^{-2} M) and the solutions were introduced into the measurement cell where the high-voltage was applied during SHG measurements. NLO measurements were calibrated with pure dichloromethane as a reference. Acquisition and data processing were performed using a computerized home-made system.

Supporting Information (see footnote on the first page of this article): Tables S1 and S2 compare selected ^1H and ^{13}C NMR chemical shifts of compounds **4** and **5** with those of pentacarbonyltungsten methylenepyran Fischer-type methoxycarbene complexes, and Table S3 lists the EFISH data of these same pentacarbonyltungsten methylenepyran Fischer-type methoxycarbene complexes.

Acknowledgments

Financial support from the Fondo Nacional de Desarrollo Científico y Tecnológico [FONDECYT, Chile; grant no. 1010318 (D. C. and C. M.)], the CNRS-CONICYT agreement no. 16771 (C. M., D. C., and J.-R. H.), the Pontificia Universidad Católica de Valparaíso, the Université de Rennes 1, and the Ministère de l'Education Nationale de la Recherche et de la Technologie (MENRT, grant to N. F.) is gratefully acknowledged.

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Received: October 28, 2005
Published Online: February 21, 2006

