



Ferrocenyl and pyridyl methylenepyrans as potential precursors of organometallic electron-rich extended bipyrans: Synthesis, characterization and crystal structure

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ABSTRACT

Ferrocenyl and pyridyl methylenepyrans were obtained from a Wittig reaction between a pyran phosphorane and ferrocenyl or pyridyl-aldehydes. The nucleophilic nature of the exocyclic C–C bond allowed the formylation of these compounds by a Vilsmeier type reaction. All the new products were characterized by IR spectroscopy, ¹H and ¹³C NMR spectroscopy, mass spectroscopy and (or) elemental analysis. Electrochemistry of representative compounds **2**, **10** and **13** was undertaken.

In addition, a crystal structure of the ferrocenylpyranylidene aldehyde **5** was described, and the pyrylium character of this compound was specified.

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1. Introduction

In comparison with their isoelectronic dithiafulvene analogs [1], which have been extensively used as precursors of extended electron-rich tetrathiafulvenes [2], chalcogenomethylenepyrans of type **A** (Fig. 1) have received relatively scant attention [3]. Nevertheless the chalcogenomethylenepyrans core has been punctually implicated as molecular framework in various domains such as molecular material science [4], medicinal technology [5], liquid crystal field [6], nonlinear optic [7], molecular machine [8]. Particular attention has been devoted to electron-rich tetraphenylidithiopyranylidene **B** (Fig. 1), a useful precursor of organic one-dimensional conductor which displays interesting electrical and magnetic properties [4g,4p].

Curiously, despite the great potential of this class of molecules, organometallic chalcogenomethylenepyrans compounds are rare and their chemistry and physical properties remain to explore.

In addition to our interest in organometallic heterocyclic pyrylium salts as marker for biological molecules such as amino acids

and proteins [9], we have explored the chemistry of unsaturated chalcogenomethylenepyrans Fischer-type carbene complexes ($R' = (-CH=CH-)_n-C(OCH_3)W(CO)_5$, X = O, S, Te, $n = 1-3$, Fig. 1A) [10]. Simple and efficient routes to these complexes have been opened using pyrylium salts [10] or methylenechalcogenopyrans bearing an aldehyde function ($R' = CHO$, Fig. 1A) [11]. These push–pull organometallic molecules which have a noticeable pyrylium character have shown their efficiency as NLO phores [11]. They have been advantageously used as precursors of extended electron-rich bischalcogenopyrans (Fig. 1C) with interesting redox properties, because calculations have predicted molecular movement upon electrochemical oxidation [12]. More recently, we have shown that electro or chemical oxidative coupling of methylenepyrans substituted by a ferrocenyl group (Fig. 1A, R = Fc) allowed the reversible formation of diferrocenylbispyrylium salt via a ferrocenylpyran radical intermediate. Subsequent reversible deprotonation of this salt afforded an extended electron-rich diferrocenyl bischalcogenopyran bearing metallocenic group (s) which gave conjugated diferrocenyl bispyrylium salt by subsequent reversible oxidation [13]. Having in mind the development of the solid-state chemistry of extended electron-rich bichalcogenopyrans bearing metallocenic group (s) or group (s) having a coordination site, we chose to explore an access to various ferrocenyl methylenepyrans

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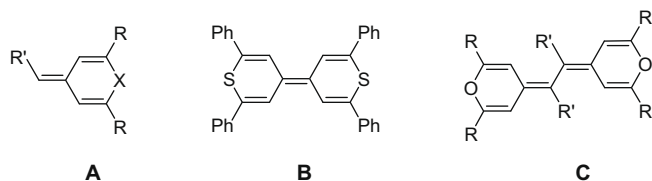


Fig. 1. Unsaturated chalcogenopyran compounds.

and pyridyl methylenepyran. Herein, we reported on the formation and characterization of such compounds using a Wittig synthetic methodology.

2. Results and discussion: synthesis of the pyran compounds

To synthesize new metallocenic heterocyclic compounds, we have chosen in first to exploit the reactivity in basic medium of the easy accessible 2,6-diphenyl-4*H*-pyran-4-yl triphenylphosphonium tetrafluoroborate salt [14] with ferrocenecarboxaldehyde and ferrocene-1,1'-dicarboxaldehyde [15]. At -78°C , addition of formylferrocene to a THF solution of the heterocyclic phosphorane, generated *in situ* by reaction of the phosphonium salt with *n*-BuLi (2.5 M solution in hexane), afforded the ferrocenyl methylenepyran **1** in good yield. A careful control of the temperature is required, since above -40°C (Scheme 1), the phosphorane reacted with the phosphonium salt and led to a bipyran [14c].

The analogous reaction involving ferrocene-1,1'-dicarboxaldehyde and two equivalents of the phosphorane have provided the ferrocenyl bispyran **2** (Fig. 2) in low yield (20%). Similarly, the ferrocenylmethylenepyran **3** (Fig. 2) was obtained from the mono-protected ferrocene-1,1'-dicarboxaldehyde [16] (39% yield). Subsequent acid hydrolysis of the acetal function led to the ferrocenylpyran aldehyde **4** in 57% yield (Fig. 2). A more expedient and efficient route to **4** consisted in using a 1/1 phosphonium salt/ferrocene-1,1'-dicarboxaldehyde ratio. Under these experimental conditions, small quantities of the bispyran **2** (Fig. 2) were also formed (<10%) and **4** was isolated upon chromatographic workup in an overall improved yield (45%).

Unsaturated Fischer-type carbene complexes would be accessible from a reaction involving the carbanion of $\text{Me}(\text{OMe})\text{C}=\text{W}(\text{CO})_5$ carbene and the formyl group of **4** [11]. Therefore, a route to electron-rich extended diferrocenyl bispyrans seems open, as it is well established that unsaturated Fischer carbenes undergo a self-dimerization reaction under Pd^{d} catalysis [17]. In addition, hybrid

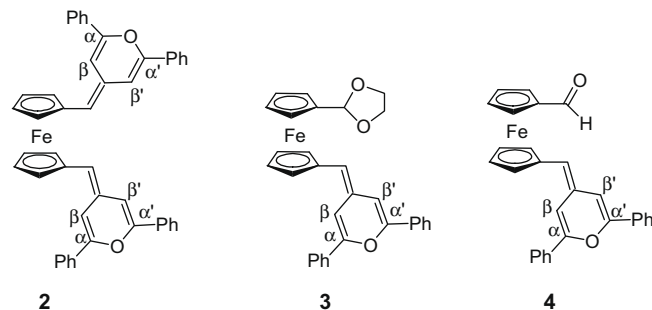


Fig. 2. New ferrocenylmethylenepyran and bismethylenepyran.

electron-rich molecular structures bearing both pyran and 1,3-dithiafulvene rings could also be reached from **4** and 1,3-dithiole Horner–Wittig reagent [1d].

For similar goal, introduction of a formyl group in **1** was achieved using a Vilsmeier-type formylation (oxalyl chloride–DMF reagent). The ferrocenylpyranaldehyde **5** was isolated in good yield (70%) (Scheme 2).

Incorporation of hydroxyl group in electron-rich TTF have attracted considerable interest with the aim of increasing the dimensionality of cation radical salts or charge transfer complexes by establishment of intermolecular hydrogen bond [18], therefore alcohol **6** was also synthesized in good yield by reduction of **4** using NaBH_4 in ethanol (74% yield) (Scheme 3).

Access to more extended π systems and systems having more than one ferrocenyl group, was achieved by a reaction between aldehyde **D** or **E** and the pyran phosphorane derivative, respectively (Schemes 4 and 5).

In the first case (aldehyde **D**), an unseparable mixture of the ferrocenylmethylenepyran **7** and aldehyde **D** was obtained. To circumvent this experimental difficulty, $\text{Co}_2(\text{CO})_8$ was added to the mixture to give the expected $\text{Co}_2(\text{CO})_6$ -acetylenic complexes of **7** and **D** [19], which are easily separated by chromatographic work-up. By this way, the trinuclear complex **8** was obtained in 74% yield (Scheme 4).

On the other hand, aldehyde **E** (mixture of stereoisomers) [20] gave the diferrocenyl unsaturated pyran **9** in low yield (20%) as one isomer (Scheme 5).

Oxidative coupling of **8** and **9** followed in the later case by a decomplexation of the dicobalt carbonyl fragment could open a route to a new class of dendralenes. These cross-conjugated molecules should have possible applications as soliton valves and switches in molecular electronic devices [21]. Finally, the pyridine–pyran complex **10** was obtained similarly from pyridine carboxaldehyde and the phosphorane derivative (85% isolated yield). Subsequent formylation using Vilsmeier-type reaction afforded **11** in 55% yield (Scheme 6).

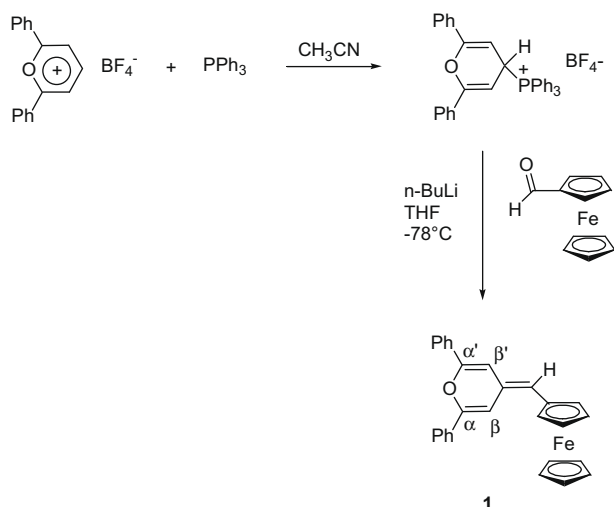
Moreover, to test the coordinative propensity of the pyridine ring [22], compound **10** was added to a $\text{W}(\text{CO})_5(\text{THF})$, generated photochemically from $\text{W}(\text{CO})_6$ and THF, to yield the expected pentacarbonyl complex **12** (57% yield).

3. Characterization

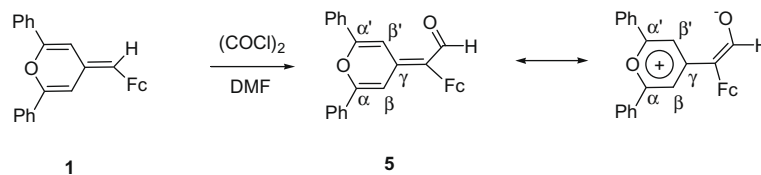
3.1. Spectroscopic studies

The new ferrocenylpyrans **1**, **3**, **4**, **5**, **6**, **8**, **9** and ferrocenylbispyran **2** were fully characterized by IR, ^1H and ^{13}C NMR spectroscopy, mass spectroscopy, elemental analysis (for **6** and **10**) and X-ray analysis for **5**.

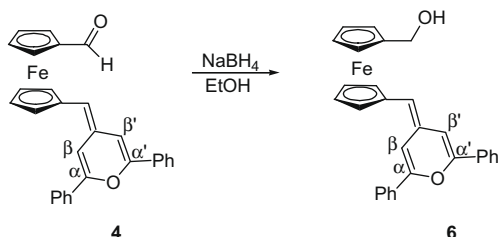
The solid-state IR spectra (KBr plates) of the ferrocenylpyran compounds **1–6**, **8**, **9** exhibit the typical features previously



Scheme 1. Synthesis of ferrocenylmethylenepyran complex.



Fc = Ferrocenyl group

Scheme 2. Formylation of **1** by $(\text{COCl})_2$ DMF reagent.**Scheme 3.** Reduction of **4** by NaBH_4 .

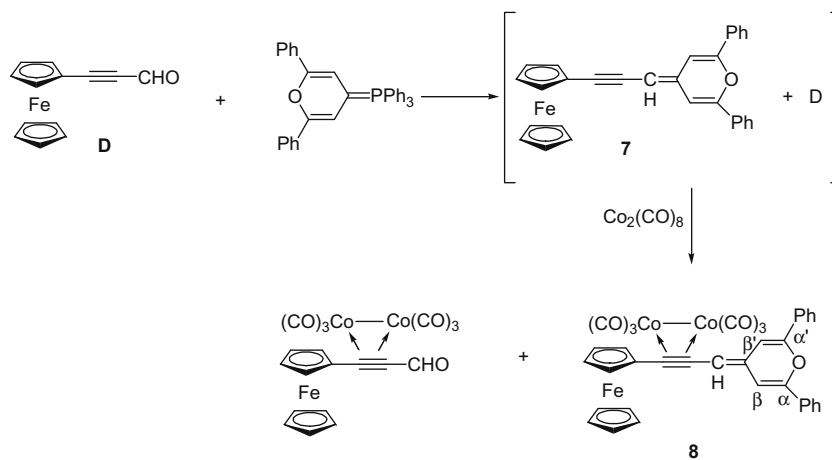
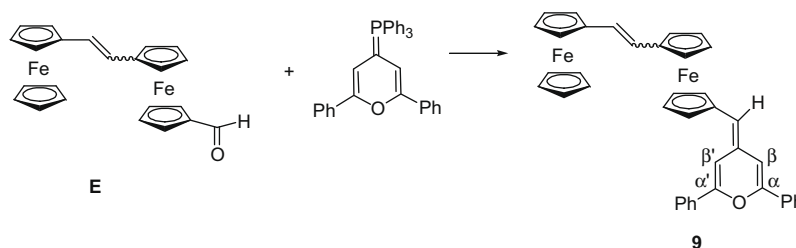
observed for related methylenepyran complexes [10,11]. In particular, the IR spectra show a medium sharp band in the 1620–1667 cm^{-1} region assigned to the $\text{C}=\text{C}$ stretching mode of the pyran ring. As expected, supplementary broad band appears at 3331 cm^{-1} for alcohol **6**, which is characteristic of OH intermolecular hydrogen bond. The IR spectrum of the cobalt carbonyl complex **8** displays three intense bands at 2073, 2042 and 2006 cm^{-1} attributed to the metal carbonyl stretching mode.

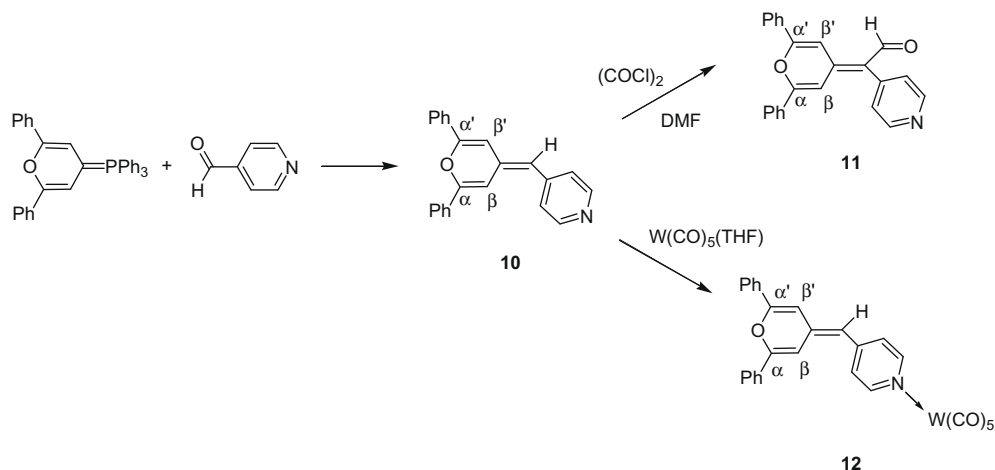
In addition to the pyran absorption band, supplementary bands appear at 2819 cm^{-1} (weak) and 1682 cm^{-1} (sharp intense) for aldehyde **4** and at 2755 cm^{-1} (weak) and 1627 cm^{-1} (sharp intense) for aldehyde **5** assigned to the $\text{C}-\text{H}$ and $\text{C}=\text{O}$ aldehyde stretching modes, respectively. The difference found between the $\nu_{(\text{C}=\text{O})}$ values of **4** and **5** suggests a contribution of the pyrylium resonance form to the ground state structure of **5**, in agreement with the findings of NMR studies (see below).

The IR spectra of the pyridine methylenepyran compounds **10–12** display several intense bands in the 1660–1500 cm^{-1} region, attributable to the vibration of the $\text{C}=\text{N}$ of pyridine ring and to the $\text{C}=\text{C}$ of the pyran ring. In addition, compound **11** displays the stretching modes characteristic of the aldehyde function (2742 cm^{-1} weak and 1666 cm^{-1} intense). Finally, consistent with the presence of a $\text{W}(\text{CO})_5$ groups, the IR spectrum of complex **12** exhibits expected intense bands for the carbonyl linked to the tungsten atom at 2069, 1969, 1914, 1913, 1866 cm^{-1} .

^1H and ^{13}C NMR spectra were recorded after recrystallization of the compounds and their analysis confirms the proposed structures.

For the ferrocenyl complexes, comparison of the ^1H and ^{13}C chemical shift values is in accordance with the electronic influence

**Scheme 4.** Synthesis of the $\text{Co}_2(\text{CO})_6$ acetylenic complex **8**.**Scheme 5.** Access to diferrocenylmethylenepyran **9**.



Scheme 6. Access to pyridylmethylenepyran compounds.

Table 1

Selected chemical shift values for pyran compounds (δ ppm, solvent CDCl_3).

Compounds	$\delta C_{\alpha'}$	δC_{α}	$\delta H_{\beta'}$	δH_{β}
1	149.0	151.0	6.30	6.92
2	149.0	151.1	6.22	6.82
3	149.1	151.6	6.31	6.88
4	150.0	152.1	6.32	6.79
5	156.1	157.1	8.70	7.23
6	149.6	151.8	6.32	6.87
8	151.6	153.0	6.26	6.59
9	149.6	151.5	6.21	6.84
10	152.2	154.1	6.45	7.04
11	157.8	158.3	8.45	6.71
12	154.1	156.4	6.83	7.31

of the aldehyde function in **5**. As stated previously, one can expect a deshielding effect for the H_{β} proton ($H_{\beta'}$) and the C_{α} atom ($C_{\alpha'}$) as the pyrylium resonance form contributes more to the ground state structure of the molecule [11c].

As exemplified in Table 1, the C_{α} ($C_{\alpha'}$) and H_{β} ($H_{\beta'}$) atoms of **5** resonate at lower field than the analogous atoms in **1**, **2**, **3**, **4**, **6**, **8**, and **9**. However the ($H_{\beta'}$) atom is clearly under the anisotropic influence of the aldehyde function and therefore cannot be taken into account for comparison. Moreover, it can be noted that a part of the deshielding effect found for **5** should be the consequence of the inductive effect of the carbonyl group.

On the other hand, the presence of the aldehyde function on the sandwich fragment in complex **4** has no detectable influence on the pyran ring chemical shift values. This observation emphasizes the lack of electronic communication *via* the iron atom between the two cyclopentadienyl rings. Concerning the ^1H and ^{13}C chemical shift values of the pyridyl pyrans **10**, **11** and **12** (Table 1), one can take note of the low deshielding effect of the pyridyl ring (comparison with analogous complexes **1** and **5**).

Again, we observe the deshielding of the C_{α} ($C_{\alpha'}$) atoms due to the presence of an aldehyde function in **11**. As in **5**, the $H_{\beta'}$ atom resonates at low field. Curiously, the electron withdrawing ability of the carbonyl group has no influence on the chemical shift of the H_{β} atom.

Consequently, X-ray analysis was performed in order to gain more information on the electronic of **5**.

3.2. X-ray crystal structure

Crystals suitable for structure determination were grown from dichloromethane/diethylether solution by slow evaporation of

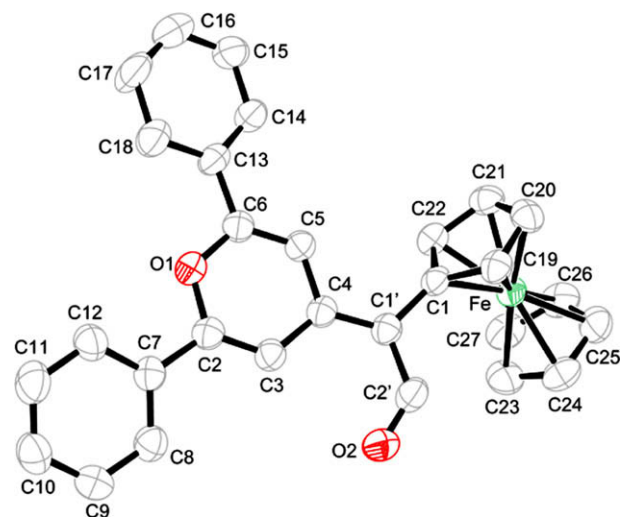


Fig. 3. ORTEP diagram of compound **5**.

Table 2

Selected bond lengths (Å) and angles ($^\circ$) for compound **5**.

C1–C1'	1.486(4)	C3–C4	1.445(4)
C4–C1'	1.384(4)	C4–C5	1.440(4)
C1'–C2'	1.461(4)	C5–C6	1.341(4)
C2'–O2	1.219(4)	C2–O1	1.375(3)
C2–C3	1.338(4)	C6–O1	1.365(3)
C1'–C4–C5	122.1(3)	C4–C1'–C2'	122.8(3)
C4–C1'–C1	120.8(2)	C1'–C2'–O2	128.6(3)
C2'–C1'–C1	116.1(2)		

the solvent at low temperature. The structure of the organometallic moiety, along with the atom labelling, is presented in Fig. 3. Selected bond lengths and angles are listed in Table 2. Details of the data collection and refinement are provided in Section 5.

The main feature of the solid-state structure is the low deviation from planarity between the pyran ring and the carbonyl group ($\text{C4–C1'–C2'–O2} = 10.4(5)^\circ$), a situation which should allow conjugation between the two parts of the molecules. On the other hand, in order to minimize the steric strain with the pyran ring and the carbonyl group, the ferrocenyl group deviates from the plane formed by the methylenepyran moiety. An angle of $53.64(9)^\circ$ is observed between the mean planes of the pyran and cyclopentadienyl rings. As in other 2,6-diphenylmethylenepyran, the phenyl

rings deviate slightly from the pyran ring (C5–C6–C13–C14 = 15.2(5)° and C3–C2–C7–C8 = –19.5(5)°). The iron distances to the Cp rings and the C–C distances and angles of the Cp lie in the expected range. On the methylenepyran side, we observe that the exocyclic bond C4–C1' is 1.384(4) Å long, suggesting a weak pyrylium character. In fact, exocyclic C–C bond lengths lying in the range of 1.39–1.40 Å have been found for push–pull methylene pyran Fischer-type carbene complexes for which, due to the electron withdrawing effect of the carbene fragment, the ground state structure are closed to cyanin limit.[10a,10b,10d] On the other hand, lower values 1.375(5) and 1.352(6) Å were found for low conjugated symmetrical bis-methylenepyran [23,13]. Finally, the C2–O2 distance (1.219(4) Å) confirmed the low intermolecular charge transfer between the intracyclic pyran oxygen atom and the aldehyde carbonyl group.

3.3. Electrochemical studies

The redox behaviour of representative compounds ferrocenyl bispyran **2**, pyridyl pyran **10** and phenylpyran **13** [24] (Fig. 1, R = R' = Ph) was investigated by cyclic voltammetry in CH₂Cl₂ in the presence of Bu₄NPF₆ as supporting electrolyte, to determine parameters which lead to the formation of extended bispyran *via* a radical cation, as observed for compound **1**. The data are collated in Table 3. For comparison, values obtained for **1** are also reported [13]. Voltammetric curves are displayed in Supplementary information.

The compound **1** displays on the anodic scan an irreversible peak at $E_{pa}(1) = -0.15$ V (vs. FeCp₂⁺/FeCp₂) followed by two reversible systems ($E_{1/2}(2) = 0.12$ V and $E_{1/2}(3) = 0.28$ V). On the reverse scan, an irreversible peak appears at –0.76 V. This peak is absent when starting the scan cathodically from $E \leq 0.20$ V. As previously discussed [13], these observations are consistent with the formation of a ferrocenyl radical cation **1**^{•+} [25], which evolves by dimerization to form a diferrocenylbispyrylium salt **14** (Scheme 7). This was confirmed by electrochemical studies performed on compound **14**, obtained by chemical oxidation using ferricinium salt. Indeed, the reduction of the diferrocenylbispyrylium salt **14** occurs at $E_{pc} = -0.76$ V to give compound **1** by a subsequent C–C bond breaking.

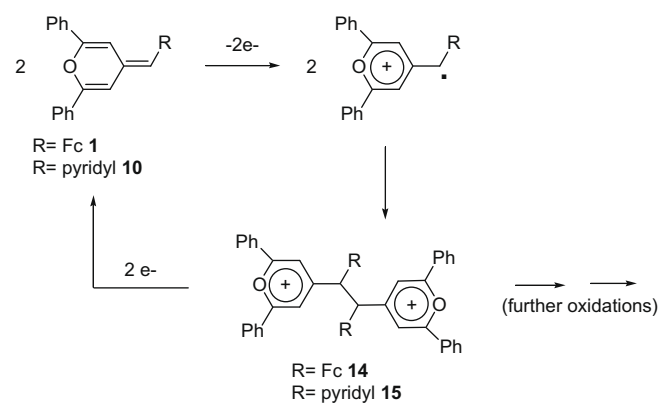
A similar behaviour was observed with the pyridyl pyran compound **10** for which irreversible oxidation at $E_{pa}(1) = 0.50$ V leads to the formation of a species irreversibly reduced at –0.77 V. As described for compound **1**, it seems likely that the chemical reaction which follows electrochemical oxidation is the dimerization of pyrylium radical cation to form a bispyrylium compound **15**. The main difference between **1** and **10** originates from the nature of the oxidized site which seems to be the ferrocenyl for **1** and the pyran for **10**.

Substituting the pyridyl moiety by a phenyl group gives a different situation: the compound **13** shows a reversible system at $E_{1/2}(2) = -0.32$ V. This redox behaviour suggest the absence of any dimerization from phenylpyrylium radical cation (no EC mechanism), in contrast to the pyridyl derivative **10**. The oxidized form of **13**, namely **13**^{•+}, is thus stable. Such behaviour highlights the importance of the electronic properties of the substituting group

Table 3

Electrochemical data for pyran and bispyran compounds, (E vs. FeCp₂⁺/FeCp₂) in CH₂Cl₂ with Bu₄NPF₆ as supporting electrolyte at 0.1 V s^{–1} (a) on the reverse cathodic scan (b) irreversible peak.

	E_{pc}	$E_{pa}(1)$ (b)	$E_{1/2}(2)$	$E_{1/2}(3)$
1	–0.76 ^(a)	–0.15	0.12	0.28
2	–0.81 ^(a)		–0.24	0.05 ^(b)
10	–0.77 ^(a)	0.50	0.85 ^(b)	
13			–0.32	



Scheme 7. Electrochemical behaviour of pyran compounds **1** and **10**.

for tuning the oxidation potential (820 mV), and allowing a dimerization process. Probably, delocalisation of the positive charge through the phenyl network inhibits this specific reaction.

To pursue the comparison with compound **1**, a voltammetric study of the ferrocenyl bispyran **2** was also performed. On the anodic scan, compound **2** exhibits a chemically reversible (but kinetically slow) system at $E_{1/2}(2) = -0.24$ V, followed by irreversible anodic peaks (Table 3). As for compounds **1** and **10**, an irreversible cathodic peak appears on the reverse scan (–0.81 V). Interestingly, this peak appears only if the potential is raised above the second anodic peak. Also, maintaining the potential at –0.03 V for few seconds leads to an increase of the cathodic peak suggesting that a chemical reaction occurred after the second oxidation. The quantitative electrolysis of compound **2** at –0.20 V shows that the electron transfer is monoelectronic ($n = 1e^-$) with the formation of a stable oxidized compound. On the basis of previous work on compound **1** [13], it appears likely that the reversible system at –0.24 V peak corresponds to the oxidation of the ferrocenyl moiety of the bispyran. This allows us to make three remarks by comparison with compound **1**: (i) the reversibility of the first oxidation and the stability of the oxidized bispyran indicates that dimerization does not occur at this stage, (ii) the first oxidation potential which is observed at lower potential than for **1** is consistent with the formation of a highly delocalised d- π electron system (iii) the appearance, after the first irreversible oxidation peak, of a reduction peak (on the reverse scan) suggests that the dioxidized species evolves by a dimerization process to ferrocenyl pyrylium salts in a similar way than **1** [26].

This electrochemical study highlights the specificity of ferrocenyl-substituted pyrans by comparison with dithiafulvene analogous compounds to undergo oxidative dimerization *via* radical cation coupling. Interestingly, a deep contrast appears between the ferrocenylpyran **1** and its isoelectronic ferrocenyl-1,4-substituted dithiafulvene analog reported by Bryce's group [27]. Whatever substituent borne by the dithiole ring (R = H, Me, SMe, CO₂Me), voltammograms of these compounds display two well separated reversible oxidation waves. The radical cation coupling is only feasible for the dithiafulvene derivative when using acid, suggesting that the deprotonation of the dithiolium salt to extended TTF is the key step for allowing dimerization. This contrasts with the ferrocenylpyran **1** for which deprotonation is not necessary to undergo dimerization after oxidation [13]. The case of non-ferrocenyl substituted pyran, such as aryl, is also different. Voltammetric studies of aryl dithiafulvene derivatives reported few years ago by Lorcy's group, showed an irreversible oxidation peak [2d–g,i–k,o]. In this case, the dimerization of the radical cation gives a dithiolium salt, which leads to a vinylogous TTF by a deprotonation process. This compound is reversibly oxidized at a lower potential than the starting 1,4-dithiafulvene.

For the ferrocenyl dithiafulvene analogous to compound **2** [27], the two reversible oxidation waves are followed by an irreversible peak.

In conclusion, it appears from these electrochemical studies that the behaviour is fully dependent, but not only, on the substituting group which can tune (or not) the delocalisation of the cationic charge on the molecule, thus allowing formation of dimers.

4. Concluding remarks

In summary, new electron-rich ferrocenyl methylenepyrans and pyridyl methylenepyran have been prepared from Wittig reaction of 2,6-diphenyl-4H-pyran-4-yl triphenylphosphonium tetrafluoroborate salt with ferrocenyl aldehydes and pyridylcarboxaldehyde. Similarly, the same reaction performed with ferrocenyldicarboxaldehyde afforded the first bispyran known today.

The presence of the sandwich fragment should favour the oxidative coupling of these molecules while incorporation of a pyridyl group into the pyranilidene framework should open a route to a coordination chemistry of this type of compounds as exemplified by the complexation of the nitrogen atom of **10** with the pentacarbonyl tungsten group.

The electron-rich nature of complexes **1** and **10** allowed the formylation of the exocyclic C=C bond using a Vilsmeier-type reaction to give aldehydes **5** and **11**. The red/ox behaviour of methylenepyran **1**, **2**, **10** and **13** was studied by cyclic voltammetry. This first approach showed that these compounds are readily oxidized to radical cation or dication, which evolves by dimerization. Attempts to isolate the bispyrylium salts and electron-rich extended bispyrans isoelectronic of vinylogous TTF are underway in our laboratory.

5. Experimental

5.1. General procedures

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. IR spectra were recorded on a Perkin-Elmer spectrum1000 FTIR using KBr plates.

All NMR data are reported in ppm (δ) relative to tetramethylsilane as external reference. 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 experiments. Spectra were recorded at room temperature in CDCl_3 on a Bruker DRX 500 spectrometer and a Bruker Advance 400 spectrometer at the "Service Commun de Recherche de Résonance Magnétique Nucléaire et de Résonance Paramagnétique Electronique de l'Université de Bretagne Occidentale". Mass spectra or elemental analyses were performed at the "Centre Régional de Mesures Physiques de l'Ouest" (CRMPO, University of Rennes). Microanalytical data were obtained with a Thermo-Finnigan Flasch EA 1112 CHNS/O analyzer. Mass spectra were obtained with a high resolution MS/MS Zab spectra Tof micromass.

5.1.1. Materials

Solvents were dried and distilled under dinitrogen by standard methods prior to use. Reagents were purchased from commercial suppliers and used without purification. Ferrocene-1,1'-dicarboxaldehyde was obtained from Ref. [15] and mono-protected ferrocene-1,1'-dicarboxaldehyde was synthesized as described previously by Balavoine and coll. [16]. Ferrocenyl acetylene and the corresponding aldehyde **D** were prepared according to Ref. [28]. Diferrocenyldicarboxaldehyde **E** was synthesized using the method described by Peris and coll. [20]. 2,6-Diphenyl-4H-pyran-

4-yl triphenylphosphonium tetrafluoroborate salt was obtained from the method previously described [14].

5.2. Crystallographic data

Crystals of **5** suitable for X Ray analysis were obtained by slow evaporation of a $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ solution at 4 °C. Single crystal was mounted on a Nonius four-circle diffractometer equipped with a CCD camera and a graphite monochromated Mo $K\alpha$ radiation source ($\lambda = 0.71073 \text{ \AA}$) from the Centre de Diffraction (CDFIX), Université de Rennes 1, France.

5.2.1. X-ray crystal data for **5**

Data collection was performed at 293(2)K. $\text{C}_{29}\text{H}_{22}\text{FeO}_2$, $M = 458.32$, monoclinic, space group $P2_1/a$, $a = 7.2729(2) \text{ \AA}$, $b = 25.0694(7) \text{ \AA}$, $c = 11.8922(4) \text{ \AA}$, $\beta = 94.613(1)^\circ$, $V = 2161.25(11) \text{ \AA}^3$, $T = 293(2) \text{ K}$, $Z = 4$, $d_{\text{calcd}} = 1.409$, 7808 structure factors were collected before merging gave 4408 unique intensities ($R_{\text{int}} = 0.0343$). Structure was solved with SHELXS-97 [29]. The refinement of 289 parameters against F^2 of unique intensities [2971 observed intensities $I > 2\sigma(I)$] was performed with SHELXL-97 [29] with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure model on calculated positions. Final residues $R = 0.0474$, $wR = 0.1177$.

5.3. Electrochemical studies

All experiments were performed under an atmosphere of nitrogen (in a glovebox) at ambient temperature using a 0.1 M solution of $[\text{NBu}_4][\text{PF}_6]$ in extra-dry CH_2Cl_2 ($[\text{H}_2\text{O}] < 30 \text{ ppm}$, Acros). A three electrode system was used with a platinum disk, a platinum wire auxiliary electrode and a platinum wire dipping in a 10 mM electrolytic solution (with supporting electrolyte) of equimolar FcPF_6 and Fc as reference electrode. Cyclic voltammetry experiments were performed with a μ -AUTOLAB III potentiostat or with an AUTOLAB PGSTAT 100 potentiostat, monitored by a computer. All the potential are quoted against the ferrocene-ferricinium couple.

5.4. General procedure for the Wittig reaction: SYNTHESIS of methylenepyran **1**, **2**, **3**, **9**, **10**

Small excess of *n*-butyllithium (1.1 equiv.; 2.5 M in hexanes) was added dropwise at -78°C , under a nitrogen atmosphere, to a degassed solution of 2,6-diphenyl-4H-pyran-4-yl triphenylphosphonium tetrafluoroborate salt (1 equiv.) in dry THF. After 5 min, the suitable metallocenyl aldehyde or pyridine carboxaldehyde (1 equiv.) was added. The solution was stirred at room temperature for 1 h and poured into cold water. Extraction with ether ($3 \times 50 \text{ mL}$), drying over MgSO_4 and evaporation of the solution under vacuum gave a solid residue. The residue was purified by chromatography on silica gel (eluent ether-petroleum ether) to give the expected pyrans.

5.4.1. Synthesis of ferrocenylpyran **1** (Scheme 1)

1.200 g of tetrafluoroborate phosphonium salt (2.0 mmol), 0.9 mL of *n*-butyllithium (2.2 mmol) and 0.428 g of ferrocenecarboxaldehyde (2.0 mmol) gave after chromatography on silica gel (eluant: perolum ether-diethylether 40/60 v/v) 0.556 g of **1** as a red-orange solid. Yield: 65%, red-orange solid. ^1H NMR (500 MHz, CDCl_3): $\delta = 4.16$ (s, 5H, C_5H_5), 4.26 (s, 2H, C_5H_4), 4.40 (s, 2H, C_5H_4), 5.59 (s, 1H, CH), 6.30 (s, 1H, H_β), 6.92 (s, 1H, H_β), 7.43 (m, 6H, $\text{H}_{\text{Ph}(\text{meta and para})}$), 7.75 (d, $J = 7.5 \text{ Hz}$, 2H, $\text{H}_{\text{Ph}(\text{ortho})}$), 7.80 (d, $J = 8.0 \text{ Hz}$, 2H, $\text{H}_{\text{Ph}(\text{ortho})}$) ppm. ^{13}C NMR (125 MHz, CDCl_3): $\delta = 68.2$; 68.8 (C_5H_4), 69.1 (C_5H_5), 84.0 ($\text{C}_{\text{Fc}(\text{quat})}$), 103.0 (C_β), 108.4 (C_β), 111.6 (CH), 124.3; 124.7 ($\text{C}_{\text{Ph}(\text{ortho})}$), 128.5; 128.9 ($\text{C}_{\text{Ph}(\text{meta and para})}$), 134.2 (C_γ), 139.2 ($\text{C}_{\text{Ph}(\text{quat})}$), 149.0 ($\text{C}_{\alpha'}$), 151.0 (C_{α}) ppm. IR (KBr):

$\bar{\nu}$ = 1658, 1493, 1445, 1278, 809, 760, 689 cm^{-1} . HRMS (ESI): calcd. for $\text{C}_{28}\text{H}_{22}\text{FeO}$: 430.1020; found: 430.1007.

5.4.2. Synthesis of ferrocenylbispyran **2** (Fig. 2)

1.200 g of tetrafluoroborate phosphonium salt (2.0 mmol), 0.9 mL of *n*-butyllithium (2.2 mmol) and 0.242 g of ferrocene-1,1'-dicarboxaldehyde (1.0 mmol) gave after chromatography (eluent: petroleum ether–diethylether 65/35 v/v) 0.134 g of an orange solid in low yield. Yield: 20%, red-orange solid. ^1H NMR (500 MHz, CDCl_3): δ = 4.28 (s, 4H, C_5H_4), 4.46 (s, 4H, C_5H_4), 5.46 (s, 2H, CH), 6.22 (s, 2H, $\text{H}_{\beta'}$), 6.82 (s, 2H, H_{β}), 7.29 (m, 8H, $\text{H}_{\text{Ph}(\text{meta})}$), 7.34 (t, J = 7.0 Hz, 4H, $\text{H}_{\text{Ph}(\text{para})}$), 7.50 (d, J = 6.1 Hz, 4H, $\text{H}_{\text{Ph}(\text{ortho})}$), 7.65 (d, J = 7.0 Hz, 4H, $\text{H}_{\text{Ph}(\text{ortho})}$) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 69.0; 69.1 (C_5H_4), 85.1 ($\text{C}_{\text{Fc}(\text{quat})}$), 103.0 ($\text{C}_{\beta'}$), 108.5 (C_{β}), 110.8 (CH), 124.1; 124.5 ($\text{C}_{\text{Ph}(\text{ortho})}$), 128.3; 128.4 ($\text{C}_{\text{Ph}(\text{meta})}$), 127.5; 128.7 ($\text{C}_{\text{Ph}(\text{para})}$), 133.3; 133.7 ($\text{C}_{\text{Ph}(\text{quat})}$), 149.0 ($\text{C}_{\alpha'}$), 151.1 (C_{α}) ppm. IR (KBr): $\bar{\nu}$ = 1654, 1495, 1446, 1281, 946, 758, 689 cm^{-1} . HRMS (ESI): calcd. for $\text{C}_{46}\text{H}_{34}\text{FeO}_2$: 674.1908; found: 674.1899.

5.4.3. Synthesis of ferrocenylpyran **3** (Fig. 2)

1.200 g of tetrafluoroborate phosphonium salt (2.0 mmol), 0.9 mL of *n*-butyllithium (2.2 mmol) and 0.572 g of ferrocene-1-formyl-1,3-dioxolane (2.0 mmol) afforded after chromatography on silica gel (eluant: petroleum ether–diethylether 55/45 v/v) 0.450 g of a red-orange solid.

Yield: 45%, red-orange solid. ^1H NMR (500 MHz, CDCl_3): δ = 3.92 (t, J = 3.0 Hz, 2H, CH_2), 4.02 (t, J = 3.0 Hz, 2H, CH_2), 4.17 (t, J = 1.5 Hz, 2H, C_5H_4), 4.29 (t, J = 1.5 Hz, 2H, C_5H_4), 4.31 (t, J = 1.5 Hz, 2H, C_5H_4), 4.44 (t, J = 1.5 Hz, 2H, C_5H_4), 5.59 (s, 1H, CH), 5.75 (s, 1H, CH), 6.31 (d, J = 1.5 Hz, 1H, $\text{H}_{\beta'}$), 6.88 (d, J = 1.5 Hz, 1H, H_{β}), 7.43 (m, 6H, $\text{H}_{\text{Ph}(\text{meta and para})}$), 7.75 (d, J = 7.5 Hz, 2H, $\text{H}_{\text{Ph}(\text{ortho})}$), 7.80 (d, J = 7.0 Hz, 2H, $\text{H}_{\text{Ph}(\text{ortho})}$) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 65.2 (CH_2), 65.3 (CH_2), 67.8; 69.2 (C_5H_4), 84.4 ($\text{C}_{\text{Fc}(\text{quat})}$), 84.6 ($\text{C}_{\text{Fc}(\text{quat})}$), 102.8 (CH), 103.0 ($\text{C}_{\beta'}$), 108.5 (C_{β}), 111.3 (CH), 124.3; 124.7 ($\text{C}_{\text{Ph}(\text{ortho})}$), 128.6–129.0 ($\text{C}_{\text{Ph}(\text{meta and para})}$), 133.8 ($\text{C}_{\text{Ph}(\text{quat})}$), 149.1 ($\text{C}_{\alpha'}$), 151.6 (C_{α}) ppm. HRMS (ESI): calcd. for $\text{C}_{31}\text{H}_{26}\text{FeO}_3$: 502.1231; found: 502.1192, calcd. for $[\text{M}-\text{CH}_2\text{CH}_2\text{O}^+]$: 458.0969; found: 458.0949.

5.4.4. Synthesis of the aldehyde ferrocenylpyran **4** (Fig. 2)

From compound **3**: A solution of **3** in CH_2Cl_2 (0.500 g, 9.96×10^{-4} mol) is warmed at 60 °C. 0.171 g of paratoluenesulfonic acid was then added and stirred until the starting material had disappeared as indicated by TLC. The mixture was poured on cold water. After extraction with ether (3 \times 50 mL) drying over MgSO_4 , evaporation of the solution under vacuum gave a solid residue. The residue was purified by chromatography on silica gel (petroleum ether–diethylether 40/60 v/v) to afford 0.270 g of **4** (yield 60%).

From ferrocene-1,1'-dicarboxaldehyde: 1.200 g of tetrafluoroborate phosphonium salt (2.0 mmol), 0.9 mL of *n*-butyllithium (2.2 mmol) and 0.484 g of ferrocene-1,1'-dicarboxaldehyde (2.0 mmol) gave 0.129 g of **2** (yield: 10 %) and 0.412 g of the expected compound **4** (yield: 45%). ^1H NMR (500 MHz, CDCl_3): δ = 4.36 (t, J = 1.5 Hz, 2H, C_5H_4), 4.50 (t, J = 1.5 Hz, 2H, C_5H_4), 4.58 (t, J = 1.5 Hz, 2H, C_5H_4), 4.78 (t, J = 2.0 Hz, 2H, C_5H_4), 5.46 (s, 1H, CH), 6.32 (d, J = 1.5 Hz, 1H, $\text{H}_{\beta'}$), 6.79 (d, J = 1.5 Hz, 1H, H_{β}), 7.45 (m, 6H, $\text{H}_{\text{Ph}(\text{meta and para})}$), 7.74 (d, J = 7.0 Hz, 2H, $\text{H}_{\text{Ph}(\text{ortho})}$), 7.76 (d, J = 7.0 Hz, 2H, $\text{H}_{\text{Ph}(\text{ortho})}$), 9.93 (s, 1H, CHO) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 69.2; 74.5 (C_5H_4), 85.2; 86.5 ($\text{C}_{\text{Fc}(\text{quat})}$), 102.5 ($\text{C}_{\beta'}$), 108.2 (C_{β}), 109.5 (CH), 124.4; 124.8 ($\text{C}_{\text{Ph}(\text{ortho})}$), 128.6; 128.7 ($\text{C}_{\text{Ph}(\text{meta})}$), 128.9; 129.3 ($\text{C}_{\text{Ph}(\text{para})}$), 133.3 ($\text{C}_{\text{Ph}(\text{quat})}$), 150.0 ($\text{C}_{\alpha'}$), 152.1 (C_{α}), 193.7 (CHO) ppm. IR (KBr): $\bar{\nu}$ = 2819, 1681, 1661, 1494, 1457, 1282, 1241, 767, 693 cm^{-1} . HRMS (ESI): calcd. for $\text{C}_{28}\text{H}_{22}\text{FeO}_2$: 458.0969; found: 458.1012, calcd. for $[\text{M}-\text{CO}^+]$: 430.1020; found: 430.1040. $\text{C}_{29}\text{H}_{22}\text{FeO}_2$: (458.15).

5.4.5. Formylation of **1**: synthesis of the ferrocenyl formyl methylenepyran **5** (Scheme 2)

(0.06 mL, 0.70 mmol) of $(\text{COCl})_2$ was added under nitrogen dropwise to 5 mL of cooled DMF (0 °C). The mixture was stirred for 15 min. Methylenepyran **1** was then added (0.200 g, 0.46 mmol) and the mixture warmed to room temperature and stirred for 1 h. The solution was poured into water and extracted with diethylether (3 \times 50 mL). The organic phase was washed with Na_2CO_3 solution in water, dried over MgSO_4 and evaporated under vacuum. The solid was then dissolved in petroleum ether/diethylether mixture and the obtained solution was cooled. Compound **5** was isolated as an orange microcrystalline solid (0.165 g, 77% yield). ^1H NMR (500 MHz, CDCl_3): δ = 4.16 (s, 5H, C_5H_5), 4.23 (s, 2H, C_5H_4), 4.37 (s, 2H, C_5H_4), 7.23 (d, J = 1.7 Hz, 1H, H_{β}), 7.48 (m, 6H, $\text{H}_{\text{Ph}(\text{meta and para})}$), 7.77 (m, 2H, $\text{H}_{\text{Ph}(\text{ortho})}$), 7.92 (m, 2H, $\text{H}_{\text{Ph}(\text{ortho})}$), 8.70 (d, J = 1.7 Hz, 1H, $\text{H}_{\beta'}$), 10.25 (s, 1H, CHO) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 67.5 (C_5H_4), 69.0 (C_5H_5), 70.0 (C_5H_4), 86.0 ($\text{C}_{\text{Fc}(\text{quat})}$), 105.3 ($\text{C}_{\beta'}$), 106.3 (C_{β}), 126.0; 126.1 ($\text{C}_{\text{Ph}(\text{ortho})}$), 129.7 ($\text{C}_{\text{Ph}(\text{meta})}$), 130.9; 131.0 ($\text{C}_{\text{Ph}(\text{para})}$), 134.1 ($\text{C}_{\text{Ph}(\text{quat})}$), 140.2 (C_{γ}), 156.1 ($\text{C}_{\alpha'}$), 157.1 (C_{α}), 191.6 (CHO) ppm. IR (KBr): $\bar{\nu}$ = 2755, 1663, 1627, 1577, 1522, 1103, 938, 765, 680 cm^{-1} . HRMS (ESI): calcd. for $\text{C}_{29}\text{H}_{22}\text{FeO}_2$: 458.0969; found: 458.0969. $\text{C}_{29}\text{H}_{22}\text{FeO}_2$ (458.15): calcd. C, 76.00; H, 4.84; found: C, 76.57; H 4.85.

5.4.6. NaBH_4 reduction of aldehyde **4**: synthesis of the alcohol **6** (Scheme 3)

NaBH_4 (0.049 g, 1.31 mmol) was added to a solution of aldehyde **4** (0.500 g, 1.09 mmol) in 15 mL of ethanol. The solution was stirred until the starting material had disappeared as indicated by TLC. The mixture was poured into water and extracted with diethylether. After drying over MgSO_4 concentration of the solution under vacuum, chromatographic work up (silica gel; eluent: petroleum–ether–diethylether 70/30 v/v) afforded an orange solid (0.370 g, yield: 74%). ^1H NMR (500 MHz, CDCl_3): δ = 1.75 (t, J = 5.2 Hz, 1H, CH_2OH), 4.17 (s, 2H, C_5H_4), 4.24 (s, 2H, C_5H_4), 4.29 (s, 2H, C_5H_4), 4.35 (d, J = 5.2 Hz, 2H, CH_2OH), 4.42 (s, 2H, C_5H_4), 5.55 (s, 1H, CH), 6.32 (s, J = 1.8 Hz, 1H, $\text{H}_{\beta'}$), 6.87 (s, J = 1.6 Hz, 1H, H_{β}), 7.36 (m, 2H, $\text{H}_{\text{Ph}(\text{para})}$), 7.43 (m, 4H, $\text{H}_{\text{Ph}(\text{meta})}$), 7.75 (d, J = 7.2 Hz, 2H, $\text{H}_{\text{Ph}(\text{ortho})}$), 7.79 (d, J = 7.1 Hz, 2H, $\text{H}_{\text{Ph}(\text{ortho})}$) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 60.7 (CH_2OH), 68.3; 68.5 (C_5H_4), 68.6; 69.2 (C_5H_4), 84.2 ($\text{C}_{\text{Fc}(\text{quat})}$), 89.2 ($\text{C}_{\text{Fc}(\text{quat})}$), 102.6 ($\text{C}_{\beta'}$), 108.2 (C_{β}), 110.1 (CH), 124.3; 124.7 ($\text{C}_{\text{Ph}(\text{ortho})}$), 128.6; 128.8 ($\text{C}_{\text{Ph}(\text{meta})}$), 128.0; 129.1 ($\text{C}_{\text{Ph}(\text{para})}$), 133.4; 133.6 ($\text{C}_{\text{Ph}(\text{quat})}$), 149.6 (C_{α}), 151.8 (C_{α}) ppm. IR (KBr): $\bar{\nu}$ = 3331, 1663, 1493, 1446, 1285, 1234, 1075, 1026, 946, 927, 818, 691 cm^{-1} . HRMS (ESI): calcd. for $\text{C}_{28}\text{H}_{22}\text{FeO}$: 460.1125; found: 460.1115. $\text{C}_{28}\text{H}_{22}\text{FeO}_2$ (460.30) calcd: C, 75.66, H 5.25; found: C, 75.66, H, 5.86.

5.4.7. Synthesis of the ferrocenyl methylenepyran acetylenic $\text{Co}_2(\text{CO})_6$ complex **8** (Scheme 4)

A schlenk tube was charged with 2,6-diphenyl-4H-pyran-4-yl triphenylphosphonium tetrafluoroborate salt (1.200 g, 2.0 mmol) and 20 mL of degassed THF at -78 °C. *n*-Butyllithium was added (0.9 mL, 2.2 mmol) and the solution was stirred for 5 min. The aldehyde **D** (0.476 g, 2.0 mmol) was added and the solution was warmed to room temperature and stirred for 1 h. 0.683 g of $\text{Co}_2(\text{CO})_8$ (2.0 mmol) was added to the reaction mixture. After 1 h, the mixture was poured into water. Extraction with diethylether, drying over MgSO_4 and evaporation of the solvent under vacuum afforded a solid residue. Chromatographic work up on silica gel yield complex **8** as a green solid (eluent: petroleum ether–diethylether 90/10 v/v, 1.090 g yield: 74%). A blue solid was also isolated (0.073 g yield 7%). ^1H NMR spectrum confirms the complexation of aldehyde **D** with $\text{Co}_2(\text{CO})_6$. ^1H NMR (500 MHz, CDCl_3): δ = 4.26 (s, 5H, C_5H_5), 4.40–4.49 (s, 4H, C_5H_4), 6.26 (s, 1H, CH), 6.59 (s, 1H, H_{β}), 7.08 (s, 1H, H_{β}), 7.48 (m, 6H, $\text{H}_{\text{Ph}(\text{meta and para})}$), 7.83 (s,

4H, $H_{\text{Ph(ortho)}}$ ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 68.4; 68.5 (C_5H_4), 69.6 (C_5H_5), 86.9 ($\text{C}_{\text{Fc(quat)}}$), 87.6 ($\text{C}_{\text{Ph(quat)}}$), 106.6 ($\text{C}_{\beta'}$), 109.1 (C_{β}), 111.4 (CH), 125.0 ($\text{C}_{\text{Ph(meta and para)}}$), 133.0 ($\text{C}_{\text{Ph(quat)}}$), 137.5 (C_{γ}), 151.6 ($\text{C}_{\alpha'}$), 153.0 (C_{α}), 184.2; 200.4 (CO) ppm. IR (KBr): $\bar{\nu}$ = 2073, 2042, 2006, 1652, 1597, 1578, 1543, 1493, 1448, 1106, 935, 763 cm^{-1} . HRMS (ESI): calcd. for $\text{C}_{36}\text{H}_{22}\text{FeO}_7\text{Co}_2$: 739.9378; found: 739.9398, calcd. for $[\text{M}+\text{H}^+]$: 740.9457; found: 740.9449.

5.4.8. Synthesis of ferrocenylpyran **9** (Scheme 5)

0.274 g of tetrafluoroborate phosphonium salt (4.7 mmol), 0.9 mL of *n*-butyllithium (5.6 mmol) and 0.200 g of diferrocenecarboxaldehyde (4.7 mmol) gave after chromatography (eluant: petroleum ether–diethylether 70/30 v/v) 0.077 g of a red–orange solid (yield: 25%). ^1H NMR (500 MHz, CDCl_3): δ = 4.03 (s, 2H, C_5H_4), 4.08 (s, 5H, C_5H_5), 4.10 (s, 2H, C_5H_4), 4.22 (s, 2H, C_5H_4), 4.32 (s, 2H, C_5H_4), 4.35 (s, 2H, C_5H_4), 4.36 (s, 2H, C_5H_4), 5.46 (s, 1H, CH), 6.21 (s, 1H, $H_{\beta'}$), 6.36 (d, J = 6.0 Hz, 2H, CH=CH), 6.84 (s, 1H, H_{β}), 7.37–7.43 (m, 6H, $H_{\text{Ph(meta and para)}}$), 7.67 (m, 2H, $H_{\text{Ph(ortho)}}$), 7.77 (m, 2H, $H_{\text{Ph(ortho)}}$) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 68.2; 68.8 (C_5H_4), 69.0 (C_5H_4), 69.1 (C_5H_5), 69.2; 69.4 (C_5H_4), 84.1 ($\text{C}_{\text{Fc(quat)}}$), 85.1 ($\text{C}_{\text{Fc(quat)}}$), 86.0 ($\text{C}_{\text{Fc(quat)}}$), 103.0 ($\text{C}_{\beta'}$), 108.6 (C_{β}), 111.3 (CH), 124.5; 124.6 ($\text{C}_{\text{Ph(ortho)}}$), 128.0; 129.0 ($\text{C}_{\text{Ph(meta and para)}}$), 134.0 ($\text{C}_{\text{Ph(quat)}}$), 149.6 ($\text{C}_{\alpha'}$), 151.5 (C_{α}) ppm. IR (KBr): $\bar{\nu}$ = 1660, 1495, 1440, 1269, 811, 754, 679 cm^{-1} . HRMS (ESI): calcd. for $\text{C}_{40}\text{H}_{32}\text{Fe}_2\text{O}$: 640.1151; found: 640.1179.

5.4.9. Synthesis of pyridyl pyran **10** (Scheme 6)

1.200 g of tetrafluoroborate phosphonium salt (2.0 mmol), 0.9 mL of *n*-butyllithium (2.2 mmol) and 0.19 mL of pyridinecarboxaldehyde (2.0 mmol) gave 0.549 g of a yellow solid (yield: 85%). ^1H NMR (500 MHz, CDCl_3): δ = 5.78 (s, 1H, CH), 6.45 (d, J = 1.7 Hz, 1H, $H_{\beta'}$), 7.04 (d, J = 1.7 Hz, 1H, H_{β}), 7.24 (d, J = 4.7 Hz, 2H, H_{pyrid}), 7.46 (m, 6H, $H_{\text{Ph(meta and para)}}$), 7.82 (m, 4H, $H_{\text{Ph(ortho)}}$), 8.51 (d, J = 4.7 Hz, 2H, H_{pyrid}) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 101.7 ($\text{C}_{\beta'}$), 108.4 (C_{β}), 110.8 (CH), 122.0 (C_{pyrid}), 125.4 ($\text{C}_{\text{Ph(ortho)}}$), 128.5 ($\text{C}_{\text{Ph(meta and para)}}$), 132.8 (C_{γ}), 133.2; 133.8 ($\text{C}_{\text{Ph(para)}}$), 146.0 (C_{pyrid}), 149.8 (C_{pyrid}), 152.2 ($\text{C}_{\alpha'}$), 154.1 (C_{α}) ppm. IR (KBr): $\bar{\nu}$ = 1663, 1658, 1579, 1489, 1445, 1281, 1075, 916, 761, 687 cm^{-1} . HRMS (ESI): calcd. for $\text{C}_{23}\text{H}_{17}\text{NO}$: 323.1310; found: 323.1304. $\text{C}_{23}\text{H}_{17}\text{NO}$ (323.05): calcd: C, 85.42; H, 5.30; N, 4.33; found: C, 85.02; H, 5.18; N, 3.91.

5.4.10. Formylation of **10** – synthesis of the pyridyl-methylenepyran aldehyde **11** (Scheme 6)

As described above, 0.06 mL (0.75 mmol) of oxalyl chloride, 5 mL of DMF and 0.161 g of **10** afforded the expected compound **11** as a brown solid (0.122 g, 70% yield). ^1H NMR (500 MHz, CDCl_3): 6.71 (s, 1H, H_{β}), 7.28 (d, J = 4.9 Hz, 2H, H_{pyrid}), 7.40 (m, 6H, $H_{\text{Ph(meta and para)}}$), 7.68 (d, J = 7.5 Hz, 2H, $H_{\text{Ph(ortho)}}$), 7.92 (d, J = 7.0 Hz, 2H, $H_{\text{Ph(ortho)}}$), 8.45 (s, 1H, $H_{\beta'}$), 8.70 (d, J = 4.9 Hz, 2H, H_{pyrid}), 9.91 (s, 1H, CHO) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 103.3 ($\text{C}_{\beta'}$), 104.9 (C_{β}), 118.7 (C_{quat}), 125.4 ($\text{C}_{\text{Ph(ortho)}}$), 125.8 ($\text{C}_{\text{Ph(ortho)}}$), 128.5 ($\text{C}_{\text{Ph(meta and para)}}$), 131.6; 132.0 ($\text{C}_{\text{Ph(quat)}}$), 145.6 (C_{pyrid}), 150.4 (C_{pyrid}), 157.8 (C_{α}), 158.3 (C_{α}), 187.5 (CHO) ppm. IR (KBr): $\bar{\nu}$ = 2742, 1666, 1622, 1589, 1445, 1228, 1078, 916, 763, 689 cm^{-1} . HRMS (ESI): calcd. for $\text{C}_{24}\text{H}_{17}\text{NO}_2$: 351.1259; found: 351.1259, calcd. for $[\text{M}-\text{H}^+]$: 350.1180; found: 350.1196; calcd. for $[\text{M}-\text{CO}^+]$: 323.1310; found: 323.1305.

5.4.11. Complexation of pyridyl pyran **11** by $\text{W}(\text{CO})_5(\text{THF})$ reagent: synthesis of the pentacarbonyl complex **12** (Scheme 6)

$\text{W}(\text{CO})_6$ (1.00 g, 3.0 mmol) was dissolved in 75 mL of degassed THF. The solution was irradiated with a medium pressure mercury vapour lamp under a slight N_2 positive pressure for 2 h30. The yellow solution of $\text{W}(\text{CO})_5\text{THF}$ was transferred via cannula to a

schlenk tube charged with 0.995 g of **11**. The solution was stirred over 12 h. Concentration of the solvent under vacuum afforded an orange solid which was recrystallized in CH_2Cl_2 (1.100 g, yellow solid, yield: 57%). ^1H NMR (500 MHz, CDCl_3): δ = 5.90 (s, 1H, CH), 6.83 (s, 1H, $H_{\beta'}$), 7.31 (s, 1H, H_{β}), 7.37 (d, J = 5.9 Hz, 2H, H_{pyrid}), 7.53 (m, 6H, $H_{\text{Ph(meta and para)}}$), 7.90 (d, J = 7.6 Hz, 2H, $H_{\text{Ph(ortho)}}$), 7.96 (d, J = 7.6 Hz, 2H, $H_{\text{Ph(ortho)}}$), 8.68 (d, J = 5.9 Hz, 2H, H_{pyrid}) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 102.6 ($\text{C}_{\beta'}$), 109.6 (C_{β}), 110.2 (CH), 124.0 (C_{pyrid}), 125.7; 126.2 ($\text{C}_{\text{Ph(ortho)}}$), 129.6–132.8 ($\text{C}_{\text{Ph(meta and para)}}$), 133.4; 133.6 ($\text{C}_{\text{Ph(quat)}}$), 148.5 (C_{pyrid}), 154.1 (C_{α}), 156.4 (C_{α}), 156.6 (C_{pyrid}), 199.8; 202.6 (CO) ppm. IR (KBr): $\bar{\nu}$ = 2069, 1969, 1914, 1913, 1866, 1654, 1578, 1560, 768, 692 cm^{-1} . HRMS (ESI): calcd. for $\text{C}_{28}\text{H}_{17}\text{NO}_6\text{W}$: 647.0565; found: 647.0570.

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Appendix A. Supplementary data

CCDC 732060 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.10.006.

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