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Reactivity of carbanions of Fischer-type carbene complexes with pyrylium salts. Synthesis and characterization of new γ-methylenepyran carbene complexes via an addition–oxidation–deprotonation process

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Abstract—The condensation reaction between γ-unsubstituted pyrylium salts and carbanions of Fischer-type carbene complexes allowed the synthesis of new γ-methylenepyran carbene complexes. NMR data, single crystal X-ray analysis, and DFT calculations suggest that these complexes have a partial pyrylium character due to the π electron-accepting ability of the carbenic fragment and to the electron-releasing properties of the methylenepyran part. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Pyrylium salts are unique oxygenated heterocyclic aromatic compounds, which possess a carbocationic character at the 2, 4, and 6 positions[1] (Fig. 1).

As a consequence they react readily with a great variety of nucleophiles, including carbon nucleophiles.[1]

Addition of nucleophiles to the pyrylium cations at C_2, gives 2-substituted 2*H*-pyrans that rearrange to dienones or dienals. This synthetic methodology has been successfully applied to the stereoselective synthesis of natural acyclic products such as leukotriene and retinal analogues.[2] In some cases, the dienones formed undergo a ring closure to give benzenic compounds.[3] We have reported recently that the C_2-addition of the readily available carbanions of Fischer-type carbene complexes to 2,4,6-triarylpyrylium salts leads to highly substituted benzophenones.[4] This formation arises from an unstable organometallic dienone which evolves by ring closure, followed by an aromatization step as the result of a double metal hydrogen β-elimination.

Addition of carbone nucleophiles to C_4 of pyrylium ring, gives 4-substituted pyrans.[1–5] When the carbanions bear electron-withdrawing groups (for example $-CO_2R$ groups), the condensation products undergo an oxidation to pyrylium salt followed by a deprotonation to γ-methylenepyrans.[1–6]

Given that the pentacarbonylmetal carbene unit in Fischer-type carbene complexes behaves as a strong electron-withdrawing groups,[7] that is similar to a Lewis acid-complexed carbonyl function, it seems likely that the condensation of their stabilized α-carbanions[8] with γ-unsubstituted pyrylium salts may provide a simple route to a new class of unsaturated carbene complexes of group 6 transition metalcarbonyl.

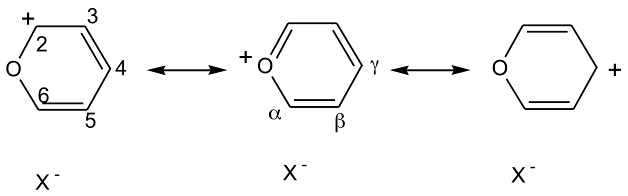

Figure 1. Resonance formula for pyrylium ring.

Keywords: pyrylium salts; methylenepyran Fischer-type carbene complexes; tungsten and chromium carbenes; DFT calculations.

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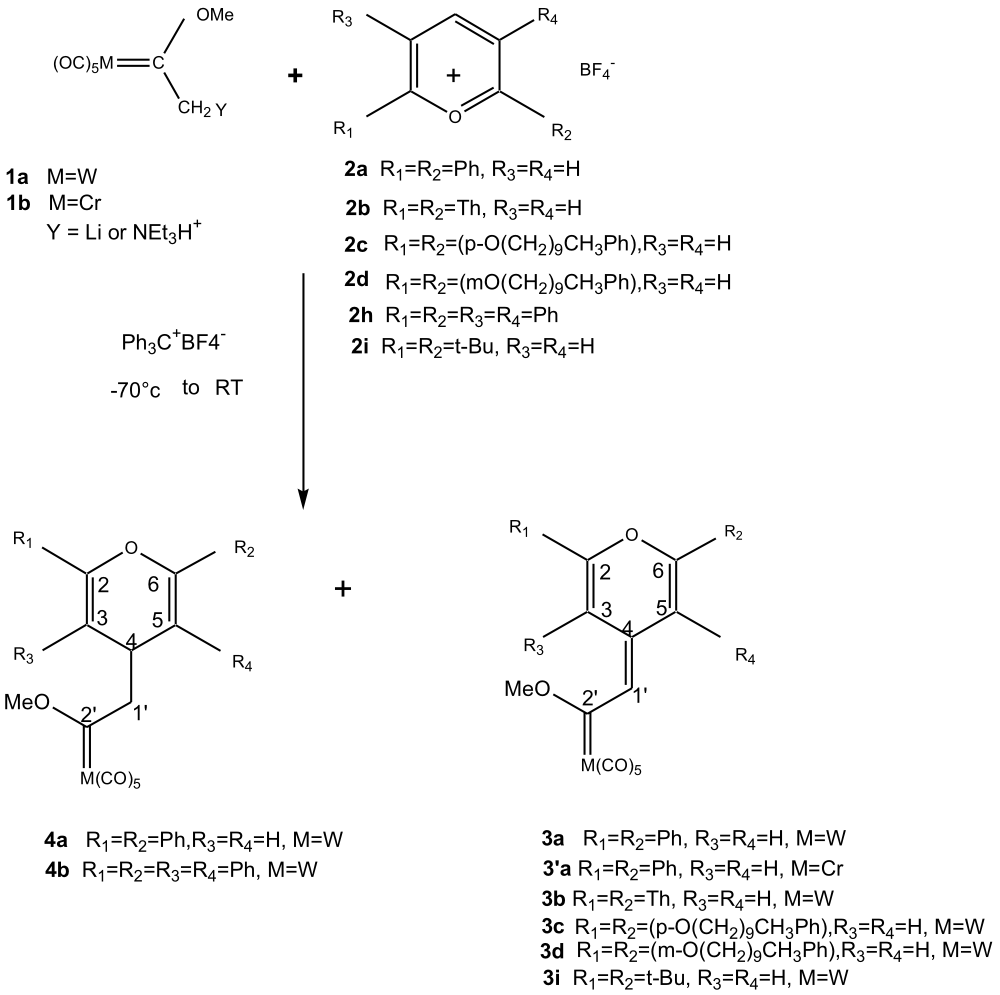


Scheme 1.

Access to new unsaturated carbene complexes is of interest as they are widely used in organic and organometallic synthesis.[9]

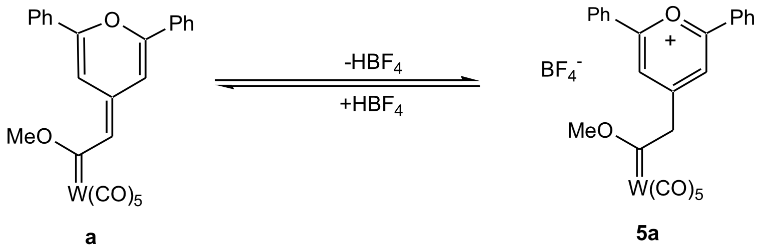
In this paper we will report on the preparation of new methylenepyran Fischer-type carbene complexes.[10] Experimental and theoretical probes of the partial pyrylium character of these complexes will be presented.

2. Results and discussion

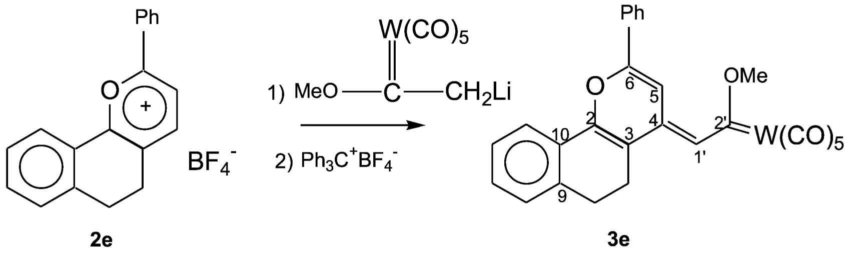
2.1. Synthesis of methylenepyran carbene complexes

Carbanion **1a** (Scheme 1), generated from *n*-butyllithium and the corresponding Fischer-type carbene complex ($CH_3C(OCH_3)W(CO)_5$), was reacted with 2,6-diphenyltetrafluoroborate pyrylium salt **2a**. After chromatography (silica gel, eluent: ether/petroleum ether), deep purple methylenepyran complex **3a** (43% yield) was obtained. A small quantity of yellow pyran complex **4a** (13% yield) was also produced. By using 2 equiv. of **2a** and adding triphenylcarbenium tetrafluoroborate salt to the reaction mixture, led to **3a** as the sole isolated product (85% yield). The formation of **3a** was the result of **4a** oxidation to pyrylium salt **5a** by the excess of **2a**, or more efficiently by the triphenylcarbenium tetrafluoroborate salt. The intermediate pyrylium salt **5a** could be obtained in the form of a yellow precipitate by adding HBF_4 to a solution of **3a** in diethylether (Scheme 2).

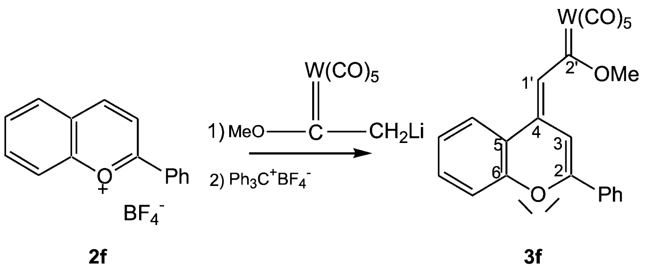
With regards to **4a**, we have observed that the transformation



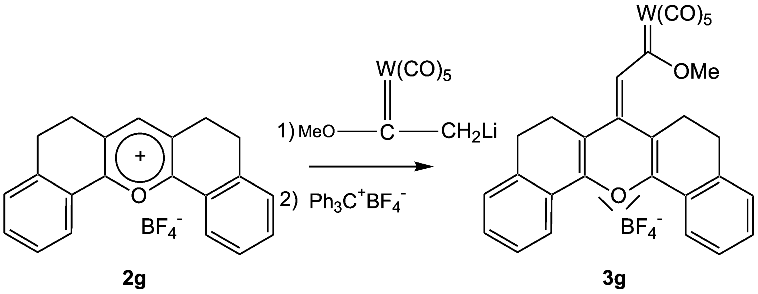
Scheme 2.



Scheme 3.



Scheme 4.



Scheme 5.

to methylenepyran **3a**, via the pyrylium salt **5a**, occurs also by the dioxygen action in diethylether solution or in solid state incorporated into a thin layer chromatography plate (silica gel) and by the action of the nonhydrid acceptor one electron transfer ferrocenium salt.

In order to obtain a wide range of γ-methylenepyran carbene complexes, we used the more efficient and commercially available triphenylcarbenium oxidizing reagent. Thus, the reaction between the pyrylium salt **2a** and the carbanion **1b** of the chromium carbene complex ($CH_3C(OCH_3)Cr(CO)_5$) resulted in the methylenepyran chromium carbene complex **3′a** in 55% yield (Scheme 1). In the tungsten series, the reaction was extended without any modification to 2,6-dithienylpyrylium salt **2b** and to 2,6-diarylpyrylium salts **2c** and **2d** that are known to exhibit a thermotropic liquid crystalline behavior.[11] γ-methylenepyran complexes **3b**, **3c** and **3d** were obtained in moderate yields (25, 20 and 30%, respectively).

In addition, the reaction of carbanion **1a** with the fused ring pyrylium salt **2e** (Scheme 3) and with the flavinium salt **2f** (Scheme 4) produced, respectively, the expected tricyclic γ-methylenepyran complex **3e** (54% yield) and the bicyclic benzopyran complex **3f** (55% yield) as the only isomers (see Section 2.2).

Under the reaction conditions we employed, only small amount (5% yield) of the tetracyclic methylenepyran carbene complex **3g** (Scheme 5) could be obtained from the pentacyclic salt **2g**. Unreacted pyrylium salt **2g** was recovered from the reaction mixture. This significant lowering in reactivity might be the consequence of the steric requirement of the two CH_2 groups in **2g**, which partly prevents the carbanion approach (Fig. 2).

Another limitation to the methylenepyran carbene complex formation was found when the β positions of the pyrylium salt were substituted by phenyl groups (pyrylium salt **2h**, Scheme 1). In this case, the reaction, perhaps for steric reasons, stopped at the pyran stage (obtention of **4b**, 40% yield).

Finally, when the standard procedure (*n*-BuLi as base and tritylcation as oxidizing reagent) was applied to the 2,6-ditertiobutylpyrylium cation **2i** (Scheme 1) a complex mixture of products was obtained. Using triethylamine as base,[12] in place of *n*-BuLi, and trityl cation as the oxidizing reagent, allowed the formation of the ditertiobutyl analogue of **3a** in a high yield (Scheme 1, $Y{=}NEt_3H^+$, **3i**, 79% yield).

Next, we examined the action of carbanion **1c** of the diethylamino complex ($CH_3C(N(Et)_2)W(CO)_5$) (Scheme 6).

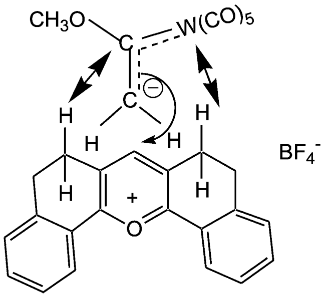
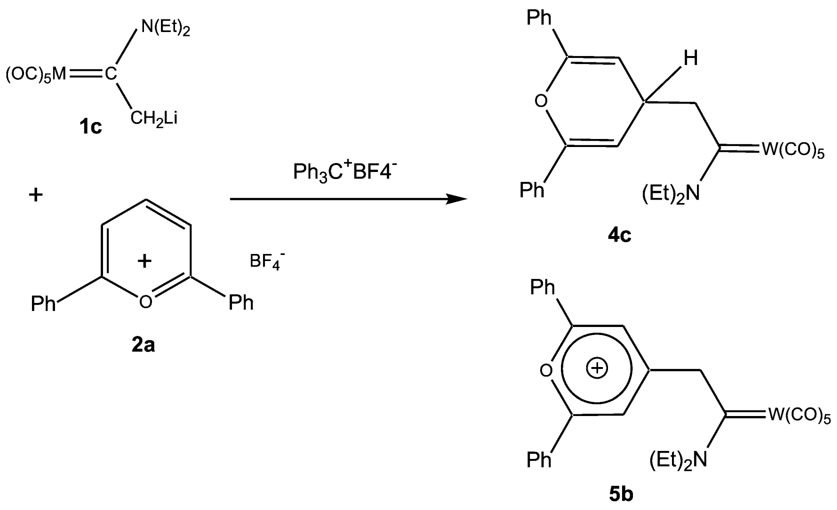
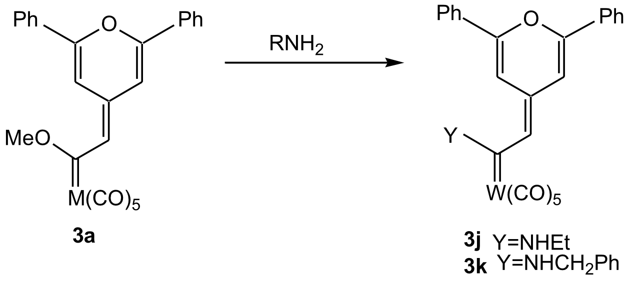


Figure 2. Addition of **1a** on pyrylium salt **2g**.



Scheme 6.



Scheme 7.

Treating pyrylium salt **2a** with carbanion **1c**, followed by the addition of trityl salt gave the yellow pyran complex **4c** in 43% yield. In this case, no formation of the aminocarbene γ-methylenepyran complex analogous to **3a** was observed. The use of a large excess of trityl cation gave only a small yield of the pyrylium salt **5b** (characterized by IR and mass spectroscopy). To date, the reasons (electronic or steric) of this behavior remain unclear. However, the substitution from **3a** of the methoxy group by an ethylamino, or a benzylamino group[13] (Scheme 7), provides easy access to the expected ethylamino and benzylamino unsaturated carbene complexes **3j** and **3k**. The transformation performed using diethylamine was unsuccessful.

2.2. Structural assignment of the methylenepyran carbene complexes. Pyran-pyrylium character

The structural assignment of new methylenepyran complexes is based on ^{1}H, ^{13}C NMR data and on X-ray structure analyses.

New compounds **3a**–**3g**, **3i**–**3k** (Schemes 1, 3–5, 7) can be described by the extreme resonance methylenepyran **A**, **C** and pyrylium **B** structures (Fig. 3).

Determining the pyrylium character of these complexes is interesting, as it was found that the pyranylidene carbene complexes, the metal analogues of the α-pyrones, exhibit this behavior depending on the ring substitution.[14] In addition, it was shown that methylenepyrans bearing two electron-withdrawing groups have a pronounced pyrylium character.[15] The color of the methylenepyranalcoxycarbene complexes dark purple, (dark red for **3i**), together with the high field resonances of the carbenic carbon atoms (δ=282–286 ppm for **3a**, **3b**–**3g**, **3i**, M=W; δ=307 ppm for **3′a**, M=Cr) compared with those observed for simple unsaturated Fischer-type carbene complexes[13] (δ=305 ppm, M=W, δ=324 ppm, M=Cr), indicate a certain delocalization of the heterocyclic oxygen lone pair.[16] Furthermore, it is notable that the α–δ unsaturated carbene complexes **6a** and **6b** formed by *n*-BuLi addition on **3a** and **3′a**[14c] (Scheme 8), show carbon carbenic chemical shift values of 302 ppm (**6a**, M=W) and 327 ppm (**6b**, M=Cr).

This difference clearly reflects, for the methylenepyran complexes, the extra delocalization of π electrons, and

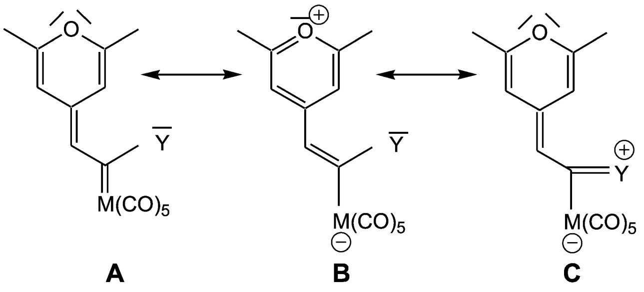
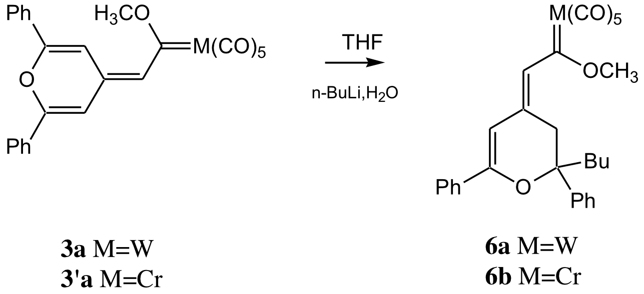


Figure 3. Resonance formula for methylenepyran complexes.



Scheme 8.

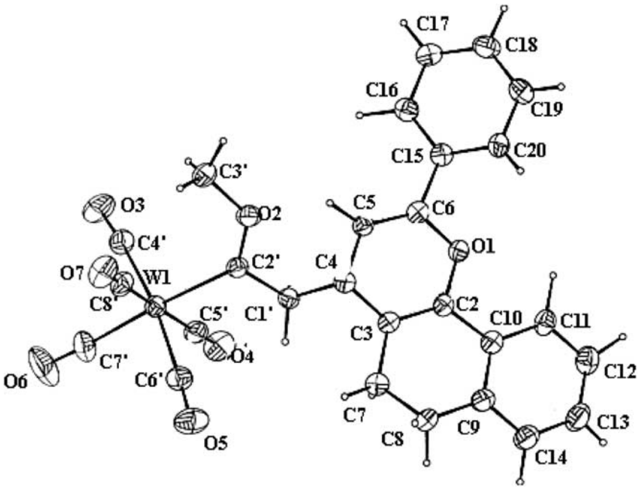


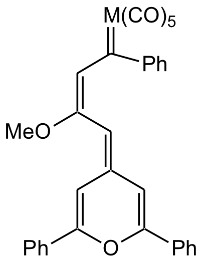
Figure 4. Ortep drawing of complex **3e**. Selected bond distances (Å): W–C2′, 2.218(7); C2′–C1′, 1.43(1); C2′–O2, 1.318(9); C1′–C4, 1.40(1); C4–C5, 1.44(1); C5–C6, 1.33(1); C6–O1, 1.372(9); C2–C3, 1.36(1); C3–C4, 1.43(1). Bond angles (°): W1–C2′–O2, 130.0(6); W1–C2′–C1′, 120.1(5); C1′–C2′–O2, 109.9(7); C2′–C1′–C4, 131.2(7); C1′–C4–C3, 120.3(6); C5–C4–C3, 115.2(6); C4–C5–C6, 121.2(7); C5–C6–O1, 122.4(6), C6–O1–C2, 119.0(5); O1–C2–C3, 122.2(6); C2–C3–C4, 119.9(6).

therefore the partial pyrylium character of these molecules (structure **B**, Fig. 3).

Single crystal X-ray analysis gives additional information relating to the methylenepyran-pyrylium duality of alcoxy carbene complexes.

Purple crystals of **3e** suitable for the X-ray analysis were obtained by slow evaporation from ether/petroleum–ether solution. The molecular view with the atom labeling is shown in Fig. 4.

In a solid state, the exocyclic carbon–carbon double bond is in s-*trans* conformation with respect to the metalcarbonyl group, and the carbene fragment is located far from the bicyclic part of the molecule. The carbon–tungsten bond and the heterocyclic ring lie in the same plane, a situation which allows the conjugation between the intracyclic oxygen atom and the metal. The W–C2′ carbenic carbon bond length (2.218 Å) proves to be significantly longer than the W–C distance found in the $(CO)_5W{=}C(OMe)Ph$ complex (2.05 Å).[17] This result, together with the weak double bond character of the C–C exocyclic bond (1.40 Å), also suggests some contribution of the resonance structure **B** (Fig. 3). In addition, the alternating bond distance pattern between the carbon atoms of the heterocyclic is not very different from that found in pyrylium salts substituted in γ position by *para*-dimethylaminophenyl[18] or the cymentrenyl electron-donating group.[19] In these salts, the pyran resonance structure contributes significantly to the valence bond description.



Scheme 9.

Furthermore, the $C_{carbenic}$–O bond length (1.32 Å) shows the presence of a π donation from the oxygen to the carbene carbon atom[20] (Fig. 3, structure **C**). It is interesting to note that a better methylenepyran electron-releasing effect occurs in carbene complexes not directly stabilized by a methoxy group (Scheme 9, more pyrylium character).[14c]

Among the methylenepyran complexes described here, the alcoxybenzomethylenepyran carbene complex **3f** seems to be a special case. The down field ^{13}C chemical shift value of the carbenic carbon (294 ppm) suggests that the contribution of the benzopyrylium resonance structure is less important. A similar trend of the carbon carbenic chemical shifts was previously observed when going from the pyran-2-ylidene complexes,[14b,c] for which the pyrylium character dominates, to the benzopyran-2-ylidene complexes, for which this contribution appears insignificant.[14a]

Further information relating to the pyrylium character of the methylenepyrans can be drawn from ^1H NMR spectroscopy analysis. It has been previously reported that at room temperature ^1H NMR spectra of γ-methylenepyrans substituted by two different electron-withdrawing groups exhibit a singlet for the pyran Hβ (Fig. 5). This phenomena arises from fast thermal isomerization around the exocyclic C–C double bond, as the consequence of the strong pyrylium character of these molecules. However, monosubstituted derivatives give rise to two chemical shift signals at room temperature.[15]

As expected, the ^1H 300 or 500 MHz NMR spectra of **3a**, **3′a**, **3b–3d**, **3i** recorded at room temperature, in $CDCl_3$ for **3b–3d** acetone-d_6 for **3a**, **3′a** and THF-d_8 for **3a** and **3i**, contained two distinct doublets in the range of 8.20–7.90 ppm and 7.33–7.00 ppm assigned to the heterocyclic β hydrogens.

As the only β hydrogen in **3e**, being geometrically disposed to the anisotropic effect of the organometallic fragment, resonates at 8.14 ppm (Fig. 4) the low field signals (8.20–

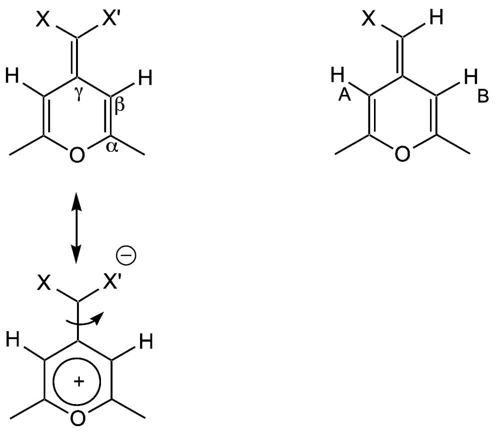


Figure 5. Representation of mono and disubstituted methylenepyrans.

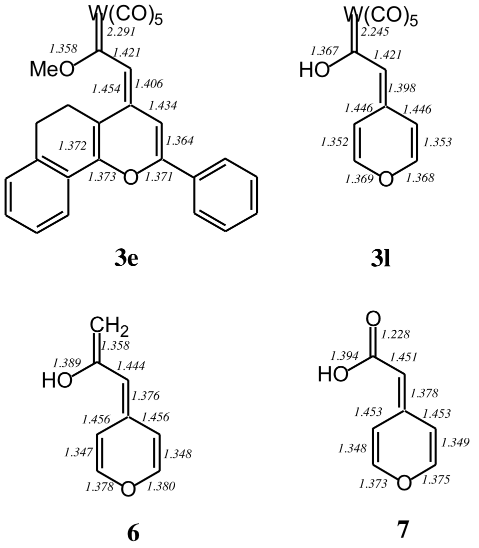


Figure 6. Major DFT optimized bond distances for **3e**, **3l**, **6** and **7**.

7.90 ppm) in **3a**, **3′a**, **3b–3d**, **3i** were assigned to the β hydrogen opposed to the metalcarbonyl fragment. According to the weak double bond character of the C–C exocyclic bond (1.40 Å) and therefore to a certain pyrylium character, 2D ^{1}H Exsy experiments performed on **3a** at 25°C in THF-d_8 have shown a low exchange process between the β hydrogens H_A and H_B (Fig. 5, X=(MeO)C=W(CO)$_5$).

On the other hand, the situation appears to be different for the aminocarbene complexes **3j**, **3k**. The yellow color of these molecules in solid state or in solution, together with the ^{13}C carbenic carbon resonances (δ=242 ppm) which are close to that found in the other unsaturated aminocarbene complexes,[13] suggest that, in this case, the pyrylium character is less developed, because of the greater contribution of resonance structure **C**. The reason of this might be because of the better π back bonding ability of nitrogen vs oxygen (Fig. 3C). The low difference observed for the chemical shift values of the β hydrogens H_A and H_B (Fig. 5, X=(NHR)C=W(CO)$_5$ (0.01 ppm for **3j** and 0.14 ppm for **3k**) may be another consequence of this electronic feature.

In order to obtain additional informations about the electronic structure of theses complexes DFT calculations were performed.

2.3. DFT calculations

The electronic structure of compounds of type **3** has been analyzed through DFT calculations on complex **3e** and on a simplified model, noted **3l** in the following, in which R_1=R_2=H, Y=OH and M=W. Geometry optimizations of **3e** were carried out assuming both C_s and C_1 symmetries, leading to very similar results. The nearly planar optimized C_1 structure is the most stable by only 0.12 eV. Its main metrical data are reported in Fig. 6. Most of the optimized bond distances do not differ significantly from the experimental ones, owing to the standard deviations of the X-ray values. The main differences are obtained for W–C$_2'$ and C$_2'$–OMe for which the optimized value is larger than the X-ray one. While we have no clear explanation for the latter, the discrepancy associated with the former was expected. Indeed, DFT calculations carried out at the generalized gradient approximation level usually over-estimate bond distances in which metal atoms are involved. Calculations on **3l** were done assuming C_s symmetry. The optimized bond distances are close to those obtained for **3e**, suggesting similar electronic properties for all complexes of type **3**, at least all of them for which Y=OR. This is also supported by the MO diagrams of **3e** and **3l** which are shown in Fig. 7. In both compounds, the three highest occupied orbitals are the so-called metallic 't_{2g}' set of the octa-hedrally coordinated W (d^6) atom. Due to a rather large mixing with the π*(CO) orbitals, their W character lies in the range 45–60%. The LUMOs of **3e** and **3l** are rather low lying and separated from the other unoccupied MOs by a significant energy gap. Such a situation suggests that the reduction of compounds **3** should lead to a stable species. This is in agreement with the cyclic voltammetry experi-ments which show that these complexes exhibit reversible reduction waves (see below). A similar result was also computed for compounds with a longer conjugated chain such as that of Scheme 9.[14c] This type of LUMO derives principally from the LUMO of the heterocycle, with some participation of the metal and carbenic atoms, as schema-tized in Fig. 7 for **3e** and **3l**. From the LUMOs localization

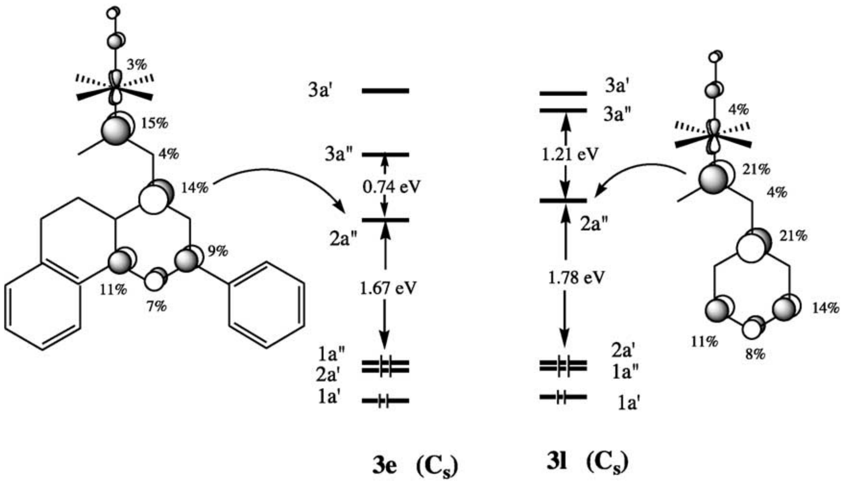


Figure 7. MO diagrams and LUMOs of **3e** and **3l**.

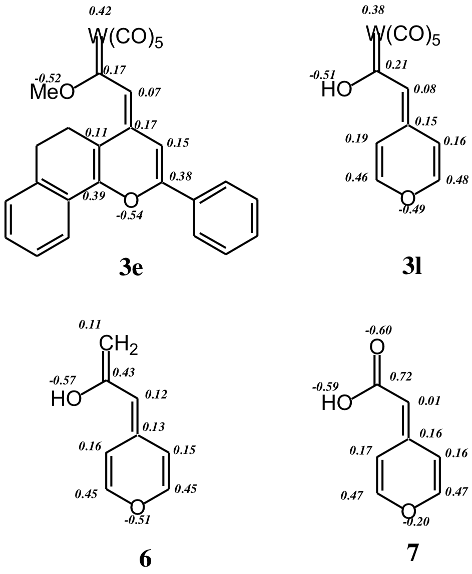


Figure 8. Mulliken atomic net charges for **3e**, **3l**, **6** and **7**.

one expects that an orbital-controlled nucleophilic attack of compounds **3** should occur in the $C_2' > C_4 > C_2 \approx C_6$ preferential order. On the other hand, from the Mulliken atomic charges given in Fig. 8 one expects that an orbital-controlled nucleophilic attack should occur in the $C_2 \approx C_6 > C_2' \approx C_4$ preferential order. Interestingly, lithium acetylide is shown to attack the carbenic C_2' atom whereas alkyl and aryl lithium reagents usually attack at C_2 or C_6.[14c] Obviously, the product of a nucleophilic attack of **3** results from a delicate balance between orbital, charge and steric effects.

In order to evaluate the effect electron accepting ability of the organometallic moiety in **3l**, we have also carried out calculations on C_s models resulting from the isolobal substitution of $W(CO)_5$ by CH_2 and O, noted **6** and **7**, respectively. The major results are shown in Figs. 6 and 8. One can see that bond alternation along the conjugated pathway is significantly less pronounced in **3l**, as compared to **6** and **7**, indicating stronger conjugation in **3** and therefore a more pyrylium character. However the net charge of the whole heterocycle varies in the order **6**>**3l**>**7**, indicating that the global electron withdrawing properties of $W(CO)_5$ are between those of CH_2 and O. Finally the computed dipole moments are (in Debye) 11.09, 8.87, 0.51 and 4.44 for **3e**, **3l**, **6** and **7**, respectively. The particularly large values computed for complexes of type **3**, are indicative of strong push–pull effects between both ends of the molecule (including the CO ligands) and support potential use of this type of complexes for NLO applications.

2.4. Electrochemical studies

The electrochemical properties of the carbenes **4a**, **3a**, **3′a** (Scheme 1) have been studied by cyclic voltammetry (Table 1). The reduction part of the **3a**, **3′a** cyclic voltammograms shows a quasi-reversible system at −1.12 and −1.15 V vs SCE. This electrochemical behavior is in line with the results of the DFT calculations (see Section 2.3) which predict the formation of stable radical anion species. Similar data for electrochemical reduction of $ArC(OMe){=}M(CO)_5$ (M=Cr, M=W) has been reported by Casey et al.[21]

Table 1. Cyclic voltammogram values for **4a**, **3a**, **3′a**

	$E_{p3}{}^{a,b}$ (V)	$E_{p2}{}^{a,b}$ (V)	$E_{p1}{}^{a}$ (V)	E'° (vs. ref)^{a,c} (V)
4a	1.75	1.45		
3a	1.80	1.26	1.04	−1.12
3′a	1.76	1.44	1.05	−1.15
$CH_3C(OCH_3)W(CO)_5$		1.39(1.21)^{d}		

[a] All CVs were run in CH_2Cl_2 with 0.1 M tetrabutylammonium tetrafluoroborate at 298 K, without correcting ohmic drop.
[b] Scan rate 0.2 V/s.
[c] Scan rate 0.1 V/s.
[d] Scan rate 0.02 V/s.

The anodic part of the **4a** voltammogram reveals, in the range of 0, +2 V vs SCE, two irreversible oxidation waves (see Table 1). As the saturated carbene complex $(CH_3(OCH_3)C{=}W(CO)_5)$ undergoes, under the same conditions, a single oxidation reaction at +1.39 V vs SCE, the wave at +1.45 V vs SCE was therefore ascribed to the oxidation of the metal[22] and the wave at highest potential to the oxidation of the phenyl rings.

Similar conclusions can be drawn for carbene complexes **3a** and **3′a**, for which similar oxidation waves were found (Table 1). However, owing to the presence of an extra exocyclic double bond, a further oxidation wave at lower potentials was observed (+1.04 and +1.05 V vs SCE).

3. Conclusion

To sum up, we have described in this paper an easy access to a new series of unsaturated Fischer-type carbene complexes, based on the high reactivity of carbanions of Fischer-type carbene complexes with pyrylium salts. This reactivity scheme will be applied to other heterocyclic cations.

The alcoxymethylenepyran carbene complexes obtained show a partial pyrylium character owing to the π electron-accepting ability of the carbenic fragment and to the electron-releasing properties of the methylenepyran part. The polarized structure of this type of complexes, which attributes them solvatochromism properties,[14c−23] suggests that they are good candidates for NLO.[24]

Finally, Pd^0 catalytic self-dimerization of these molecules,[25] to obtain electron rich unsaturated structures, are currently being undertaken in our laboratory.

4. Experimental

4.1. General

All preparations involving organometallic methylenepyrans were carried out in an atmosphere of dry nitrogen. Solvents were dried and distilled according to standard procedure.[26] ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$, in acetone-d_6, or in THF-d_8 on a Brücker 60, 300 or 500 MHz spectrometer. Infrared spectra were recorded on a Perkin–Elmer spectrometer FTIR-1000 using KBr plates. Elemental analysis were performed by the Service Central de Microanalyses du CNRS at Lyon, France.

Mass spectra were obtained on a High Resolution MS/MS Zab spec Tof micromass (Centre Regional de Mesures Physiques de l'Ouest Université de Rennes 1).

Optical absorption spectra were measured with a Pye Unicam SP 7-500 spectrophotometer.

Cyclic voltammetry measurement were performed on a potentiostat EGG 273 monitored by computer software Princeton 275.

The pyrylium salts were prepared according to the standard literature.[1]

4.2. X-Ray crystallography

Complex **3e** was crystallized from an ether/petroleum–ether mixture. The crystal was set up on an automatic four-circle diffractometer. The structure was solved by using the Patterson method with the aid of the program CRYSTALS.[27]

The crystallographic data collection parameters appear in Table 2. Bond lengths (Å) and angles (°) are reported in Tables 3 and 4.

Table 2. Crystallographic data parameters of **3e**

Empirical formula	$C_{27}H_{18}O_7$
Fw	638.3
Lattice parameters	
7.442(4)	
b (Å)	24.256(4)
c (Å)	13.324(4)
α (°)	90
β (°)	97.1(3)
γ (°)	90
V (Å^3)	2384(1)
Z-value	4
Crystal system	Monoclinic
Space group	$P2_1/c$
μ (cm^{-1})	49.9
D (g cm^{-3})	1.78
Diffractometer	CAD4 Enraf-Nonius
Radiation	Mo Kα (λ=0.71069 Å)
Scan type	ω/20
Range of scan (°)	$0.8+0.345t_g\theta$
Limits θ (°)	1–25
Temperature	Room temperature
Octants réunis	0.8, 0.28, −15.15
Number of tables	4647
Number of single table	4179
Number of single table used for refinement	$3171(F_o)^2>3\sigma(F_o)^2$
R (int)	0.0198
$R=\sum\lvert\lvert F_o\rvert-\lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$	0.0480
Rw[a]$=[\sum w(\lvert F_o\rvert-\lvert F_c\rvert)^2/\sum wF_o^2]^{1/2}$	0.0555
Absorbance correction	Psi-scan
Extinction parameter	131
Goodness of fit s	1.07
Number of variables	372
$\Delta\rho_{min}$ (e Å^{-3})	−1.13
$\Delta\rho_{max}$ (e Å^{-3})	2.59

[a] $w=w'[1-((\lvert\lvert F_o\rvert-\lvert F_c\rvert\rvert)/6\sigma(F_o))^2]^2$ with $w'=1/\sum rA_rT_r(X)$ with three coefficients, 7.59, −1.13 and 5.98 for a Chebychev' series, for which X is $F_o/F_{o(max)}$.

Table 3. Bond lengths (Å) for **3e**

W(1)–C(2′)	2.218(7)	O(2)–C(2′)	1.318(9)
W(1)–C(8′)	2.04(1)	O(2)–C(3′)	1.44(1)
W(1)–C(6′)	2.017(9)	O(1)–C(2)	1.372(9)
W(1)–C(4′)	2.029(9)	O(1)–C(6)	1.346(8)
W(1)–C(7′)	2.016(9)	O(3)–C(4′)	1.13(1)
W(1)–C(5′)	2.09(1)	O(6)–C(7′)	1.13(1)
C(2′)–C(1′)	1.43(1)	O(4)–C(5′)	1.10(1)
C(1′)–C(4)	1.40(1)	O(7)–C(8′)	1.14(1)
C(4)–C(5)	1.44(1)	O(5)–C(6′)	1.14(1)
C(4)–C(3)	1.43(1)	C(7)–C(8)	1.53(1)
C(5)–C(6)	1.33(1)	C(8)–C(9)	1.48(1)
C(3)–C(2)	1.36(1)	C(9)–C(14)	1.38(1)
C(6)–C(15)	1.49(1)	C(9)–C(10)	1.41(1)
C(2)–C(10)	1.45(1)	C(14)–C(13)	1.38(1)
C(3)–C(7)	1.50(1)	C(13)–C(12)	1.37(1)
C(15)–C(16)	1.38(1)	C(12)–C(11)	1.38(1)
C(15)–C(20)	1.38(1)	C(11)–C(10)	1.39(1)
C(16)–C(17)	1.40(1)	C(18)–C(19)	1.37(1)
C(19)–C(20)	1.38(1)	C(17)–C(18)	1.38(1)

Table 4. Angles of bonds (°) for **3e**

C(2′)–W(1)–C(4′)	97.6(3)	C(2′)–W(1)–C(8′)	90.9(3)
C(4′)–W(1)–C(8′)	93.4(4)	C(2′)–W(1)–C(7′)	176.6(4)
C(4′)–W(1)–C(7′)	84.1(4)	C(8′)–W(1)–C(7′)	92.0(4)
C(2′)–W(1)–C(6′)	90.8(3)	C(4′)–W(1)–C(6′)	171.5(4)
C(8′)–W(1)–C(6′)	87.6(3)	C(7′)–W(1)–C(6′)	87.5(4)
C(2′)–W(1)–C(5′)	86.0(3)	C(4′)–W(1)–C(5′)	90.0(3)
C(8′)–W(1)–C(5′)	17.7(3)	C(7′)–W(1)–C(5′)	91.0(4)
C(6′)–W(1)–C(5′)	89.4(3)	C(2′)–O(2)–C(3′)	121.2(7)
C(6)–O(1)–C(2)	119.0(5)	W(1)–C(2′)–O(2)	130.0(6)
W(1)–C(2′)–C(1′)	120.1(5)	O(2)–C(2′)–C(1′)	109.9(7)
C(2′)–C(1′)–C(4)	131.2(7)	C(1′)–C(4)–C(5)	124.3(7)
C(1′)–C(4)–C(3)	120.3(6)	C(5)–C(4)–C(3)	115.2(6)
C(4)–C(5)–C(6)	121.2(7)	O(1)–C(6)–C(5)	122.4(6)
O(1)–C(6)–C(15)	111.8(6)	C(5)–C(6)–C(15)	125.8(7)
O(1)–C(2)–C(3)	122.2(6)	O(1)–C(2)–C(10)	112.1(6)
C(3)–C(2)–C(10)	125.5(7)	C(4)–C(3)–C(2)	119.9(6)
C(4)–C(3)–C(7)	122.6(6)	C(2)–C(3)–C(7)	117.5(7)
C(3)–C(7)–C(8)	114.5(7)	C(7)–C(8)–C(9)	114.5(7)
C(8)–C(9)–C(14)	121.2(8)	C(8)–C(9)–C(10)	119.4(7)
C(14)–C(9)–C(10)	119.4(8)	C(9)–C(14)–C(13)	119.8(9)
C(14)–C(13)–C(12)	120.9(9)	C(13)–C(12)–C(11)	120.7(9)
C(12)–C(11)–C(10)	119.2(8)	C(2)–C(10)–C(9)	117.2(7)
C(2)–C(10)–C(11)	122.9(7)	C(9)–C(10)–C(11)	119.9(8)
W(1)–C(4′)–O(3)	174.0(9)	W(1)–C(8′)–O(7)	179.5(8)
W(1)–C(7′)–O(6)	176.5(13)	W(1)–C(6′)–O(5)	176.0(8)
W(1)–C(5′)–O(4)	177.2(8)	C(6)–C(15)–C(16)	119.7(7)
C(6)–C(15)–C(20)	120.6(7)	C(16)–C(15)–C(20)	119.7(7)
C(15)–C(16)–C(17)	119.8(8)	C(16)–C(17)–C(18)	119.0(9)
C(17)–C(18)–C(19)	121.1(9)	C(18)–C(19)–C(20)	119.6(9)
C(15)–C(20)–C(19)	120.7(8)		

Detailed crystallographic data for compound **3e** have been deposited at the Cambridge Crystallographic Data Centre (No. CCDC 182873) and are available of request.

4.3. Computational details

DFT calculations were carried out using the Amsterdam Density Functional (ADF) program[28] developed by Baerends and co-workers.[29] Electron correlation was treated within the local density approximation (LDA) in the Vosko–Wilk–Nusair parametrization.[30] The nonlocal corrections of Becke[31] and of Perdew[32] were added to the exchange and correlation energies, respectively. The numerical integration procedure applied for the calculations where developed by te Velde et al.[29] The atom electronic configurations were described by a triple-ζ Slater-type orbital (STO) basis set for H 1s, C 2s and 2p, O 2s and 2p and W 4f, 5d and 6s, augmented with a 3d single-ζ polarization for C and O and atoms and with a 2p single-ζ polarization for H atom. A double-ζ STO basis set was used for W 5s and 5p. A single-ζ STO basis set was used for W 6p. A frozen-core approximation was used to treat the core shells up to 1s for C, N and O and up to 4d for W.[29a] The geometries were fully optimized using the analytical gradient method implemented by Verluis and Ziegler.[33]

4.4. Preparation of new heterocyclic organometallic carbenes

4.4.1. General procedure for the preparation of methylenepyran carbene complexes. At −78°C, 0.75 ml of a 2.1 M solution of *n*-butyllithium (1.6×10^{-3} mol) was added to a solution of methoxymethylpentacarbonylcarbene complex (1.6×10^{-3} mol), in dry THF(10 ml), in a N_2 atmosphere. Pyrylium salt (3.2×10^{-3} mol), was then added. The solution was stirred during 1 h at room temperature. Removal of the THF at low pressure left a dark purple residue which was diluted in 20 ml of CH_2Cl_2. Triphenylcarbenium salt was then added. Removal the solvent left a residue which was subsequently subjected to column chromatography on Kieselgel (0.063–0.200 mm) employing 80/20 v/v petroleum–ether/diethylether as eluent. Methylenepyrans were isolated and recrystallized from diethyl ether.

3a. (Scheme 1) 85% yield; FTIR (KBr) ν (cm^{-1}): 2052, 1964, 1888, 1641, 1489, 1224. ^{1}H NMR (acetone-d_6, 300 MHz) δ: 4.61 (s, 3H, OCH_3), 7.21 (s, 1H, H(1′)), 7.33 (d, 1H, J^4=1.6 Hz, H(5)), 7.62 (m, 6H, H(Ph), 8.12 (m, 4H, H(Ph)), 8.22 (d, 1H, J^4=1.6 Hz, H(3)). ^{1}H NMR (THF-d_8, 500 MHz) δ: 4.56 (s, 3H, OCH_3), 7.09 (d, 1H, J^4=1.6 Hz, H(5)), 7.12 (s, 1H, H(1′)), 7.56 (m, 6H, H(Ph), 8.02 (m, 4H, H(Ph)), 8.13 (d, 1H, J^4=1.6 Hz, H(3)).

2D NMR (HMQC, HMBC) (THF-d_8, 500 MHz) δ ^{13}C: 68.3 (C(OCH_3)), 108.3 C(3), 110.6 C(5),126.5 C(Ph), 126.9 C(Ph), 129.8 C(Ph), 129.9 C(Ph), 132.0 C(Ph), 132.2 C(Ph), 132.6 C(4), 161.4 C(6), 162.4 C(2), 285.3 C(2′). ^{13}C NMR (acetone-d_6, 75 MHz) δ: 67.7 (q, J^1=146 Hz, C(OCH_3)), 107.7 (d, J^1=166 Hz, C(3)), 109.8 (d, J^1=169 Hz, C(5)), 125.5 (d, J^1=164 Hz, C(1′)), 125.8 (d, J^1=166 Hz, C), 128.18 (d, J^1=160 Hz, C), 129.0 (d, J^1=160 Hz, C), 129.02 (d, J^1=160 Hz, C), 129.1 (s, C(Ph)), 131.4 (d, J^1=162 Hz, C), 131.5 (d, J^1=160 Hz, C), 131.9 (d, J^1=161 Hz, C), 132.3 (s, C(Ph)), 137.1 (s, C(4)), 159.9 (s, C(6)), 161.2 (s, C(2)), 199.0 (s, C(CO)), 204.0 (s, C(CO)), 284.0 (s, C(2′)). UV–Vis (nm): CCl_4: 542 (ε=23200); 389 (ε=10770); 334 (ε=11950); DMSO: 515 (ε=17700); 387 (sh); 356 (ε=8790); MS *m/z* Calcd for $C_{25}H_{16}O_7W$: 612.0406 (M+). Found 612.0422. Mp 110°C.

3′a. (Scheme 1) 55% yield; FTIR (KBr) ν (cm^{-1}): 2043, 1967, 1891, 1641, 1488, 1201. ^{1}H NMR (acetone-d_6, 300 MHz) δ: 4.75 (s, 3H, OCH_3), 7.14 (s, 1H, H(1′)), 7.27 (d, 1H, J^4=1.6 Hz, H(5)), 7.62 (m, 6H, Ph), 8.10 (m, 4H, Ph), 8.14 (d, 1H, J^4=1.6 Hz, H(3)). ^{13}C NMR (acetone-d_6, 75 MHz) δ: 65.9 (q, J^1=146 Hz, C(OCH_3)), 108.0 (d, J^1=178 Hz, C(3)), 110.4 (d, J^1=178 Hz, C(5)), 126.6 (d, J^1=160 Hz, C(1′)), 127.1 (d, J^1=160 Hz, C), 128.1 (s, C(Ph)), 128.3 (d, J^1=160 Hz, C), 128.5 (d, J^1=160 Hz, C), 130.0 (d, J^1=159 Hz, C), 130.1 (d, J^1=160 Hz, C), 131.0 (d, J^1=156 Hz, C), 132.3 (d, J^1=159 Hz, C(Ph)), 132.4 (d, J^1=160 Hz, C(Ph)), 132.6 (s, C(Ph)), 136.8 (s, C(4)), 161.6 (s, C(2)), 162.8 (s, C(6)), 219.3 (s, C(CO)), 225.5 (s, C(CO)), 307.1 (s, C(2′)). UV–Vis (nm): CCl_4: 543 (ε=22550); 395 (ε=17110); 329 (ε=16300); DMSO: 523 (ε=21350); 392 (ε=11590); 350 (ε=13930); MS *m/z* Calcd for $C_{25}H_{16}OCr$: 480.0301 (M+). Found 480.031. Anal. $C_{25}H_{16}O_7Cr$: calcd C 62.55; H 3.36; found C 62.51; H 3.36. Mp 105°C.

3b. (Scheme 1) 25% yield; FTIR (KBr) ν (cm^{-1}): 2067, 2053, 1929, 1631, 1486, 1414. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 4.60 (s, 3H, OCH_3), 7.07 (d, 1H, J^4=1.6 Hz, H(5)), 7.12 (s, 1H, H(1′)), 7.20–7.30 (m, 3H, H(Th)), 8.01 (d, 1H, J^4=1.6 Hz, H(3)). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 68.5 (q, J^1=145 Hz, C(OCH_3)), 106.9 (d, J^1=162 Hz, C(3)), 109.0 (d, J^1=160 Hz, C(5)), 129.1 (d, J^1=157 Hz, C), 129.7 (d, J^1=160 Hz, C(1′)), 129.6 (d, J^1=160 Hz, C), 129.7 (d, J^1=160 Hz, C), 129.8 (d, J^1=160 Hz, C), 130.02 (d, J^1=160 Hz, C), 131.2 (d, J^1=160 Hz, C), 131.3 (d, J^1=160 Hz, C), 131.8 (d, J^1=160 Hz, C), 135.4 (s, C(Ph)), 135.6 (s, C(Ph)), 139.4 (s, C(4)), 156.8 (s, C(2)), 158.0 (s, C(6)), 199.9 (s, C(CO)), 204.2 (s, C(CO)), 288.8 (s, C(2′)); MS *m/z* Calcd for $C_{21}H_{12}O_7S_2W$: 623.9534 (M+). Found 623.9536. Anal. $C_{21}H_{12}O_7S_2W$: calcd C 40.42; H 1.93; found C 40.40; H 1.94.

3c. (Scheme 1) 20% yield; FTIR (KBr) ν (cm^{-1}): 2921, 2849, 2054, 1963, 1912, 1892, 1633, 1604, 1480, 1173. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.90 (t, 6H, H(CH_3)), 1.30–2.00 (m, 32H, H(CH_2)), 4.10 (t, 4H, OCH_2), 4.50 (s, 3H, OCH_3), 6.50 (d, 1H, J^4=1.3 Hz, H(5)), 6.90 (s, 1H, H(1′)), 7.02 (dd, 4H, *J*=8.8, 5.9 Hz, H(Ph)), 7.80 (dd, 4H, *J*=8.8, 1.8 Hz, H(Ph)), 7.90 (d, 1H, J^4=1.3 Hz, H(3)). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 14.1 (q, J^1=119 Hz, C(CH_3)), 22.7 (t, J^1=125 Hz, C(CH_2)), 26.0 (t, J^1=112 Hz, C(CH_2), 29.1 (t, C(CH_2)), 29.3 (t, C(CH_2)), 29.4 (t, C(CH_2)), 29.6 (t, C(CH_2)), 31.9 (t, C(CH_2)), 66.4 (t, J^1=142 Hz, C(OCH_2)), 67.4 (t, J^1=133 Hz, C(OCH_2)), 106.3 (d, J^1=133 Hz, C(3)), 108.1 (d, J^1=128 Hz, C(5)), 115.10 (d, J^1=161 Hz, C(Ph)), 115.15 (d, J^1=161 Hz, C(Ph)), 123.7 (s, C(Ph)), 123.9 (s, C(Ph)), 127.2 (d, J^1=159 Hz), 127.5 (d, J^1=160 Hz), 129.9 (d, J^1=159 Hz, C(1′)), 138.9 (s, C(4)), 160.2 (s, C(6)), 161.4 (s, C(2)), 161.7 (s, C(Ph)), 161.9 (s, C(Ph)), 199.0 (s, C(CO)), 204.0 (s, C(CO), 282.1 (s, C(2′)). MS *m/z* Calcd for $C_{45}H_{56}O_9W$: 924.3442 (M+). Found 924.3490. Anal. $C_{45}H_{56}O_9W$: calcd C 60.54; H 6.32; found C 58.47; H 6.11.

3d. (Scheme 1) 30% yield; FTIR (KBr) ν (cm^{-1}): 2922, 2851, 2055, 1969, 1894, 1638, 1581, 1493, 1225. ^{1}H NMR ($CDCl_3$, 125 MHz) δ: 0.90 (t, 6H, H(CH_3)), 1.30–2.00 (m, 32H, H(CH_2)), 4.03 (t, 4H, OCH_2), 4.52 (s, 3H, OCH_3), 6.61 (d, 1H, J^4=1.7 Hz, H(5)), 7.00 (s, 1H, H(1′), 7.05 (m, 2H, H(Ph)), 7.33 (m, 2H, H(Ph)), 7.41 (m, 4H, H(Ph)), 7.92 (d, 1H, J^4=1.3 Hz, H(3)). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 14.1

(q, J^1=123 Hz, C(CH$_3$)), 22.7 (t, J^1=124 Hz, C(CH$_2$)), 26.1 (t, J^1=124 Hz, C(CH$_2$)), 29.3 (t, C(CH$_2$)), 29.40 (t, C(CH$_2$)), 29.45 (t, C(CH$_2$)), 29.6 (t, C(CH$_2$)), 31.9 (t, C(CH$_2$)), 67.8 (t, J^1=146 Hz, C(OCH$_2$)), 68.4 (t, J^1=157 Hz, C(OCH$_2$)), 108.0 (d, J^1=156 Hz, C(3)), 110.0 (d, J^1=144 Hz, C(5)), 111.7 (d, J^1=160 Hz, C(Ph)), 112.3 (d, J^1=160 Hz, C(Ph)), 130.3 (d, J^1=161 Hz), 130.3 (d, J^1=161 Hz), 131.0 (d, J^1=157 Hz, C(1′)), 132.8 (s, C(Ph)), 133.3 (s, C(Ph)), 137.3 (s, C(4)), 159.7 (s, C(6)), 159.8 (s, C(2)), 159.9 (s, C(Ph)), 161.2 (s, C(Ph)), 199.1 (s, C(CO)), 204.0 (s, C(CO)), 282.8 (s, C(2′)). MS *m/z* Calcd for $C_{45}H_{56}O_9W$: 868.3536 (M−2CO)+. Found 868.3529.

3e. (Scheme 3) 54% yield; FTIR (KBr) ν (cm^{-1}): 2053, 1967, 1899, 1631, 1575, 1481, 1216. ^{1}H NMR (acetone-d_6, 300 MHz) δ: 2.85 (t, 2H, J^3=7.9 Hz, CH$_2$), 3.05 (t, 2H, J^3=7.9 Hz, CH$_2$), 4.55 (s, 3H, OCH$_3$), 7.10 (s, 1H, H(1′), 7.40 (m, 2H, Ph), 7.54 (m, 4H, Ph), 7.87 (m, 3H, Ph), 8.15 (s, 1H, H(5)). ^{13}C NMR (acetone-d_6, 125 MHz) δ: 67.9 (q, J^1=145 Hz, C(OCH$_3$)), 107.8 (d, J^1=177 Hz, C(5)), 117.0 (s, C(3)), 123.0 (d, J^1=159 Hz, C), 127.2 (d, J^1=154 Hz, C), 128.0 (d, J^1=159 Hz, C), 128.3 (s, C(9)), 129.2 (d, J^1=160 Hz, C(1′)), 130.9 (d, J^1=160 Hz, C), 131.1 (d, J^1=160 Hz, C), 132.1 (s, C(Ph)), 136.7 (s, C(10)), 137.8 (s, C(4)), 155.7 (s, C(2)), 158.9 (s, C(6)), 199.2 (s, C(CO)), 204.3 (s, C(CO)), 286.2 (s, C(2′)). MS *m/z* Calcd for $C_{27}H_{18}O_7W$: 638.0562 (M+). Found 638.0585.

3f. (Scheme 4) 55% yield; FTIR (KBr) ν (cm^{-1}): 2054, 1894, 1616, 1504, 1225. ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 4.63 (s, 3H, OCH$_3$), 7.28 (s, 1H, H(1′)), 7.40–7.80 (m, 9H, Ph), 8.05 (s, 1H, H(3)). ^{13}C NMR (CDCl$_3$, 75 MHz) δ: 68.4 (q, J^1=146 Hz, C(OCH$_3$)), 105.2 (d, J^1=168 Hz, C(3)), 118.5 (d, J^1=160 Hz, C(1′)), 120.0 (s, C(5)), 124.2 (d, J^1=160 Hz, C), 126.1 (d, J^1=160 Hz, C), 126.2 (d, J^1=160 Hz), 127.9 (d, J^1=160 Hz), 128.3 (d, J^1=160 Hz), 128.5 (s, C(Ph)), 128.7 (d, J^1=160 Hz), 129.1 (d, J^1=160 Hz), 131.0 (d, J^1=160 Hz), 132.0 (s, C(4)), 132.3 (d, J^1=160 Hz), 155.4 (s, C(6)), 159.3 (s, C(2)), 198.8 (s, C(CO)), 204.2 (s, C(CO)), 294.0 (s, C(2′)). MS *m/z* Calcd for $C_{23}H_{14}O_7W$: 586.0249 (M+). Found 586.0222.

3g. 5% yield; FTIR (KBr) ν (cm^{-1}): 2052, 1893, 1621, 1469, 1241. MS *m/z* Calcd for $C_{29}H_{20}O_7W$: 664.0719 (M+). Found 664.0723.

4.4.2. Synthesis of the pyranmethoxycarbene complex 4a (Scheme 1). At −78°C, 0.75 ml of a 2.1 M solution of *n*-butyllithium (1.6×10^{-3} mol) was added to a solution of methoxymethylpentacarbonyl carbene complex (M=W) (0.600 g, 1.6×10^{-3} mol) in dry THF in a N$_2$ atmosphere. The mixture was stirred quickly for 10 min, 2,6-diphenylpyryliumtetrafluoroborate (0.470 g, 1.44×10^{-3} mol) was then added slowly. The mixture was allowed to warm up to room temperature, and was stirred for 1 h. Removal of the THF at low pressure left a purple residue. Separation on silica gel plates (eluent: petroleum ether/diethyl ether 80/20%) afforded **4a** (0.15 g, 13% yield), and the methylenepyran complex **3a** (0.42 g, 43% yield).

4a. FTIR (KBr) ν (cm^{-1}): 2071, 1899, 1685, 1446, 1283, 759. ^{1}H NMR (acetone-d_6, 60 MHz) δ: 3.60 (s, 3H, H(1′) and H(4)), 4.70 (s, 3H, OCH$_3$), 5.60 (s, 2H, H(5.3)), 7.30 (m, 6H(Ph)), 7.70 (m, 4H(Ph)). MS *m/z* Calcd for $C_{25}H_{18}O_7W$: 613.0484 (M−H$^+$). Found 613.0484. Mp 100°C.

The same procedure was applied to synthesize **4b**.

4b. FTIR (KBr) ν (cm^{-1}): 2068, 1917, 1638, 1494, 1444, 1226, 696. ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 3.70 (d, 2H, J^3=6.7 Hz, H(1′)), 3.90 (s, 3H, OCH$_3$), 4.20 (t, 1H, J^3=6.7 Hz, H(4)), 7.10–7.40 (m, 20H, Ph). ^{13}C NMR (CDCl$_3$, 75 MHz) δ: 44.0 (dd, J^1=137 Hz, J^2=5.6 Hz, C(1′)), 69.5 (q, J^1=147 Hz, C(OCH$_3$)), 70.9 (td, J^1=129 Hz, J^3=4.9 Hz, C(4))), 114.9 (s, C(3)), 115.7 (s, C(3)), 134.5 (s, C(Ph)), 135.2 (s, C(Ph)), 139.2 (s, C(Ph)), 139.4 (s, C(Ph)), 147.0 (s, C(6)), 149.1 (s, C(2)), 197.2 (s, C(CO)), 203.4 (s, C(CO)), 337.40 (s, C(2′)). MS *m/z* Calcd for $C_{37}H_{26}O_7W$: 767.1266 (M+H$^+$). Found 767.1273.

4.4.3. Synthesis of the pyrandimethylamino carbene complex 4c (Scheme 6). To a solution of dimethylaminomethylpentacarbonylcarbene complex (M=W) (0.400 g; 1.04×10^{-3} mol) in dry THF under N$_2$ atmosphere, was added at −78°C, 0.42 ml of a 2.1 M solution of *n*-butyllithium (1.04×10^{-3} mol). After the mixture was stirred rapidly at −78°C for 10 min, 2,6-diphenylpyryliumtetrafluoroborate (0.350 g, 1.1×10^{-3} mol) was added. The mixture was allowed to warm to room temperature, and was stirred for 1 h. Removal of the THF at low pressure left a yellow residue. Chromatography on silica gel plates (eluent: petroleum ether–diethylether 50/50%) produced **4c** (0.260 g; 43% yield) as yellow material.

4c. FTIR (KBr) ν (cm^{-1}): 2059, 1920, 1894, 1639, 1519, 1356, 1284, 765. ^{1}H NMR (acetone-d_6, 300 MHz) δ: 1.34 (t, 3H, J^3=7.2 Hz, H(CH$_3$)), 1.55 (t, 3H, J^3=7.5 Hz, H(CH$_3$)), 3.60 (d, 2H, J^3=7.7 Hz, H(1′)), 4.02 (q, 2H, J^3=7.5 Hz, H(CH$_2$)), 4.11 (m, 1H, H(4)), 4.32 (q, 2H, J^3=7.2 Hz, H(CH$_2$)), 5.50 (d, 2H, J^4=4 Hz, H(3,5)), 7.35–7.50 (m, 6H, H(Ph)), 7.75 (m, 4H, H(Ph)). ^{13}C NMR (acetone-d_6, 75 MHz) δ: 14.5 (q, J^1=146 Hz, C(OCH$_3$)), 107.7 (d, J^1=166 Hz, C(3)), 109.8 (d, J^1=169 Hz, C(5)), 125.5 (d, J^1=164 Hz, C(1′)), 125.8 (d, J^1=166 Hz, C), 128.18 (d, J^1=160 Hz, C), 129.0 (d, J^1=160 Hz, C), 129.02 (d, J^1=160 Hz, C), 129.1 (s, C(Ph)), 131.4 (d, J^1=162 Hz, C), 131.5 (d, J^1=160 Hz, C), 131.9 (d, J^1=161 Hz, C), 132.3 (s, C(Ph)), 137.1 (s, C(4)), 159.9 (s, C(6)), 161.2 (s, C(2)), 199.0 (s, C(CO)), 204.0 (s, C(CO)), 284.0 (s, C(2′)). MS *m/z* Calcd for $C_{28}H_{25}NO_6W$: 655.1190 (M+). Found 655.1180. Mp 130°C.

4.4.4. Synthesis of the aminocarbenepyrylium salt 5b (Scheme 6). The methylenepyranaminocarbene complex **4c** (0.200 g, 3.05×10^{-4} mol) in CH$_2$Cl$_2$ solution was treated with a large excess of triphenylcarbeniumtetrafluoroborate. After being stirred for 8 h, the mixture was diluted with ether, and filtered to give **5b** as yellow solid (0.100 g, 5% yield). FTIR (KBr) ν (cm^{-1}): 1960, 1855, 1629, 1578, 1083. MS *m/z* Calcd for $C_{28}H_{24}NO_6WBF_4$: 330.1858 (M−W(CO)$_5$)$^+$. Found 330.1866.

4.4.5. Synthesis of the ditertiobutylmethylenepyranmethoxycarbene complex 3i (using triphenylcarbeniumhexafluorophosphate salt as oxidizing reagent) (Scheme 1). Methoxymethylpentacarbonylcarbene (M=W) (0.400 g;

9.8×10^{-4} mol), 2,6-ditertiobutylpyryliumtetrafluoroborate and triethylamine (0.35 ml; 1.090×10^{-3} mol), were stirred in 15 ml of THF at room temperature for 30 min. Following hydrolysis, extraction with ether, drying over $MgSO_4$ and distillation of the solvent, the yellow residue obtained was dissolved in 10 ml of CH_2Cl_2· and triphenylcarbeniumhexafluorophosphate salt (0.420 g; 1.08×10^{-3} mol) was added. After being stirred for 30 min, the mixture was hydrolyzed. Extraction with ether, drying over $MgSO_4$, and distillation of the solvent left a red residue. The residue was subjected to column chromatography on silica gel with petroleum ether as an eluent to finally produced **3i** (0.445 g; 79% yield).

3i. FTIR (KBr) ν (cm^{-1}): 2970, 2055, 1892, 1643, 1494, 1244, 1201, 939, 698. ^1H NMR (THF-d_8, 500 MHz) δ: 1.73 (s, 9H, H(CH_3)), 4.43 (s, 3H, OCH_3), 6.26 (s, 1H, H(5)), 6.90 (s, 1H, H(1′), 7.50 (s, 1H, H(3)). ^{13}C NMR (THF-d_8, 125 MHz) δ: 28.0 (C(CH_3)), 67.6 (C(OCH_3)), 106.5 (C(3)), 108.3 (C(5)), 142.0 (C(4)), 174.0 (C(6)), 175.3 (C(2)), 200.1 (t, J_{CW}=125 Hz, C(CO)), 204.3 (t, J_{CW}=125 Hz, C(CO)), 283.1 (C(2′)). MS *m/z* Calcd for $C_{21}H_{24}O_7W$: 572.1032 (M+). Found 572.1037.

4.4.6. Synthesis of the ditertiobutylmethylenepyranemethoxy carbene complex 3i (using ferrocenium salt as oxidizing reagent). Methoxymethylpentacarbonylcarbene complex (M=W) (0.500 g; 1.22×10^{-3} mol), 2,6-ditertiobutylpyryliumhexafluorophosphate (0.515 g; 1.22 mol) and triethylamine (0.38 ml; 2.44×10^{-3} mol), were stirred in 15 ml of THF for 30 min. Following hydrolysis, extraction with ether, drying over $MgSO_4$ and distillation of the solvent, the yellow residue obtained was dissolved in 15 ml of CH_2Cl_2 and ferroceniumhexafluorophosphate salt (0.420 g; 1.08×10^{-3} mol) was added. After being stirred for 45 min, the mixture was hydrolyzed. Following extraction with ether, drying over $MgSO_4$ and distillation of the solvent, the yellow residue was subjected to column chromatography on silica gel (eluent: petroleum ether) to produce **3i** (0.102 g; 16% yield) and ferrocene (0.130 g; 53% yield).

4.4.7. Aminolysis of the methylenepyran carbene complex 3a (Scheme 7)

4.4.7.1. Synthesis of aminocarbene 3j. A solution of **3a** (0.145 g; 2.3×10^{-4} mol) in 15 ml of diethylether/petroleum ether mixture was treated with a large excess of diethylamine (10^{-2} mol) at room temperature, until the solution became yellow. Water was poured on to the reaction mixture and the product was extracted with ether. The extract was dried over $MgSO_4$ and the solvent was removed under reduced pressure. Chromatography on silica gel plates (eluent: petroleum ether/diethylether 80/20% produced **3j** as yellow solid (0.060 g; 41% yield).

FTIR (KBr) ν (cm^{-1}): 2055, 1897, 1654, 1516. ^1H NMR (acetone-d_6, 300 MHz) δ: 1.56 (t, 3H, J^3=7.2 Hz, H(CH_3)), 4.01 (m, 2H, J^3=6.0 Hz, H(CH_2)), 6.44 (s, 1H, H(1′)), 6.74 (dd, 1H, J^4=1.9, 0.7 Hz, H(5)), 6.75 (d, 1H, J^4=1.8 Hz, H(3)), 7.40–7.60 (m, 6H, 2H(Ph)), 7.90 (m, 4H, H(Ph)), 10.14 (s, 1H(NH)). ^{13}C NMR (acetone-d_6, 75 MHz) (two isomers appear during the analysis) δ: 14.5 and 15.2 (q, J^1=127.9 Hz, C(CH_3)), 51.3 and 51.4 (t, J^1=139 Hz, C(CH_2)), 102.7 and 102.9 (d, J^1=176 Hz, C(3)), 107.4 and 107.8 (d, J^1=174 Hz, C(5)), 123.6 and 123.8 (s, C(Ph)), 125.3 and 125.4 (s, C(Ph)), 125.6 (d, J^1=155 Hz, C), 125.9 (d, J^1=150 Hz, C), 130.8 (d, J^1=159 Hz, C), 129.5 (d, J^1=163 Hz, C), 129.7 (d, J^1=160 Hz, C), 129.8 (d, J^1=159 Hz, C), 130.4 (d, J^1=156 Hz, C), 130.6 (d, J^1=160 Hz, C), 153.3 and 154.1 (s, C(2)), 154.4 and 155.0 (s, C(6)), 133.4 and 133.5 (s, C(4)), 199.5 (s, C(CO)), 205.8 (s, C(CO)), 242.0 (s, C(2′)). MS *m/z* Calcd for $C_{26}H_{19}NO_6W$: 652.0722 (M+). Found 625.0731.

4.4.8. Synthesis of aminocarbene 3k (Scheme 7). 0.200 g of **3a** (3.2×10^{-4} mol) and (3.2×10^{-3} mol) of benzylamine produced 0.770 g of **3k** (35% yield).

FTIR (KBr) ν (cm^{-1}): 2054, 1912, 1651, 1493. ^1H NMR (acetone-d_6, 300 MHz) δ: 5.28 (s, 2H, H(CH_2)), 6.50 (s, 1H, H(1′)), 6.64 (d, 1H, J^4=2.0 Hz, H(5)), 6.78 (d, 1H, J^4=2.0 Hz, H(3)), 7.40–7.60 (m, 11H, H(Ph)), 7.80–8.10 (m, 4H, H(Ph)), 10.05 (s, 1H(NH)). ^{13}C NMR (acetone-d_6, 125 MHz) δ: 38.3 (t, J^1=125.6 Hz, C(CH_2)), 102.7 and 103.1 (d, J^1=159.0 Hz, C(3)), 107.6 and 108.1 (d, J^1=163 Hz, C(5)), 122–133 (s, C(Ph)), 133.7 (s, C(4)), 153.6 and 154.4 (s, C(2)), 154.9 and 155.5 (s, C(6)), 199.7 (s, C(CO)), 206.2 (s, C(CO)), 242.2 (s, C(2′)). MS *m/z* Calcd for $C_{31}H_{21}NO_6W$: 687.0878 (M+). Found 687.0884.

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