

Synthesis, structure and reactivity of acetylenic $\text{Co}_2(\text{CO})_6$ pyrylium salts. Electronic influence of the $\text{Co}_2(\text{CO})_6$ acetylenic fragment

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Abstract

The formation of new pyrylium salts bearing in the γ position an acetylenic $\text{Co}_2(\text{CO})_6$ fragment is described. X-ray analysis showed that the γ carbon of the pyrylium ring does not interact with a cobalt atom. However, IR values, relating to the carbonyl stretching band, suggested that a part of the positive charge is delocalized on the cluster core. Finally, the reactivity of these cationic complexes towards nucleophiles is reported. © 1997 Elsevier Science S.A.

Keywords: Pyrylium salts; Acetylenic $\text{Co}_2(\text{CO})_6$ fragment

1. Introduction

Pyrylium salts are heterocycles which possess a carbocationic character at the α and γ positions [1]. This property not only confers to them a key role in heterocyclic chemistry, but also has led to the development of a variety of practical applications notably in photography and reprography [2].

Despite their inherent interest, organometallic pyrylium salts are rare compounds and their chemistry appears to have been little developed. The only salts to have been isolated are those substituted by one or two metallocenic groups [3].

Recently, we have (1) described an easy access to γ -phenyl $\text{Cr}(\text{CO})_3$ substituted pyrylium salts via the diacetylation of complexed alkenes by Ac_2O -Lewis acid systems; (2) studied in connection with the problem of the metal carbonyl stabilization of carbenium ion, the electronic influence of the $\text{Cr}(\text{CO})_3$ group towards the heterocyclic ring [4].

On the other hand, we have used pyrylium salts bearing an organometallic moiety at the γ -position as reagents for specific conjugation of amino acids [5] and

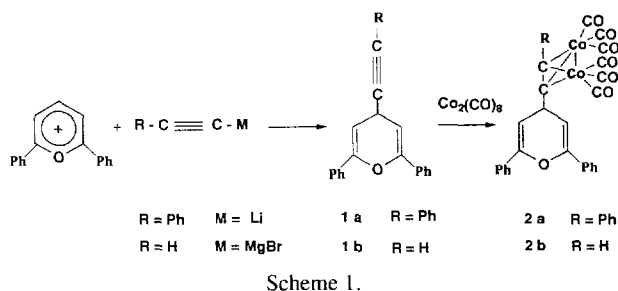
proteins [6]. Therefore we present here the synthesis and characterisation of new organometallic, non-metallocenic pyrylium salts bearing in the γ position an acetylenic $\text{Co}_2(\text{CO})_6$ fragment, in order to test their capacity to react with amino acids and proteins. The cobalt carbonyl group marker proved to be the best suited for FT-IR carbonyl metallo-immuno assay [7].

As the pyrylium ring has a positive charge, we shall also discuss its interaction towards the $\text{Co}_2(\text{CO})_6$ group, in connection with the well known stabilization mode of metal-stabilized propargylic cations [8].

2. Results and discussion

One could envisage two synthetic approaches to the γ - $\text{Co}_2(\text{CO})_6$ acetylenic derivatives of pyrylium salts. The first, tested with success in the benztrorenic series [4], involves the diacetylation of 2-substituted ethynyl $\text{Co}_2(\text{CO})_6$ propene complexes with Ac_2O in the presence of Lewis acid. The second requires the incorporation of the acetylenic fragment into the 2,6-diphenylpyrylium salt, leading to a pyran [9,10]. Subsequent complexation of the pyran by $\text{Co}_2(\text{CO})_8$ and hydride abstraction should allow the isolation of the complexed pyrylium salt. Attempts to effect the diacetylation of

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Scheme 1.

2-ethynyl $\text{Co}_2(\text{CO})_6$ propene complex in the presence of BF_3 having been unsuccessful, we chose to explore the pyran route.

The reaction of phenylethyneyllithium with the 2,6-diphenylpyrylium tetrafluoroborate salt in diethyl ether gave the expected pyran **1a** (Scheme 1). This unstable compound (in solution the formation of a dark green polar decomposition product was observed), treated with $\text{Co}_2(\text{CO})_8$ led, after chromatography, to the complexed pyran **2a** in low yield.

However, the yield increased to 51% when the complexation stage was performed without isolation of the uncomplexed pyran **1a** (Scheme 1).

In the same way, addition of ethynyl magnesium bromide to the 2,6-diphenylpyrylium salt followed by the action of $\text{Co}_2(\text{CO})_8$ allowed the isolation of the complexed pyran **2b** (36% yield).

It is noteworthy that, in contrast to the highly air sensitive pyran **1b** (which must be stored under argon in a freezer $1b^1$), the complexed one is a stable compound which can be stored in air at room temperature for several months. The complexation of the carbon–carbon triple bond not only decreases the dioxygen action [9] but also prevents the formation of the reactive allene which dimerizes at room temperature leading to a cyclobutane [10] (Scheme 2).

Finally, the complexed pyrans **2a** and **2b** react readily with the trityl cation in CH_2Cl_2 to give, after dilution, with ether a dark brown precipitate identified as the complexed pyrylium cations **3a** and **3b** (Scheme 3).

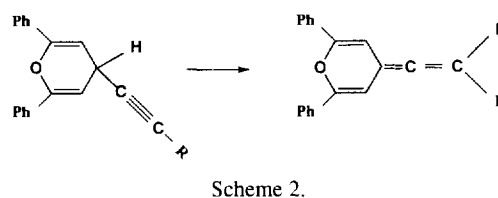
The complexes **3a**, **3b** are the first examples of organometallic non-metallocenic pyrylium salts.

3. X-ray crystal structure of **3a**. Electronic influence of the $\text{Co}_2(\text{CO})_6$ ethynyl fragment

Dark brown crystals of **3a**, were obtained by recrystallization from dichloromethane/ether.

In the solid state (Fig. 1, Table I), the acetylenic

¹ $1b^1$ ^1H NMR (CDCl_3) δ (ppm): 8.20–6.90 (m, 10H); 5.48 (d, 2H, $^3J = 4.0\text{Hz}$); 4.22 (t d, $^3J = 4.0\text{Hz}$, $^4J = 2.0\text{Hz}$); 2.25 (d, $^4J = 2.0\text{Hz}$).



Scheme 2.

$\text{Co}_2(\text{CO})_6$ fragment is comparable to complexes of neutral alkynes [11]. The $\text{Co}_1\text{--C}_3$ and the $\text{Co}_2\text{--C}_3$ distances are respectively 3.13 and 3.17 Å, too long for a viable direct interaction, involving the carbon 3, between a d orbital of a cobalt atom and the vacant π^* orbital of the pyrylium ring.

This result is reminiscent of the phenyl $\text{Cr}(\text{CO})_3$ and ferrocenyl-substituted pyrylium systems in which the stable heterocycle has no need of electronic assistance from the metal [5]. It is in contrast with the $\text{Co}_2(\text{CO})_6$ propargylium ion case, in which anchimeric assistance by the metal is required (in the absence of crystal structure determination, this proposition is supported by NMR studies [12]). The cobalt carbonyl pyrylium cation is fully comparable to the $\text{Co}_2(\text{CO})_6$ -complexed propyne iminium salt of which an X-ray structure has been reported recently [13] (Scheme 4).

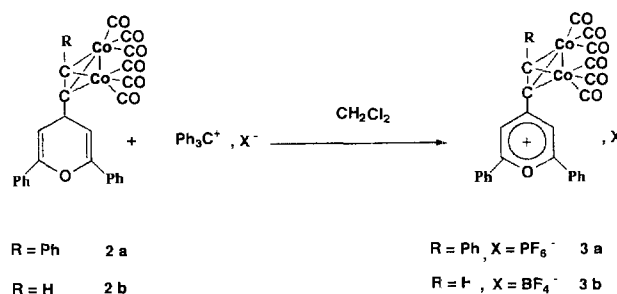
However, a comparison with the literature results relating to IR values of the carbonyl stretching bands on neutral and cationic cobalt complexes [8] (Table 2) shows that, in **3b**, the charge density on the cluster moiety appears to be between those of the $[\text{Co}_2(\text{CO})_6]$ propargylium ion and the $[\text{Co}_2(\text{CO})_6(\text{CH}\equiv\text{CCH}_2\text{X})^+]\text{BF}_4^-$ complexes [8].

This result is a consequence of the strong electron withdrawing effect of the pyrylium ring.

Finally, it is found that the α phenyls, perhaps for steric reasons and (or) for packing effects in the crystal lattice, are rotated by 21° and 32° relative to the pyrylium ring. These data are the highest observed in the known X-ray crystal structures of 2,6-diphenyl pyrylium salts [5,14].

4. Reactivity of pyrylium salts **3a**

In the absence of systematic studies relating to the chemistry of uncomplexed acetylenic pyrylium salts



Scheme 3.

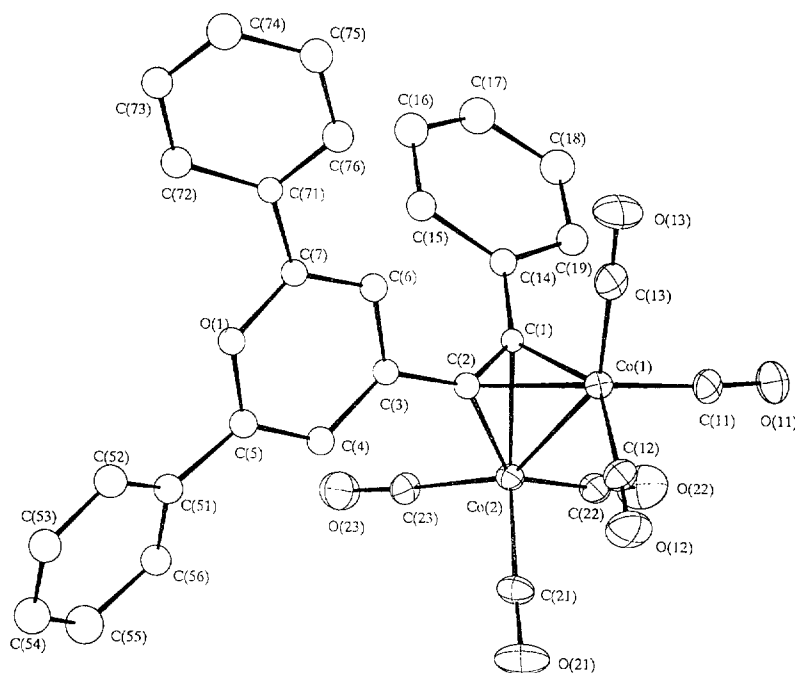
Fig. 1. Structure of **3a**.

Table 1
Selected bond distances (Å) and bond angles (deg) in **3a** [C₃₁H₁₇O₇Co₂](PF₆)

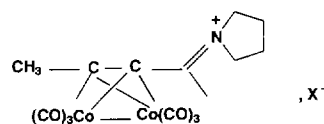
Co ₁ –Co ₂ 2.478(3); C ₁ –C ₂ 1.34(2); Co ₁ –C ₁ 1.93(1); Co ₁ –C ₂ 1.95(1); Co ₂ –C ₁ 1.99(1); Co ₂ –C ₂ 1.91(2); C ₁ –C ₁₄ 1.45(2); C ₂ –C ₃ 1.49(2); Co ₁ –C ₁₃ 1.77(2); Co ₁ –C ₁₁ 1.83(2); Co ₁ –C ₁₂ 1.87(2); Co ₁ –C ₂₁ 1.83(2); Co ₁ –C ₂₂ 1.84(2); Co ₁ –C ₂₃ 1.80(2); C–O(av.) 1.12(2); C ₃ –C ₆ 1.42(2); C ₃ –C ₄ 1.39(2); C ₄ –C ₅ 1.40(2); C ₆ –C ₇ 1.35(2); O ₁ –C ₇ 1.36(2); O ₁ –C ₅ 1.34(2); C ₁ –C ₂₁ –C ₃ 139.2(14); C ₂ –C ₁ –C ₁₄ 142.2(14); Co ₁ –C ₂ –C ₁ 69.2(9); Co ₂ –C ₂ –C ₁ 72.9(9); Co ₁ –C ₂ –C ₃ 131.1(11); Co ₂ –C ₂ –C ₃ 137.3(11); Co ₁ –C ₁ –C ₂ 70.4(9); Co ₂ –C ₁ –C ₂ 66.9(8); C ₂ –C ₃ –C ₄ 119.9(14); C ₂ –C ₃ –C ₆ 121.2(14); C ₄ –C ₃ –C ₆ 118.9(14); C ₅ –O ₁ –C ₇ 121.4(12).

(only two Russian reports are related to the reactivity of the carbon–carbon triple bond of γ -acetylenic pyrylium salts: the first shows its electrophilic character [15] and the second [16] its dienophilic property), and in order to test the ability of Co₂(CO)₆ acetylenic pyrylium salts to act as new organometallic reagents for specific conjugation of proteins, we decided to investigate the reactivity of **3a** towards some nucleophiles.

As expected **3a** reacted rapidly at the pyrylium ring in acetone–water medium, with nucleophiles such as BH₄[−], OH[−] and NH₃ [2].

With the hydroxide ion and ammonia, the reaction led to the pseudo-base **4** and to the pyridine **5**. With the borohydride ion, we observed an addition at both the α and the γ carbon atom (Scheme 5).

On the contrary, addition of aniline and benzylamine



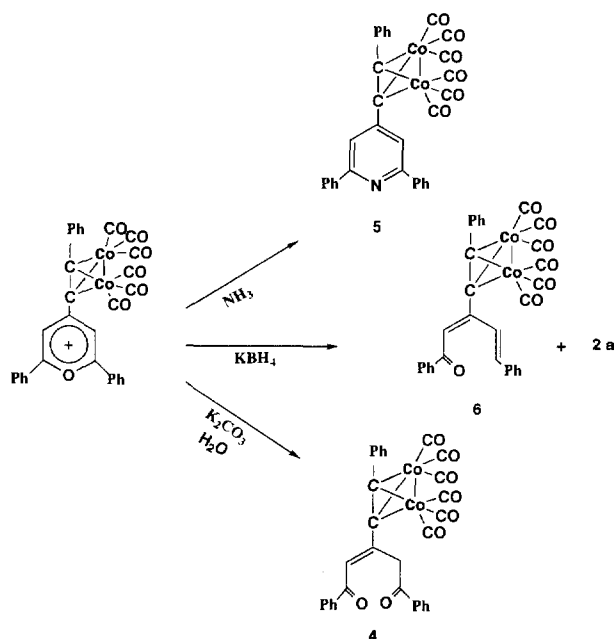
Scheme 4.

to **3a** does not allow the formation of the expected complexed pyridinium salts. The reaction gave uncharacterised uncomplexed products.

Table 2
IR values of the carbonyl bands of cobalt carbonyl complexes

Complex	ν C=O (cm ^{−1}) CH ₂ Cl ₂			Ref.
[H–C≡C–CH ₂ Co ₂ (CO) ₆] ⁺ BF ₄ [−]	2130	2105	2085	[8]
3b	2110	2080	2045	this work
[H–C≡C–CH ₂ S ⁺ (Et) ₂ Co ₂ –(CO) ₆] ⁺ BF ₄ [−]	2103	2066	2035	[8]
[H–C≡C–CH ₂ P ⁺ (Et) ₂ Co ₂ –(CO) ₆] ⁺ BF ₄ [−]	2101	2062	2037	[8]
[H–C≡C–CH ₂ PyCo ₂ (CO) ₆] ⁺ BF ₄ [−]	2103	2067	2025	[8]
[H–C≡C–CH ₂ OHC ₂ (CO) ₆] ⁺ BF ₄ [−]	2090	2050	2025	[8]

Py = pyridine



Scheme 5.

This point, and the extension of the reaction to proteins, are currently under further investigation.

5. Experimental details

All preparations involving organometallic pyrans and pyrylium complexes were carried out under an atmosphere of dry nitrogen. Solvents were dried and distilled according to standard procedures. ^1H NMR spectra were recorded in CDCl_3 or in acetone- d_6 on a Bruker A.M. 300 MHz spectrometer. Infrared spectra were recorded on a Perkin–Elmer Spectrum 1000 FTIR spectrophotometer using KBr plates. Elemental analyses were performed by the Service Central de Microanalyse du CNRS at Lyon, France.

5.1. General procedure for formation of complexed pyrans **2a** and **2b**

To a degassed diethyl ether suspension of the 2,6-diphenylpyrylium tetrafluoroborate salt (2 g, 6.25 mmol) was added at 0°C a solution of phenylethynyllithium (6.3 ml of 1 M in THF). The reaction was warmed to room temperature. When the solution turned red $\text{Co}_2(\text{CO})_8$ (2.14 g, 6.2 mmol) was added and stirring was continued for 1 h. After silica gel chromatography (petroleum) the complexed pyran **2a** was obtained. **2a**: 1.98 g (51% yield).

2,6-Diphenylpyrylium tetrafluoroborate (2 g, 6.25 mmol), ethynylmagnesium bromide (19 ml of 0.5 M in THF) and $\text{Co}_2(\text{CO})_8$ (2.14 g, 6.25 mmol) gave the pyran **2b** (1.4 g, 36% yield).

5.2. General procedure for the formation of complexed pyrylium salts **3a** and **3b**

To a degassed CH_2Cl_2 solution of **2a** (0.5 g, 0.8 mmol) was added 0.132 g (0.8 mmol) of trityl hexafluorophosphate (Ph_3CPF_6). The solution was stirred for 1 h. Addition of ether precipitates the pyrylium salts **3a** (0.415 g, 68% yield). The same procedure applied to **2b** and Ph_3CBF_4 gave **3b** (89% yield).

5.3. Reaction of nucleophiles with **3a**

To a degassed acetone–water solution of **3a** the appropriate nucleophile was added. After 5 min, water was added. After extraction with ether and drying over MgSO_4 the residue was chromatographed on a silica plate. Elution with ether–petroleum mixture gave the expected products (Scheme 5).

Table 3

Crystal data for $[\text{C}_{31}\text{H}_{17}\text{O}_7\text{Co}_2](\text{PF}_6)$

F_w	619.3
a (Å)	14.934(4)
b (Å)	9.758(2)
c (Å)	22.240(7)
α (°)	90
β (°)	106.10(2)
γ (°)	90
V (Å ³)	3114
Z	4
Crystal system	Monoclinic
Space group	Cc
Linear absorption coefficient μ (cm ⁻¹)	11.03
Density ρ (g cm ⁻³)	1.32
Diffractometer	Phillips PW 1100
Radiation	Mo K α ($\lambda = 0.71069$ Å)
Scan type	$\omega/2\theta$
Scan range	$0.8 + 0.345 \text{tg } \theta$
θ Limits (°)	2–25
Temperature of measurement	Room temperature
Octants collected	–17, 17; 0, 11; 0, 26
No. of data collected	3013
No. of unique data collected	2712
No. of unique data used for refinement	$1584 (F_o)^2 > 2.5\sigma(F_o)^2$
R_{int}	0.035
Decay of standard reflections (%)	< 1
$R = \sum F_o - F_c / \sum F_o $	0.0575
$R_w = \sum w(F_o - F_c)^2 / \sum wF_o^2$	0.0616, $w = 1.0$
Absorption correction	DIFABS (min = 0.93, max = 1.06)
Extinction parameter ($\times 10^{-6}$)	None
Goodness of fit S	0.53
No. of variables	259
$\Delta\rho_{\text{min}}$ (e Å ⁻³)	–0.51
$\Delta\rho_{\text{max}}$ (e Å ⁻³)	0.51

Table 4
Fractional atomic coordinates for $[C_{31}H_{17}O_7Co_2](PF_6)$

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq}	<i>U</i> _{iso}
Co(1)	0.3625(2)	0.0579(2)	0.0082(1)	0.0409	
Co(2)	0.3392(2)	0.3063(3)	-0.0137(1)	0.0387	
C(11)	0.423(1)	0.073(2)	0.0914(9)	0.0492	
O(11)	0.455(1)	0.082(2)	0.1429(6)	0.0810	
C(12)	0.460(1)	0.023(2)	-0.0271(9)	0.0540	
O(12)	0.516(1)	0.006(2)	-0.0504(8)	0.0850	
C(13)	0.315(1)	-0.109(2)	0.0071(9)	0.0560	
O(13)	0.282(1)	-0.216(2)	0.0069(8)	0.0785	
C(21)	0.435(1)	0.338(2)	-0.0487(8)	0.0503	
O(21)	0.495(1)	0.354(2)	-0.0685(8)	0.0762	
C(22)	0.383(1)	0.376(2)	0.0658(8)	0.0463	
O(22)	0.401(1)	0.418(2)	0.1143(7)	0.0838	
C(23)	0.261(1)	0.441(2)	-0.0503(8)	0.0449	
O(23)	0.208(1)	0.520(2)	-0.0728(8)	0.0853	
O(1)	0.1142(7)	0.051(1)	-0.2405(4)		0.038(2)
C(1)	0.2514(9)	0.166(1)	0.0011(6)		0.027(3)
C(2)	0.267(1)	0.154(2)	-0.0553(7)		0.034(4)
C(3)	0.216(1)	0.116(2)	-0.1204(7)		0.035(4)
C(4)	0.221(1)	0.200(2)	-0.1701(7)		0.041(4)
C(5)	0.169(1)	0.163(2)	-0.2308(7)		0.041(4)
C(6)	0.159(1)	-0.003(2)	-0.1331(7)		0.034(4)
C(7)	0.110(1)	-0.032(2)	-0.1925(7)		0.037(4)
C(14)	0.177(1)	0.173(2)	0.0312(7)		0.038(4)
C(15)	0.083(1)	0.165(2)	-0.0064(8)		0.047(4)
C(16)	0.011(1)	0.170(2)	0.0212(9)		0.060(5)
C(17)	0.032(1)	0.191(2)	0.0830(9)		0.068(5)
C(18)	0.121(1)	0.199(2)	0.1205(9)		0.065(5)
C(19)	0.195(1)	0.186(2)	0.0951(8)		0.051(4)
C(51)	0.166(1)	0.242(2)	-0.2877(8)		0.047(4)
C(52)	0.139(1)	0.178(2)	-0.3475(8)		0.058(5)
C(53)	0.142(1)	0.251(2)	-0.3992(9)		0.057(5)
C(54)	0.168(1)	0.383(2)	-0.395(1)		0.069(6)
C(55)	0.192(2)	0.452(2)	-0.338(1)		0.077(6)
C(56)	0.193(1)	0.375(2)	-0.2840(8)		0.049(4)
C(71)	0.049(1)	-0.150(1)	-0.2133(7)		0.034(4)
C(72)	-0.032(1)	-0.137(2)	-0.2649(8)		0.050(4)
C(73)	-0.089(1)	-0.252(2)	-0.2823(8)		0.052(4)
C(74)	-0.070(1)	-0.368(2)	-0.2501(9)		0.065(5)
C(75)	0.007(1)	-0.383(2)	-0.1980(9)		0.058(5)
C(76)	0.067(1)	-0.271(2)	-0.1805(8)		0.052(5)
P(1)	0.3607(4)	0.2777(6)	0.3138(3)		0.064(1)
F(1)	0.343(1)	0.251(2)	0.378(1)		0.181(8)
F(2)	0.255(1)	0.322(2)	0.290(1)		0.170(8)
F(3)	0.367(1)	0.315(2)	0.248(1)		0.172(7)
F(4)	0.323(2)	0.132(3)	0.292(1)		0.23(1)
F(5)	0.389(2)	0.423(3)	0.340(1)		0.26(1)
F(6)	0.464(2)	0.231(3)	0.335(1)		0.191(9)

5.4. X-ray crystallography

Complex **3a** was crystallized from CH_2Cl_2 with ether as co-solvent. The crystal was set up on an automatic four-circle diffractometer. The structures were solved by using the Patterson method with the aid of the program CRYSTALS [17]. The crystallographic data collection parameters appear in Table 3, and atomic positional parameters are collected in Table 4.

5.5. Typical NMR, IR and analytical data for the new compounds

2a 1H NMR ($CDCl_3$) δ (ppm): 7.90–7.70 (m, 6H); 7.55–7.30 (m, 9H); 5.97 (d, 2H, $^3J = 4.64$ Hz); 5.04 (t, 1H, $^3J = 4.64$ Hz). IR (KBr) ν (cm^{-1}): ν C=O 2080, 2050, 2020, 2000. Anal. Found: C, 60.12; H, 3.14. $C_{31}H_{18}O_7Co_2$ Calc.: C, 60.00; H, 2.90%.

2b 1H NMR ($CDCl_3$) δ (ppm): 7.75–7.55 (m, 4H); 7.50–7.33 (m, 6H); 6.12 (s, 1H); 5.60 (d, 2H, $^3J = 4.6$ Hz); 4.57 (t, 1H, $^3J = 4.6$ Hz). IR (KBr) ν (cm^{-1}): ν C=O 2080, 2040, 2010, 1980. Anal. Found: C, 55.03; H, 2.47. $C_{25}H_{14}O_7Co_2$ Calc.: C, 55.14; H, 2.50%.

3a 1H NMR (acetone- d_6) δ (ppm): 8.62 (s, 2H, H pyrylium ring); 8.50–8.40 (m, 4H); 7.95–7.85 (m, 2H); 7.85–7.70 (m, 6H); 7.55–7.45 (m, 3H). IR (KBr) ν (cm^{-1}): ν C=O 2100, 2070, 2040, 2020. Anal. Found: C, 48.59; H, 2.45. $C_{31}H_{17}O_7PF_6Co_2$ Calc.: C, 48.69; H, 2.25%.

3b 1H NMR (acetone- d_6) δ (ppm): 8.80–8.50 (m, 4H); 8.72 (s, 2H, H pyrylium ring); 7.90–7.70 (m, 6H); 7.40 (s, 1H, H acetylenic). IR (KBr) ν (cm^{-1}): ν C=O: 2100, 2070, 2030. Anal. Found: C, 46.62; H, 2.33. $C_{25}H_{13}O_7BF_4Co_2$ Calc.: C, 47.62; H, 2.06%.

4 1H NMR ($CDCl_3$) δ (ppm): 8.30–7.20 (m, 16H); 4.68 (s, 2H). IR (KBr) ν (cm^{-1}): ν C=O 2080, 2060, 2025, 2015; ν C=O 1685, 1640. Anal. Found: C, 58.27; H, 3.02. $C_{31}H_{20}O_8Co_2$ Calc.: C, 58.49; H, 2.83%.

5 1H NMR ($CDCl_3$) δ (ppm): 8.5–7.0 (m, 17H). IR (KBr) ν (cm^{-1}): ν C=O: 2090, 2050, 2010, 2000; ν C=N 1610. Anal. Found: C, 59.88; H, 2.93. $C_{31}H_{18}NO_6Co_2$ Calc.: C, 60.29; H, 2.75%.

6 1H NMR ($CDCl_3$) δ (ppm): 8.50 (d, 1H, $^3J = 17$ Hz); 8.20–7.90 (m, 2H); 7.80–7.10 (m, 14H); 6.86 (d, 1H, $^3J = 17$ Hz). IR (KBr) ν (cm^{-1}): ν C=O 2080, 2060, 2020, 1995; ν C=O 1640. Anal. Found: C, 58.77; H, 3.91. $C_{31}H_{18}O_7Co_2$ Calc.: C, 60.00; H, 2.90%.

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