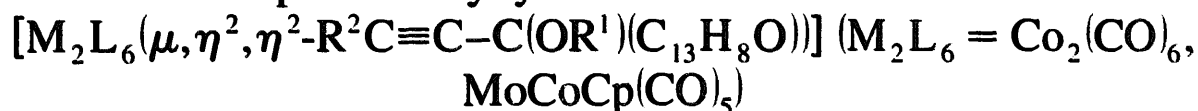


# Charge stabilization in cationic anthronyl-substituted alkynes: synthesis, characterization and X-ray molecular structures of $M_2L_6$

## Complexed alkynyl-substituted C10-anthrone



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### Abstract

A series of the novel  $M_2L_6$ -complexed alkynyl-substituted C10-anthrone derivatives were prepared and fully characterized. Furthermore, the X-ray molecular structures of three complexes belonging to this family were determined with the general formula  $[M_2L_6(\mu, \eta^2, \eta^2-R^2C \equiv C-C(OR^1)(C_{13}H_8O))]$ ,  $M_2L_6 = Co_2(CO)_6$ ,  $R^1 = CH_3$ ,  $R^2 = H$  **5**;  $M_2L_6 = MoCoCp(CO)_5$ ,  $R^1 = CH_3$ ,  $R^2 = H$  **7** and  $M_2L_6 = Co_2(CO)_6$ ,  $R^1 = CH_3$ ,  $R^2 = C_6H_5$  **8**. Addition of  $HBF_4$  to the compounds  $[MoCoCp(CO)_5(\mu, \eta^2, \eta^2-HC \equiv C-C(OR^1)(C_{13}H_8O))]$ ,  $R^1 = H$  **6**;  $R^1 = CH_3$  **7**, produced the cationic counterpart  $[MoCoCp(CO)_5(\mu, \eta^2, \eta^2-HC \equiv C-C(C_{13}H_8O))]^+ BF_4^-$  **9**. The charge stabilization in this novel carbenium ion possessing an anthrone fragment was investigated and showed that the dinuclear cluster alleviates the positive charge at the C10 carbon center. Further, the reactivity of these carbenium ion towards nucleophiles was also examined. © 1997 Elsevier Science S.A.

### 1. Introduction

The alkylation of quinones was early described and reviewed by Ried [1,2]. Mono- and di-condensation of phenyl acetylene on the anthraquinone was studied by Rio [3], Ried and Schmidt [4]. Chodkiewicz and coworkers [5–7] have determined the stereochemistry of the alkylation of anthraquinone. Other groups have studied the reactivity of anthraquinone towards alkylation [8–10] or reduction [11,12] of anthrone derivatives where an acetylenic and hydroxyl or ethereal functions were grafted at C10 of the anthrone molecule (Fig. 1).

The particular nature of the fused unsaturated rings renders possible a large electronic delocalization through

the whole system of such an anthrone derivative. Thus Cognacq and Chodkiewicz [13] have postulated the formation of a delocalized carbenium ion as intermediate in the mechanism of transannular transposition showed in Scheme 1.

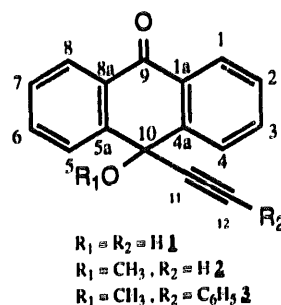
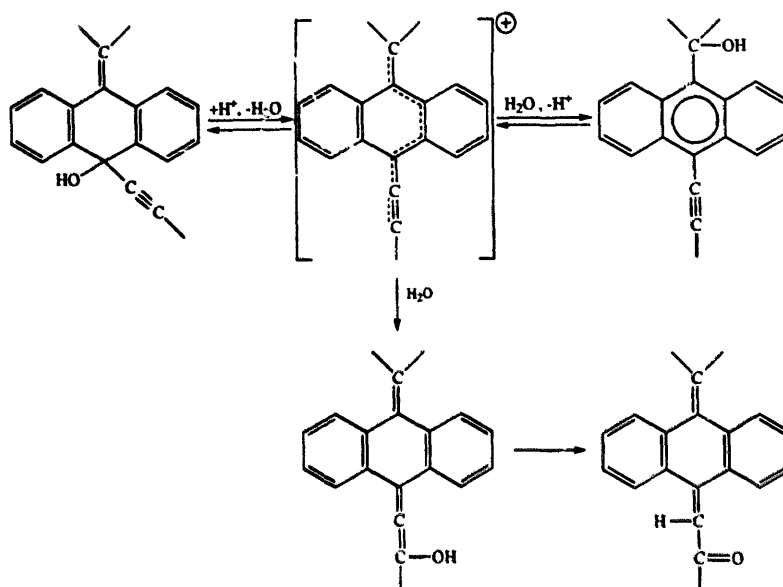


Fig. 1. Acetylenic anthrone derivatives.

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Scheme 1. Transannular transposition in free acetylenic carbenium ion.

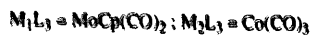
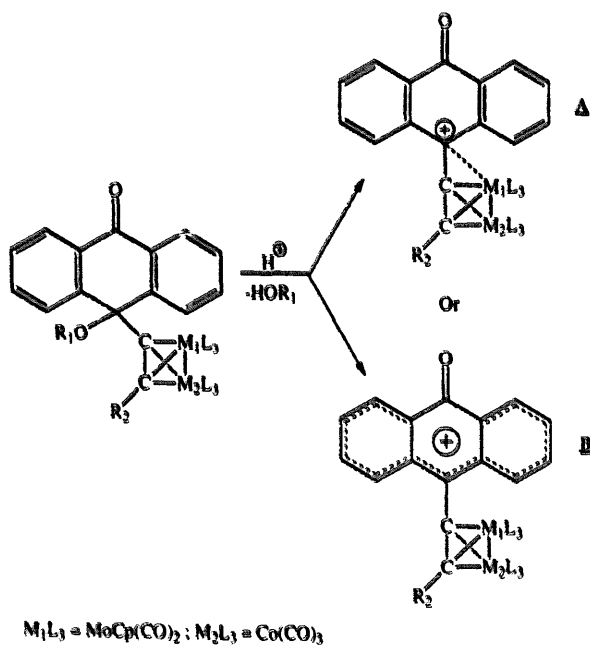
This chemistry is of interest partly because it allows the obtainment of cumulene derivatives [14] and partly their importance resides in the capacity of anthracene conjugated rings to act as an electronic reservoir.

The electronic properties of such anthrone species (Fig. 1) can be better tuned by attaching a dinuclear cluster to the alkyne unit at C10. These species can be protonated to give the corresponding carbenium complexes (see Scheme 2).

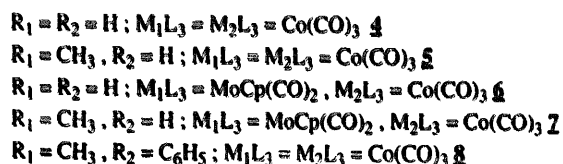
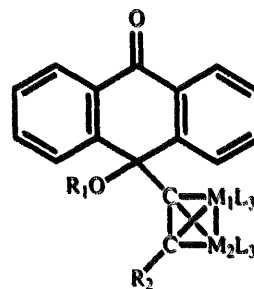
At this stage, the stabilization of the carbenium center can be achieved either (a) by an interaction with the metal center (A) or (b) through delocalization over

the anthronyl fragment (B) (Scheme 2). One of the issues under investigation here is how the carbenium center ( $C^+$ ) in this system is stabilized?

Carbenium ions stabilized by a dinuclear cluster in the  $\alpha$ -position have been widely investigated by our group and others [15–17]. Nicholas and coworkers [15,16] have shown that propargyl cations stabilized by coordination to the dicobalt hexacarbonyl group ' $Co_2(CO)_6$ ' can serve as electrophilic propargyl synthons because of their reactivity towards a variety of hetero- and carbon-centered nucleophiles. The more stable less reactive  $Cp_2M_2(CO)_4$  derivatives,  $M = Mo, W$ , provide a lot of important information concerning the stabilization of these carbenium centers. In these cases more structural studies by X-ray diffraction were reported [18].



Scheme 2. Charge stabilization in cationic anthronyl-substituted alkynes.

Fig. 2. Complexed  $Co_2(CO)_6$ ,  $Co(CO)_3$ - $MoCp(CO)_2$  acetylenic anthrone derivatives.

In this paper we describe the synthesis, identification and X-ray structures of neutral homo  $[\text{Co}_2(\text{CO})_6]$  and hetero  $[\text{MoCoCp}(\text{CO})_5]$  bimetallic acetylenic clusters possessing an anthrone fragment  $[\text{Co}_2(\text{CO})_6(\mu, \eta^2, \eta^2\text{-R}^2\text{C}\equiv\text{C}-\text{C}(\text{OR}^1)(\text{C}_{13}\text{H}_8\text{O}))]$  ( $\text{R}^1 = \text{R}^2 = \text{H}$  **4**;  $\text{R}^1 = \text{CH}_3$ ,  $\text{R}^2 = \text{H}$  **5**;  $\text{R}^1 = \text{CH}_3$ ,  $\text{R}^2 = \text{C}_6\text{H}_5$  **8**) and  $[\text{MoCoCp}(\text{CO})_5(\mu, \eta^2, \eta^2\text{-R}^2\text{C}\equiv\text{C}-\text{C}(\text{OR}^1)(\text{C}_{13}\text{H}_8\text{O}))]$  ( $\text{R}^1 = \text{R}^2 = \text{H}$  **6**;  $\text{R}^1 = \text{CH}_3$ ,  $\text{R}^2 = \text{H}$  **7**) (Fig. 2) and the formation of the corresponding stabilized carbenium ion  $[\text{MoCoCp}(\text{CO})_5(\mu, \eta^2, \eta^3\text{-HC}\equiv\text{C}-\text{CC}_{13}\text{H}_8\text{O})]^+\text{BF}_4^-$  **9**.

## 2. Results and discussion

Starting from 10-alkynyl-substituted 9-anthrones **1**, **2** and **3**, we have synthesized the dicobalt hexacarbonyl alkyne complexes **4**, **5** and **8** respectively, in the usual way, namely by reaction of stoichiometric amounts of  $\text{Co}_2(\text{CO})_8$  and alkyne in ethereal solution [19]. The heterobimetallic isolobal complexes **6** and **7** were obtained by exchanging one  $\text{Co}(\text{CO})_3$  vertex with the isolobal 'MoCp(CO)<sub>2</sub>' unit; this reaction was achieved by addition of NaMoCp(CO)<sub>3</sub> to the complexes **4** or **5** in THF solution at room temperature [20].

Treatment of the  $\text{Co}_2(\text{CO})_6$ -complexed phenylethyne

anthrone **8** with one equivalent of NaMoCp(CO)<sub>3</sub> did not produce the congeneric heterobinuclear MoCoCp(CO)<sub>5</sub> species. Further prolongation of the reaction period for 2 days under reflux resulted in the decomposition of the starting material **8**. We interpret the failure of replacing one  $\text{Co}(\text{CO})_3$  vertex by MoCp(CO)<sub>2</sub> in **8** to the steric factors generated by the anthrone fragment at C10, the phenyl substituent at C12 and the incoming organometallic NaMoCp(CO)<sub>3</sub> unit.

The complexes **4**, **5**, **6**, **7** and **8** were identified by elemental analysis, infrared, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. Furthermore, the structures of  $[\text{Co}_2(\text{CO})_6(\mu, \eta^2, \eta^2\text{-HC}\equiv\text{C}-\text{C}(\text{OCH}_3)(\text{C}_{13}\text{H}_8\text{O}))]$  **5**,  $[\text{MoCp}(\text{CO})_2\text{-Co}(\text{CO})_3(\mu, \eta^2, \eta^2\text{-HC}\equiv\text{C}-\text{C}(\text{OCH}_3)(\text{C}_{13}\text{H}_8\text{O}))]$  **7** and  $[\text{Co}_2(\text{CO})_6(\mu, \eta^2, \eta^2\text{-C}_6\text{H}_5\text{C}\equiv\text{C}-\text{C}(\text{OCH}_3)(\text{C}_{13}\text{H}_8\text{O}))]$  **8** were determined.

### 2.1. X-ray crystal structures of **5**, **7** and **8**

Suitable crystals for crystallographic studies were obtained for compounds **5**, **7** and **8** by slow evaporation of an ethereal solution at room temperature. Crystallographic data, selected distances and angles are listed in Tables 1–4. The unit cell is monoclinic for each compound **5**, **7**, and **8**. For **8**, there are two independent

Table 1  
Crystal and refinement data for **5**, **7** and **8**

Formula	$\text{C}_{27}\text{H}_{12}\text{O}_8\text{Co}_2$ <b>5</b>	$\text{C}_{27}\text{H}_{17}\text{O}_7\text{MoCo}$ <b>7</b>	$\text{C}_{29}\text{H}_{16}\text{O}_8\text{Co}_2$ <b>8</b>
Fw	534.2	608.3	610.3
Unit cell	Monoclinic	Monoclinic	Monoclinic
Space group	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	29.810(7)	13.902(2)	40.031(18)
<i>b</i> (Å)	11.662(5)	10.300(2)	16.748(7)
<i>c</i> (Å)	14.737(7)	17.414(4)	17.074(9)
$\alpha$ (deg)	90	90	90
$\beta$ (deg)	119.13(3)	106.25(2)	110.4(5)
$\gamma$ (deg)	90	90	90
<i>V</i> (Å <sup>3</sup> )	4475(73)	2394(11)	10728
<i>Z</i>	8	4	16
$\mu$ (cm <sup>-1</sup> )	15.23	12.5	12.8
$\rho$ (calc) (g cm <sup>-3</sup> )	1.58	1.69	1.51
Diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Philips PW1100
Radiation	Mo K $\alpha$ ( $\lambda = 0.71069$ Å)	Mo K $\alpha$ ( $\lambda = 0.71069$ Å)	Mo K $\alpha$ ( $\lambda = 0.71069$ Å)
<i>T</i> (°C)	20	20	20
Scan mode	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$
Scan width (deg)	$0.8 + 0.345 \tan \theta$	$0.8 + 0.345 \tan \theta$	$1.20 + 0.345 \tan \theta$
2 $\theta$ limit (deg)	1–25	1–25	2–25
No. data collected	3926	4207	8083
Unique data used in final ref	$1635 (F_o)^2 > 3\sigma(F_o)^2$	$1614 (F_o)^2 > 3\sigma(F_o)^2$	$3789 (F_o)^2 > 2.5\sigma(F_o)^2$
<i>R</i> (int)	0.0370	0.0462	0.0464
$R = \sum   F_o  -  F_c   / \sum  F_o $	0.0552	0.0366	0.0492
$R_w = [\sum w( F_o  -  F_c )^2 / \sum w F_o^2]^{1/2}$	0.0610 <i>w</i> = 1.0	0.0406 <i>w</i> = 1.0	0.0403 <i>w</i> = 1.0
Correction	DIFABS (min 0.58, max 1.25)	DIFABS (min 0.93, max 1.04)	DIFABS (mic 0.85, max 1.09)
Extinction parameter	none	none	265
Final no. of variables	300	326	706
$\Delta\rho$ min (e <sup>-</sup> Å <sup>-3</sup> )	-0.58	-0.31	-0.31
$\Delta\rho$ max (e <sup>-</sup> Å <sup>-3</sup> )	0.71	0.32	0.29

molecules (**8a** and **8b**) in the asymmetric unit; **8b** can be deduced from **8a** by a rotation around the C(10)–C(11) bond. CAMERON views are shown in Figs. 3–5 respectively.

For the [Co<sub>2</sub>] complexes **5** and **8**, we have compared the geometry of the cluster core with that of the [Co<sub>2</sub>(CO)<sub>6</sub>(μ,η<sup>2</sup>,η<sup>2</sup>-2-endo-propynylfenchol) **11** [21]. Corresponding distances and angles are very similar to each other. The structure of the [Mo–Co] complex **7** is the first hetero-bimetallic alkyne cluster of this type described in the literature. The metal–metal bond distance for **7** d<sub>Mo–Co</sub> = 2.69 Å averages that of the d<sub>Co–Co</sub> = 2.47 Å for **5** and that of the d<sub>Mo–Mo</sub> = 2.980 Å in [Mo<sub>2</sub>Cp<sub>2</sub>(CO)<sub>4</sub>(μ,η<sup>2</sup>,η<sup>2</sup>-HC≡CH)] [22] (Table 5).

A general observation concerns the conformation at the disubstituted C10 which appears clearly to bear the [C<sub>2</sub>M<sub>2</sub>] cluster in the axial position while the hydroxyl or methoxy group points in the equatorial position. This result confirms the hypothesis formulated by Cadiot and coworkers [6] based on <sup>1</sup>H NMR data. The authors investigated the diamagnetic anisotropy of aromatic rings in mono- and di-tertiary-anthraquinols and concluded that the more bulky group adopts the axial position, while the minor one is equatorial. Thus, in a 10-alkynyl-10-methyl- (or ethyl-) substituted anthrone, the acetylenic group occupies the equatorial position.

Table 2

Main interatomic distances (Å) and bond angles (deg) for C<sub>27</sub>H<sub>17</sub>O<sub>7</sub>Co<sub>2</sub> (**8**)

Co(1)–Co(2)	2.47(2)		
Co(1)–C(11)	1.95(1)	Co(2)–C(11)	1.98(1)
Co(1)–C(12)	1.98(1)	Co(2)–C(12)	1.98(1)
O(9)–C(9)	1.22(1)	O(10)–C(10)	1.44(1)
O(10)–C(13)	1.42(1)	C(10)–C(11)	1.50(1)
C(11)–C(12)	1.37(2)		
Co(2)–Co(1)–C(11)	51.5(3)	Co(2)–Co(1)–C(12)	51.3(4)
C(11)–Co(1)–C(12)	40.8(5)	Co(2)–Co(1)–C(14)	102.3(4)
C(11)–Co(1)–C(14)	105.1(5)	C(12)–Co(1)–C(14)	144.1(6)
Co(2)–Co(1)–C(15)	150.1(4)	C(11)–Co(1)–C(15)	102.3(5)
C(12)–Co(1)–C(15)	100.1(6)	C(14)–Co(1)–C(15)	98.3(6)
Co(2)–Co(1)–C(16)	95.4(5)	C(11)–Co(1)–C(16)	139.9(6)
C(12)–Co(1)–C(16)	102.7(7)	C(14)–Co(1)–C(16)	103.8(7)
C(15)–Co(1)–C(16)	100.4(7)	Co(1)–Co(2)–C(11)	50.5(3)
Co(1)–Co(2)–C(12)	51.6(3)	C(11)–Co(2)–C(12)	40.6(5)
Co(1)–Co(2)–C(17)	97.0(4)	C(11)–Co(2)–C(17)	107.2(6)
C(12)–Co(2)–C(17)	143.5(5)	Co(1)–Co(2)–C(18)	147.3(4)
C(11)–Co(2)–C(18)	97.0(5)	C(12)–Co(2)–C(18)	103.0(6)
C(17)–Co(2)–C(18)	96.8(6)	Co(1)–Co(2)–C(19)	103.8(5)
C(11)–Co(2)–C(19)	139.4(6)	C(12)–Co(2)–C(19)	99.4(7)
C(17)–Co(2)–C(19)	106.9(8)	C(18)–Co(2)–C(19)	100.3(7)
C(10)–O(10)–C(13)	115.4(8)	C(4a)–C(10)–O(10)	109.9(8)
C(4a)–C(10)–C(11)	105.2(9)	O(10)–C(10)–C(11)	103.9(8)
C(10a)–C(10)–C(11)	110.0(9)	Co(1)–C(11)–Co(2)	78.0(4)
Co(1)–C(11)–C(10)	137.7(8)	Co(2)–C(11)–C(10)	133.3(8)
Co(1)–C(11)–C(12)	71.0(7)	Co(2)–C(11)–C(12)	69.8(7)
C(10)–C(11)–C(12)	138.8(10)	Co(1)–C(12)–Co(2)	77.1(4)
Co(1)–C(12)–C(11)	68.2(6)	Co(2)–C(12)–C(11)	69.6(7)

Table 3

Main interatomic distances (Å) and bond angles (deg) for C<sub>27</sub>H<sub>17</sub>O<sub>7</sub>CoMo (**7**)

Mo(1)–Co(1)	2.691(2)	Co(1)–C(11)	1.984(8)
Mo(1)–C(11)	2.13(1)	Co(1)–C(12)	1.94(1)
Mo(1)–C(12)	2.156(9)	Co(1)–C(14)	1.79(1)
Mo(1)–C(17)	1.97(1)	Co(1)–C(15)	1.77(1)
Mo(1)–C(18)	1.99(1)	Co(1)–C(16)	1.80(1)
Mo(1)–C(19)	2.34(1)	C(10)–C(11)	1.54(1)
Mo(1)–C(20)	2.30(1)	C(11)–C(12)	1.33(1)
Mo(1)–C(21)	2.31(1)		
Mo(1)–C(22)	2.33(1)		
Mo(1)–C(23)	2.38(1)		
Co(1)–Mo(1)–C(11)	46.8(2)	Mo(1)–Co(1)–C(11)	51.5(3)
Co(1)–Mo(1)–C(12)	45.6(3)	Mo(1)–Co(1)–C(12)	52.5(3)
C(11)–Mo(1)–C(12)	36.3(3)	C(11)–Co(1)–C(12)	39.7(4)
Co(1)–Mo(1)–C(17)	85.8(3)	Mo(1)–Co(1)–C(14)	98.3(4)
C(11)–Mo(1)–C(17)	112.2(4)	C(11)–Co(1)–C(14)	105.1(4)
C(12)–Mo(1)–C(17)	76.3(4)	C(12)–Co(1)–C(14)	142.4(4)
Co(1)–Mo(1)–C(18)	126.9(4)	Mo(1)–Co(1)–C(15)	146.8(4)
C(11)–Mo(1)–C(18)	90.1(4)	C(11)–Co(1)–C(15)	98.5(5)
C(12)–Mo(1)–C(18)	81.4(4)	C(12)–Co(1)–C(15)	96.1(5)
C(17)–Mo(1)–C(18)	85.0(5)	C(14)–Co(1)–C(15)	104.1(5)
Co(1)–Mo(1)–C(19)	118.1(4)	Mo(1)–Co(1)–C(16)	99.4(4)
C(11)–Mo(1)–C(19)	150.2(4)	C(11)–Co(1)–C(16)	143.9(5)
C(12)–Mo(1)–C(19)	157.7(4)	C(12)–Co(1)–C(16)	107.7(5)
C(17)–Mo(1)–C(19)	88.4(5)	C(14)–Co(1)–C(16)	99.5(5)
C(18)–Mo(1)–C(19)	113.8(5)	C(15)–Co(1)–C(16)	100.7(5)
Co(1)–Mo(1)–C(20)	149.7(4)	Mo(1)–C(11)–Co(1)	81.6(3)
C(11)–Mo(1)–C(20)	143.7(4)	Mo(1)–C(11)–C(10)	139.8(6)
C(12)–Mo(1)–C(20)	164.5(4)	Co(1)–C(11)–C(10)	131.9(7)
C(17)–Mo(1)–C(20)	102.7(5)	Mo(1)–C(11)–C(12)	72.9(6)
Co(1)–Mo(1)–C(21)	130.9(4)	Co(1)–C(11)–C(12)	68.5(5)
C(11)–Mo(1)–C(21)	108.7(4)	C(10)–C(11)–C(12)	133.8(9)
C(12)–Mo(1)–C(21)	142.0(4)	Mo(1)–C(12)–Co(1)	81.9(4)
C(17)–Mo(1)–C(21)	138.1(5)	Mo(1)–C(12)–C(11)	70.8(6)
C(18)–Mo(1)–C(21)	85.9(5)	Co(1)–C(12)–C(11)	71.8(6)
Co(1)–Mo(1)–C(22)	98.0(3)		
C(11)–Mo(1)–C(22)	95.1(4)		
C(12)–Mo(1)–C(22)	130.1(4)		
C(17)–Mo(1)–C(22)	144.4(5)		
C(18)–Mo(1)–C(22)	118.5(5)		
Co(1)–Mo(1)–C(23)	91.8(3)		
C(11)–Mo(1)–C(23)	115.4(4)		
C(12)–Mo(1)–C(23)	137.2(4)		
C(17)–Mo(1)–C(23)	109.9(5)		
C(18)–Mo(1)–C(23)	140.1(5)		

The complexation of the alkyne unit by a bimetallic fragment renders the complexed-alkyne unit as the bulky group which would change its relative conformation by occupying the axial position (see Fig. 6).

The geometry of the conjugated rings is very similar to that found for the free 9,10-dihydroanthracene ligand [23].

## 2.2. Preparation and characterization of the dinuclear-stabilized carbenium ion [MoCoCp(CO)<sub>5</sub>(μ,η<sup>2</sup>,η<sup>1</sup>-HC≡C–CC<sub>13</sub>H<sub>8</sub>O)]<sup>+</sup> BF<sub>4</sub><sup>–</sup> **9**

Addition of HBF<sub>4</sub>–Et<sub>2</sub>O to an ethereal solution of the complexes **6** and **7** leads to the corresponding tetrafluoro-

Table 4  
Main interatomic distances (Å) and bond angles (deg) for  $C_{20}H_{16}O_8Co_2$  (**8a** and **8b**)

<b>8a</b>			
Co(1)–Co(2)	2.464(2)		
Co(1)–C(11)	1.945(8)	Co(2)–C(11)	1.945(8)
Co(1)–C(12)	1.960(8)	Co(2)–C(12)	1.977(8)
Co(1)–C(20)	1.79(1)	Co(2)–C(23)	1.80(1)
Co(1)–C(21)	1.78(1)	Co(2)–C(24)	1.80(1)
Co(1)–C(22)	1.83(1)	Co(2)–C(25)	1.81(1)
C(10)–C(11)	1.53(1)	C(11)–C(12)	1.33(1)
C(12)–C(13)	1.46(1)		
Co(2)–Co(1)–C(11)	50.7(2)	Co(2)–Co(1)–C(12)	51.6(2)
C(11)–Co(1)–C(12)	39.8(3)	Co(2)–Co(1)–C(20)	98.1(3)
C(11)–Co(1)–C(20)	142.4(4)	C(12)–Co(1)–C(20)	106.5(4)
Co(2)–Co(1)–C(21)	149.8(4)	C(11)–Co(1)–C(21)	103.4(4)
C(12)–Co(1)–C(21)	99.2(5)	C(20)–Co(1)–C(21)	97.6(5)
Co(2)–Co(1)–C(22)	101.6(4)	C(11)–Co(1)–C(22)	104.2(4)
C(12)–Co(1)–C(22)	142.6(4)	C(20)–Co(1)–C(22)	102.4(5)
C(21)–Co(1)–C(22)	99.9(5)	Co(1)–Co(2)–C(11)	50.7(2)
Co(1)–Co(2)–C(12)	50.9(2)	C(11)–Co(2)–C(12)	39.6(3)
Co(1)–Co(2)–C(23)	102.3(3)	C(11)–Co(2)–C(23)	138.8(4)
C(12)–Co(2)–C(23)	100.0(4)	Co(1)–Co(2)–C(24)	149.8(3)
C(11)–Co(2)–C(24)	99.9(4)	C(12)–Co(2)–C(24)	103.2(4)
C(23)–Co(2)–C(24)	97.3(4)	Co(1)–Co(2)–C(25)	97.3(3)
C(11)–Co(2)–C(25)	108.5(4)	C(12)–Co(2)–C(25)	143.4(4)
C(23)–Co(2)–C(25)	105.1(4)	C(24)–Co(2)–C(25)	99.6(4)
Co(1)–C(11)–Co(2)	78.6(3)	Co(1)–C(11)–C(10)	136.1(6)
Co(2)–C(11)–C(10)	135.0(6)	Co(1)–C(11)–C(12)	70.7(5)
Co(2)–C(11)–C(12)	71.5(5)	C(10)–C(11)–C(12)	137.5(8)
Co(1)–C(12)–Co(2)	77.5(3)	Co(1)–C(12)–C(11)	69.5(5)
Co(2)–C(12)–C(11)	68.9(5)	Co(1)–C(12)–C(13)	136.4(7)
Co(2)–C(12)–C(13)	130.5(6)	C(11)–C(12)–C(13)	145.0(8)
<b>8b</b>			
Co(101)–Co(102)	2.471(2)		
Co(101)–C(111)	1.949(8)	Co(102)–C(111)	1.951(8)
Co(101)–C(112)	1.974(8)	Co(102)–C(112)	1.950(8)
Co(101)–C(120)	1.78(1)	Co(102)–C(123)	1.82(1)
Co(101)–C(121)	1.81(1)	Co(102)–C(124)	1.81(1)
Co(101)–C(122)	1.83(1)	Co(102)–C(125)	1.80(1)
C(110)–C(111)	1.54(1)	C(111)–C(112)	1.33(1)
C(112)–C(113)	1.48(1)		
Co(102)–Co(101)–C(111)	50.7(2)	Co(102)–Co(101)–C(112)	50.5(2)
C(111)–Co(101)–C(112)	39.6(3)	Co(102)–Co(101)–C(120)	148.0(3)
C(111)–Co(101)–C(120)	99.0(4)	C(112)–Co(101)–C(120)	100.6(4)
Co(102)–Co(101)–C(121)	99.1(3)	C(111)–Co(101)–C(121)	107.4(4)
C(112)–Co(101)–C(121)	143.4(4)	C(120)–Co(101)–C(121)	100.4(5)
Co(102)–Co(101)–C(122)	101.2(3)	C(111)–Co(101)–C(122)	140.6(4)
C(112)–Co(101)–C(122)	102.4(4)	C(120)–Co(101)–C(122)	98.5(5)
C(121)–Co(101)–C(122)	103.8(5)	Co(101)–Co(102)–C(111)	50.7(2)
Co(101)–Co(102)–C(112)	51.4(2)	C(111)–Co(102)–C(112)	39.8(3)
Co(101)–Co(102)–C(123)	102.4(3)	C(111)–Co(102)–C(123)	104.2(4)
C(112)–Co(102)–C(123)	142.8(4)	Co(101)–Co(102)–C(124)	148.4(3)
C(111)–Co(102)–C(124)	102.8(4)	C(112)–Co(102)–C(124)	97.7(4)
C(123)–Co(102)–C(124)	100.8(4)	Co(101)–Co(102)–C(125)	97.7(3)
C(111)–Co(102)–C(125)	142.2(4)	C(112)–Co(102)–C(125)	106.4(4)
C(123)–Co(102)–C(125)	102.7(5)	C(124)–Co(102)–C(125)	97.7(5)
Co(101)–C(111)–Co(102)	78.6(3)	Co(101)–C(111)–C(110)	135.3(6)
Co(102)–C(111)–C(110)	134.9(6)	Co(101)–C(111)–C(112)	71.2(5)
Co(102)–C(111)–C(112)	70.0(5)	C(110)–C(111)–C(112)	139.1(8)
Co(101)–C(112)–Co(102)	78.1(3)	Co(101)–C(112)–C(111)	69.2(5)
Co(102)–C(112)–C(111)	70.1(5)	Co(101)–C(112)–C(113)	130.6(6)
Co(102)–C(112)–C(113)	135.9(6)	C(111)–C(112)–C(113)	144.5(9)

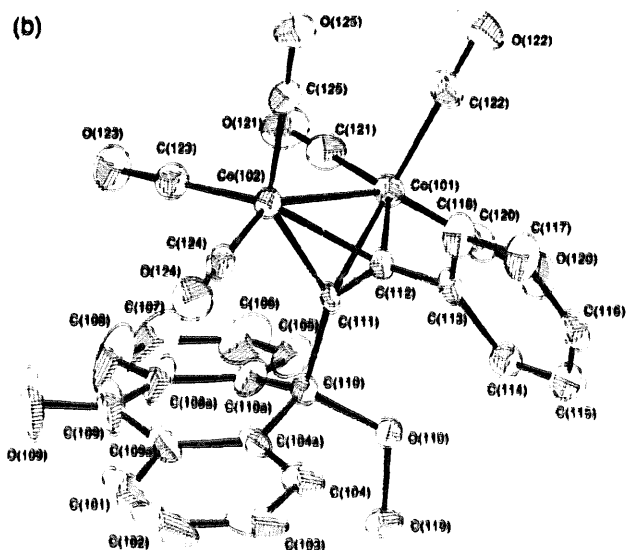
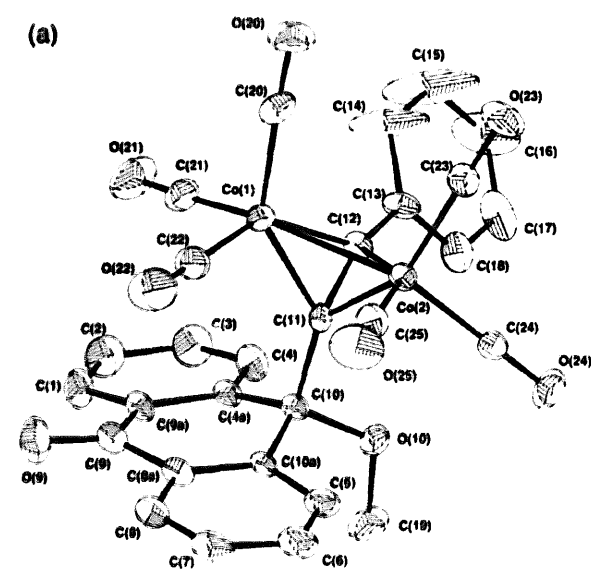


Fig. 3. CAMERON drawing of the two conformers **8a** and **8b**.

bororate salt  $[MoCp(CO)_2Co(CO)_3(\mu, \eta^2, \eta^1-HC \equiv C-CC_1, H_nO)]^+[BF_4]^-$  **9**. This carbenium ion is a yellow-brown solid, insoluble in ether and sparingly soluble in  $CH_2Cl_2$ . Attempts to obtain suitable crystals of compound **9** for an X-ray study have so far been unsuccessful.

Treatment of cation **9** with  $H_2O$  led to the corresponding complexed alcohol **6**. Furthermore, it reacts with  $NaBH_4$  to produce the reduced product **10** (Scheme 3).

These results confirm the previous observation [18] whereby the nucleophilic reagent attacks exclusively the carbenium center located in the  $\alpha$ -position of the cluster core.

A comparison of the  $\nu(CO)$  wavenumbers of the neutral acetylenic complex **7** and the carbenium ion **9** is shown in Table 6.

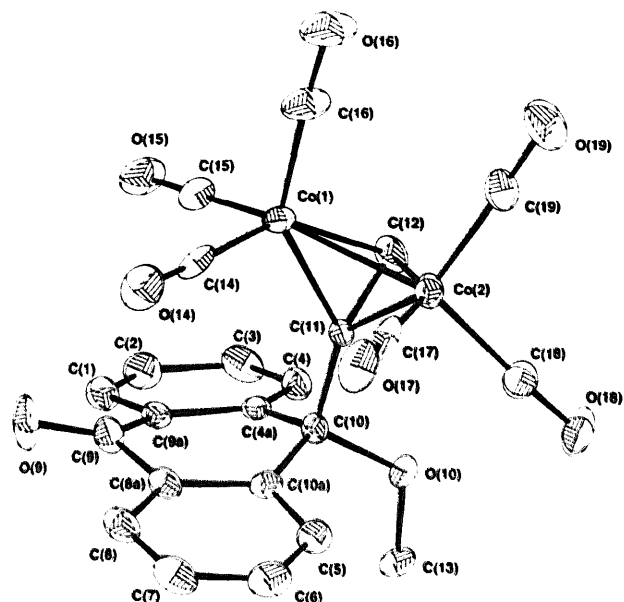


Fig. 4. CAMERON drawing of **5**.

All the frequencies for the Metal–CO vibrators are shifted by a value of  $50\text{--}60\text{ cm}^{-1}$ , which is very close to those found [21] in the tertiary  $[MoCoCp(CO)_5]$  propynyl ion **12** relative to its neutral precursor **13**. Generally the  $\nu(CO)$  wavenumbers of the complexed carbenium ions are good indications for charge delocalization onto the cluster core. Interestingly, the  $\nu(CO)$  for the ketonic C9 function is not significantly shifted ( $\pm 2\text{ cm}^{-1}$ ), indicating a very weak delocalization of the positive charge onto the anthrone skeleton.

$^{13}C$  NMR data of **9** recorded in  $CD_2Cl_2$  solution suggest also a significant delocalization of the positive

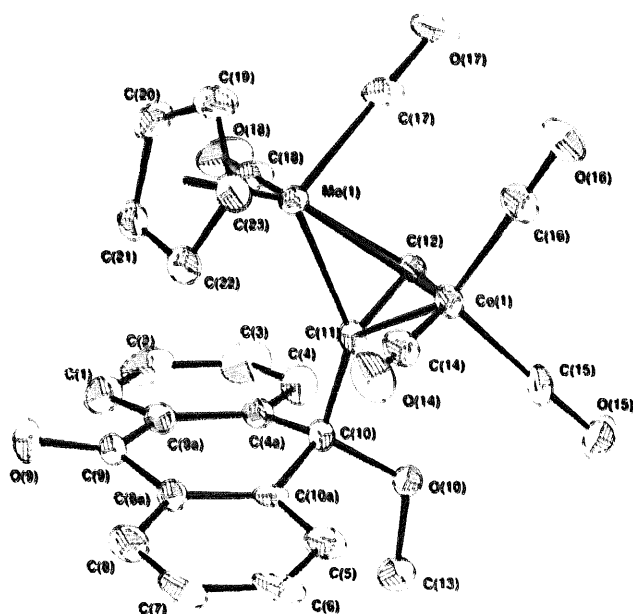


Fig. 5. CAMERON drawing of **7**.

Table 5  
Comparison of the metal–metal and metal–carbon distances in the tetrahedral clusters **5**, **7**, **8** and **11**

	<b>5</b>	<b>7</b>	<b>8</b>	<b>11</b>
	Co-Co	Co-Mo	Co-Co	Co-Co
d M-M(Å)	2.47	2.69	2.46	2.34
C11-C12	1.37	1.33	1.33	1.32
C10-C11	1.50	1.54	1.53	1.50
C11-M1	1.95	2.13	1.94	2.01
C11-M2	1.98	1.98	1.94	2.00
C12-M1	1.98	1.94	1.96	1.98
C12-M2	1.98	2.15	1.98	1.97

charge onto the cluster core. These results are listed in Table 7.

For instance the cyclopentadienyl ligand in the carbenium complex **9** is shifted by 7.3 ppm downfield relative to that of the neutral compound **7**. The metal–CO ligands for **7** appear at 225.6, 220.4 and 203.6 ppm while those of **9** appear at 216.9, 209.4, 198.8 ppm. Similar results were obtained for the heterobimetallic [MoCoCp(CO)<sub>5</sub>]-alkynyl ions and their alcohol-precursors [24]. The (C=O) function of the anthrone ligand

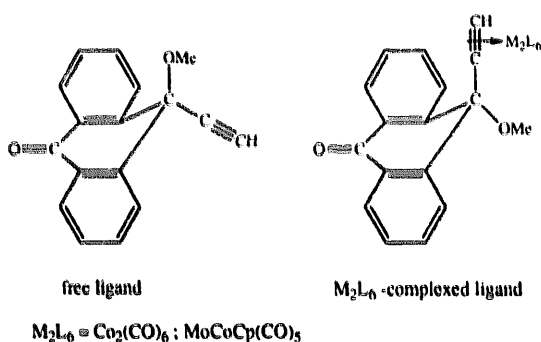
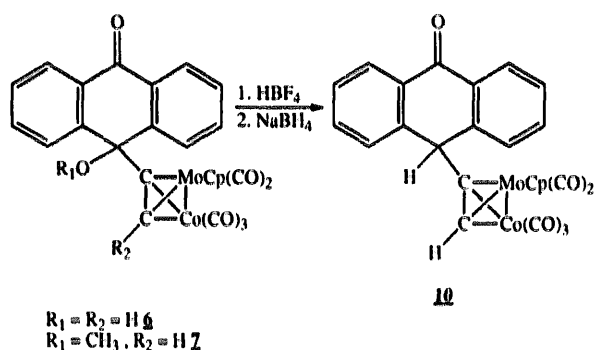


Fig. 6. Conformational change by complexation of the triple bond in acetylenic anthrone derivatives.



Scheme 3. Reduction of heterodinuclear alkyne complexes **6** and **7** by acidic treatment followed by hydride reduction.

Table 6  
Comparison of the  $\nu_{CO}$  frequencies for neutral and charged bimetallic [Mo–Co] alkyne complexes

	$\nu_{CO(M-CO)}$ ( $cm^{-1}$ )	$\nu_{C=O}$ ( $cm^{-1}$ )	ref.
<p><b>7</b></p>	2053 - 2007 1987 - 1946	1666	This work
<p><b>9</b></p>	2100 - 2069 2054 - 2029	1668	This work
<p><b>13</b></p>	2034 - 1986 1959 - 1927 1895		18
<p><b>12</b></p>	2083 - 2047 2034 - 2020 1988		18

Table 7  
<sup>13</sup>C NMR data for the neutral **7** and charged **9** bimetallic alkyne complexes [ $\delta$ , ppm]

	$^*C_9$	$^*CO$	$^*C_5H_5$	$^*C10$
<p><b>7</b></p>	184.3	225.6 220.4 203.6	90.0	81.8
<p><b>9</b></p>	190.9	216.9 209.4 198.8	96.6	139.9

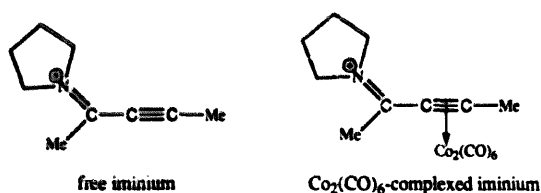


Fig. 7. Free and  $\text{Co}_2(\text{CO})_6$ -complexed iminium.

in the neutral complex **7** and its cationic counterpart **9** appear at 184.3 ppm and 190.9 ppm respectively; while the quaternary C10 signal appears at 81.8 ppm in the neutral compound **7**, it shifts to 139.9 ppm in the corresponding carbenium complex **9**. This chemical shift is consistent with those attributed to metal-stabilized tertiary carbenium centers [25]. The infrared and the  $^{13}\text{C}$  NMR data obtained for the parent alcohol-complex **7** and its corresponding carbenium species **9** suggest that the positive charge is most likely stabilized by the cluster core and not by the conjugated anthronyl-fragment. These results contrast with those reported by Maas et al. [26] on the free iminium-alkyne and its complexed counterpart (Fig. 7).

The authors have investigated the charge dispersal in these systems and found that the ligand appears to stabilize the charge density and not the dinuclear cluster  $\text{Co}_2(\text{CO})_6$  unit. The X-ray molecular structures of the free and complexed ligands were determined and found similar in terms of stabilization, where no anchimeric assistance from the neutral center to the carbenium ion was observed.

### 3. Conclusion

In this paper we have described some homo- $[\text{Co}_2(\text{CO})_6]$  and hetero- $[\text{MoCoCp}(\text{CO})_5]$  10-alkynyl anthrone cluster X-ray structures which provide information about the conformation at the C10 carbon whereby the bulky cluster group adopts an axial position while the hydroxyl or methoxy substituent is in the equatorial one. Treatment of complexes **6** and **7** with  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  produce the corresponding carbenium ion **9**. IR and NMR spectroscopic studies allow one to postulate a significant interaction between the cluster unit  $[\text{MoCoCp}(\text{CO})_5]$  and the carbenium ion. This interaction overcomes the charge delocalization ability of the conjugated rings of the anthrone ligand.

### 4. Experimental section

Derivatives **1**, **2** and **3** were obtained as described previously by Chodkiewicz and coworkers [5–7]. All reactions were carried out under argon atmosphere us-

ing standard Schlenk techniques. Solvents were purified and dried before use by conventional distillation techniques under argon.

$^1\text{H}$  and  $^{13}\text{C}$  NMR data were recorded on Bruker AC 200 and AM 250 spectrometers using a 5 mm dual frequency  $^1\text{H}$ – $^{13}\text{C}$  probe. Chemical shifts values are indicated in parts per million using TMS as reference. Infrared spectra were recorded in  $\text{CH}_2\text{Cl}_2$  on an F.T. Bomem Michelson 100 instrument. The adsorbent used for thin layer chromatography was silica-gel 60GF $_{254}$ . Elemental analyses were performed by the regional microanalysis service (Université P.M. Curie).

#### 4.1. X-ray crystal structure determinations for **5**, **7** and **8**

Accurate cell dimensions and orientation matrices were obtained by least squares refinements of 25 accurately centered reflections. No significant variations were observed in the intensities of two checked reflections during data collections. Complete crystallographic data and collection parameters are listed in Table 1. The data were corrected for Lorentz and polarization effects. Computations were performed by using the PC version of CRYSTALS [27]. Scattering factors and corrections for anomalous absorption were taken from 'International Tables for X-ray Crystallography' [28]. The structures were solved by using SHELXS [29] and refined by full-matrix least squares with anisotropic thermal parameters. Hydrogen atoms were introduced in calculated positions in the last refinement, and only an overall isotropic thermal parameter was refined. For compound **8**, the asymmetric unit contains independent molecules. The two molecules of compound **8** are shown in Fig. 3; compounds **5** and **7** are shown in Figs. 4 and 5 respectively. Selected bond lengths and bond angles are listed in Tables 2–4. Tables of atomic coordinates, thermal parameters, bond lengths and bond angles are deposited as supplementary material.

#### 4.2. $[(\text{Co}_2(\text{CO})_6)_\mu, \eta^2, \eta^2\text{-}10\text{-ethynyl-}10\text{-hydroxy-}9\text{-anthrone}]_2$ **4**

To 1 g (4.27 ml) of 10-ethynyl-10-hydroxy-9-anthrone in 20 ml of THF are added at room temperature 1.459 g of  $\text{Co}_2(\text{CO})_8$  in 10 ml THF. The mixture is allowed to react under stirring for 1 h, then filtered through silica-gel; the crude product is chromatographed on preparative plates using a mixture of pentane-ether (90/10) as eluent. After removing the solvent 1.554 g of a red solid are obtained in 70% yield. The material decomposes at 170°C.

$^1\text{H}$  NMR( $\text{CDCl}_3$ ): 8.15 (dd,  $J = 7.6, 1.2$  Hz, 2H:1,8); 8.00 (dd,  $J = 7.6, 1.2$  Hz, 2H:4,5); 7.64 (dt,  $J = 7.6, 1.2$  Hz, 2H:3,6); 7.47 (dt,  $J = 7.6, 1.2$  Hz, 2H:2,7); 5.82 (s, 1H:12).



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 198.5 (Co–CO); 184.2 (C9); 148.5 (C4a C5a); 133.5 (C3 C6); 130.5 (C1a C8a); 128.8 (C2 C7); 127.4 (C1 C8); 125.2 (C4 C5); 109.8 (C11); 73.7 (C10); 73.4 (C12).

IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu_{\text{CO}}$  = 2096, 2059, 2030, 1669  $\text{cm}^{-1}$ .  
Anal. Calcd. for  $\text{C}_{22}\text{H}_{10}\text{Co}_2\text{O}_8$ : C, 50.80; H, 1.95; found: C, 48.71; H, 2.11.

#### 4.3. [ $\text{Co}_2(\text{CO})_6(\mu, \eta^2, \eta^2\text{-10-ethynyl-10-methoxy-9-anthrone})$ ] **5**

The complex **5** was prepared in 75% yield using the same method as described for **4**. The material decomposes at 150 °C.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 8.29 (dd,  $J$  = 8.0, 1.3 Hz, 2H:1.8); 7.90 (dd,  $J$  = 8.0, 1.3 Hz, 2H:4,5); 7.70 (dt,  $J$  = 8.0, 1.8 Hz, 2H:3,6); 7.51 (dt,  $J$  = 8.0, 1.8 Hz, 2H:2,7); 6.01 (s, 1H:12); 3.18 (s, 3H:OCH<sub>3</sub>).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 198.5 (Co–CO); 183.1 (C9); 144.9 (C4a C5a); 133.6 (C3 C6); 132.0 (C1a C8a); 128.8 (C2 C7); 127.7 (C1 C8); 126.6 (C4 C5); 108.2 (C11); 78.8 (C10); 75.3 (C12); 53.7 (OCH<sub>3</sub>).

IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu_{\text{CO}}$  = 2095, 2059, 2030, 1666  $\text{cm}^{-1}$ .  
Anal. Calcd. for  $\text{C}_{23}\text{H}_{12}\text{Co}_2\text{O}_8$ : C, 52.0; H, 2.26; found: C, 51.86; H, 2.20.

#### 4.4. [ $\text{MoCoCp}(\text{CO})_5(\mu, \eta^2, \eta^2\text{-10-ethynyl-10-hydroxy-9-anthrone})$ ] **6**

To an amalgam 5% (Na–Hg) in THF is added a solution of  $\text{Mo}_2\text{Cp}_2(\text{CO})_6$  1.2 g (2.44 mmol) in 20 ml THF. The mixture is stirred until it turns yellow-brown. Then the solution is filtered under argon and added to 10 ml THF solution of **4** (1.274 g, 2.44 mmol). This mixture is refluxed until the reaction is achieved. The crude product is chromatographed on silica plates using pentane–ether as eluent (85/15). 0.890 g of a solid orange product **6** is isolated in 60% yield. Decomposes at 134 °C.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 8.14 (d,  $J$  = 7.5 Hz, 1H:1); 8.10 (d,  $J$  = 7.5 Hz, 1H:8); 7.89 (d,  $J$  = 7.5 Hz, 1H:4); 7.81 (d,  $J$  = 7.5 Hz, 1H:5); 7.61 (t,  $J$  = 7.5 Hz, 2H:3,6); 7.45 (q,  $J$  = 7.5 Hz, 2H:2,7); 5.52 (s, 1H:12); 5.13 (s, 5H:C<sub>5</sub>H<sub>5</sub>).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 225.2–220.1 (Mo–CO); 203.6 (Co–CO); 185.0 (C9); 149.6–149.1 (C4a C5a); 133.4–132.6 (C3 C6); 130.6 (C1a C8a); 128.2 (C2 C7); 127.0 (C1 C8); 125.8–125.1 (C4 C5); 100.9 (C11); 90.0 (C<sub>5</sub>H<sub>5</sub>); 83.3 (C12), 76.2 (C10).

IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu_{\text{CO}}$  = 2053, 2008, 1987, 1953, 1665  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{26}\text{H}_{15}\text{CoMoO}_7$ : C, 52.55; H, 2.54; found: C, 53.50; H, 2.70.

#### 4.5. [ $\text{MoCoCp}(\text{CO})_5(\mu, \eta^2, \eta^2\text{-10-ethynyl-10-methoxy-9-anthrone})$ ] **7**

**7** is prepared in the same way as that described for **6** and was obtained in 65% yield. Decomposes at 165 °C.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 8.26 (dd,  $J$  = 7.7, 1.2 Hz, 1H:1); 8.18 (dd,  $J$  = 7.7, 1.2 Hz, 1H:8); 7.80 (dd,  $J$  = 7.7, 0.6 Hz, 1H:4); 7.66 (m, 3H:3,5,6); 7.50 (m, 2H:2,7); 5.70 (s, 1H:12); 4.88 (s, 5H:C<sub>5</sub>H<sub>5</sub>); 3.13 (s, 3H:OCH<sub>3</sub>).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 225.6–220.4 (Mo–CO); 203.6 (Co–CO); 184.3 (C9); 146.1–145.9 (C4a C5a); 133.6–132.8 (C3 C6); 132.1–131.8 (C1a C8a); 128.2 (C2 C7); 127.2 (C1 C8); 127.1–126.4 (C4 C5); 99.4 (C11); 90.0 (C<sub>5</sub>H<sub>5</sub>); 84.9 (C12); 81.8 (C10); 53.7 (OCH<sub>3</sub>).

IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu_{\text{CO}}$  = 2053, 2007, 1987, 1946, 1666  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{27}\text{H}_{17}\text{CoMoO}_7$ : C, 53.31; H, 2.82; found: C, 52.97; H, 2.89.

#### 4.6. [ $\text{Co}_2(\text{CO})_6(\mu, \eta^2, \eta^2\text{-10-methoxy-10-phenylethynyl-9-anthrone})$ ] **8**

The complex **8** was prepared in the same way as described for **4**, in 80% yield. Melting point 138 °C.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 8.28 (dd,  $J$  = 7.5, 1.3 Hz, 2H:1,8); 7.83 (dd,  $J$  = 7.5, 1.3 Hz, 2H:4,5); 7.52 (m, 4H:3,6,14,18); 7.47 (dd,  $J$  = 7.5, 1.3 Hz, 2H:2,7); 7.30 (m, 3H:15,16,17); 3.28 (s, 3H:OCH<sub>3</sub>).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 198.5 (Co–CO); 183.2 (C9); 144.6 (C4a C5a); 138.7 (C13); 133.4 (C3 C6); 132.2 (C1a C8a); 129.4 (C2 C7); 128.8–128.6 (C14,15,17,18); 127.7 (C1 C8); 126.9 (C4 C5); 127.5 (C16); 109.4 (C11); 95.7 (C12); 80.4 (C10); 54.0 (OCH<sub>3</sub>).

IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu_{\text{CO}}$  = 2092, 2059, 2032  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{29}\text{H}_{16}\text{Co}_2\text{O}_8$ : C, 57.07; H, 2.64; found: C, 56.98; H, 2.74.

#### 4.7. [ $\text{MoCoCp}(\text{CO})_5(\mu, \eta^2, \eta^1\text{-10-ethynyl-10(9H)-oxoanthracen-9-ylidene})$ ]<sup>+</sup>BF<sub>4</sub><sup>−</sup> **9**

To 0.3 g (0.5 mmol) of **6** and **7** in 10 ml ether were added 0.25 ml of  $\text{HBF}_4\text{-Et}_2\text{O}$  complex at room temperature. After the formation of a yellow-brown precipitate, ether was removed and the solid washed five times with ether, then dried under vacuum. 0.22 g of **9** were obtained in 78% yield.

$^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 8.32 (dd,  $J$  = 7.5, 1.5 Hz, 1H:1); 8.19 (dd,  $J$  = 7.5, 1.5 Hz, 1H:8); 8.12 (dd,  $J$  = 7.5, 1.5 Hz, 1H:4); 7.82–7.64 (m, 5H:2,3,5,6,7); 7.52 (s, 1H:12); 5.14 (s, 5H:C<sub>5</sub>H<sub>5</sub>).

$^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 216.9–209.4 (Mo–CO); 198.8 (Co–CO, broad); 190.9 (C9); 143.5 (C4a C5a); 139.9 (C10); 134.3, 133.0, 132.6, 131.6 (C:2,3,6,7); 128.3–128.0 (C1 C8); 124.1–122.8 (C4 C5); 116.4 (C11); 96.6 (C<sub>5</sub>H<sub>5</sub>); 89.1 (C12).

IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu_{\text{CO}}$  = 2100, 2069, 2054, 1668  $\text{cm}^{-1}$ .

#### 4.8. [ $\text{MoCoCp}(\text{CO})_5(\mu, \eta^2, \eta^2\text{-10-ethynyl-9-anthrone})$ ] **10**

To a solution of 0.13 g ( $0.2 \times 10^{-3}$  mol) of **9** in 5 ml  $\text{CH}_2\text{Cl}_2$  were added 0.1 g  $\text{NaBH}_4$ . The solution turned

red. After hydrolysis the organic phase was extracted by ether then washed and dried on magnesium sulfate and chromatographed on silica plates using pentane as eluent. 0.08 g of a solid red product was obtained in 72% yield.

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ): 8.26 (dd,  $J = 8.5$ , 1 Hz, 1H); 8.12 (dd,  $J = 8.5$ , 1 Hz, 1H); 7.51 (m, 6H); 5.87 (s, 1H); 5.30 (s, 1H); 4.77 (s, 5H; C5H5).

IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu_{\text{CO}} = 2051$ , 2004, 1984, 1946, 1662  $\text{cm}^{-1}$ .

#### 4.9. Supporting information

For 5, 7 and 8 tables of atomic coordinates, all bond distances and angles, and anisotropic thermal parameters (42 pages) are available.

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