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Journal of Organometallic Chemistry 585 (1999) 43–52

Journal of Organometallic Chemistry

Stereoselective reactivity of diastereotopic carbon–carbon triple bonds induced by chiral orthosubstituted arene tricarbonyl chromium complexes. Diastereoselective $Co_2(CO)_8$ complexation and $LiAlH_4$ reduction

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Received 21 December 1998

Abstract

The diastereoselective $Co_2(CO)_8$ complexation and $LiAlH_4$ reduction of diastereotopic carbon–carbon triple bond, induced by chiral *ortho* substituted arene tricarbonylchromium complexes is described. The relative configuration of the obtained diastereoisomers are determined unequivocally by X-ray crystallography, ^{1}H-NMR and transition state analysis.

Keywords: Arene tricarbonylchromium complex; C–C triple bond; $Co_2(CO)_8$ complexation; $LiAlH_4$ reduction

1. Introduction

1-2 unsymmetrically disubstituted arene tricarbonylchromium complexes are chiral molecules. Since the pioneer work of the groups of Dabard [1] and Tirouflet [2], several laboratories have reported various diastereoselective and enantioselective synthesis induced by the metallocenic chirality [3]. In most known cases, the stereoselective formation of the new chiral center was produced from prochiral carbonyls [4], imines [5], C–C double bonds [6], oxonium ions [7], chromium stabilized carbocations [8], and arene tricarbonylchromium stabilized carbanions [9]. A special case was the dioxirane oxidation involving diastereotopic lone pairs of sulfinyl *ortho* substituted arene tricarbonylchromium complex [10].

The monoreactivity of diastereotopic functions in chiral arene tricarbonylchromium complexes, could be an other attractive, but to the best of our knowledge, unexplored approach to diastereoselective and enantioselective synthesis in this series.

In this paper, we disclose the diastereoselective reactivity of C–C triple bonds induced by the chirality of *ortho*-substituted arene tricarbonylchromium complexes. As first examples we have selected two classic reactions in acetylenic chemistry: the $Co_2(CO)_8$ complexation [11] and the $LiAlH_4$ reduction [12].

2. Results and discussion

2.1. Synthesis of the diacetylenic complexes

The racemic diynes **1**, **2**, **5**, **6** are easily accessible in good yield (64–90%) from the reaction of methyl, *ortho*-methoxy or *ortho*-methyl-benzoate tricarbonylchromium complexes with two equivalents of the adequate lithium acetylide (Scheme 1).

Adding NaOH to methanolic solution of **2** allowed the formation of complex **3** (yield: 88%) (Scheme 2).

Silylation of the potassium alcoholate, obtained from

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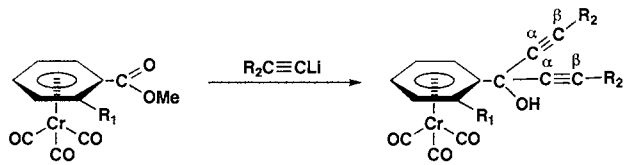
PII: S0022-328X(99)00187-4



Scheme 1.

1 by Me_3SiCl produced **4** in good yield (73,6%) (Scheme 3).

As expected for the presence of diastereotopic functions, ^{1}H-NMR spectra show two clean singlets for the acetylenic hydrogens of **3** and for the methyl protons of the $SiMe_3$ groups of **2** (**3**: $\delta \equiv C-H$ 3.20 and 3.22 ppm; **2**: $\delta \equiv C-SiMe_3$: 0.19 and 0.16 ppm).

Similar inequivalence is found for the C_β of the carbon–carbon triple bond (**3**: C_β: 74.34 and 73.64 ppm; **2**: $C_\beta Si$: 89.37 and 88.20 ppm).

2.2. Diastereoselective cobalt carbonyl complexation

The complexation of a carbon–carbon triple bond by $Co_2(CO)_8$ is a very popular reaction in organometallic chemistry. The synthetic potentiality of the obtained acetylenic cobalt–carbonyl complexes, especially in the propargylic series, has been well demonstrated [11].

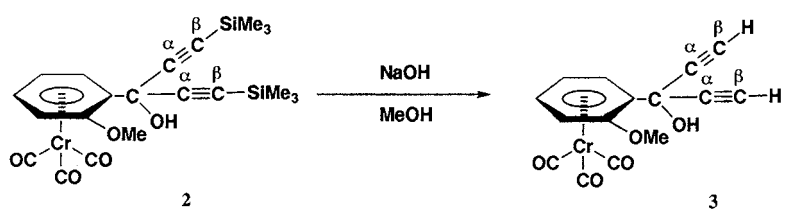
To test the stereoselectivity of the complexation, complexes **1**–**6** (one equivalent) were reacted with $Co_2(CO)_8$ (one and a half equivalents) in ether solution at room temperature (r.t.) (Scheme 4). In this condition no product resulting from a decomplexation reaction could be detected. As expected, the monocomplexation is stereoselective. The diastereoisomer ratio was determined by ^{1}H-NMR examination of the mixture obtained after chromatographic purification. For the *ortho*-methoxy complexes case, the diastereoselectivity is dependent on the acetylenic carbon–carbon triple bond substitution and insensitive apparently to the substitution of the hydroxy hydrogen by a $SiMe_3$ group. The diastereoisomeric mixture of **7a**–**7b**, **8a**–**8b**, **9a**–**9b**, **10a**–**10b** were separated easily by chromatography on silica gel plates (eluent: ether–petroleum ether).

The complexation of **5** and **6** (*ortho*-methyl complexes case) was less stereoselective and the chromatographic separation of the diastereoisomeric mixture was unsuccessful.

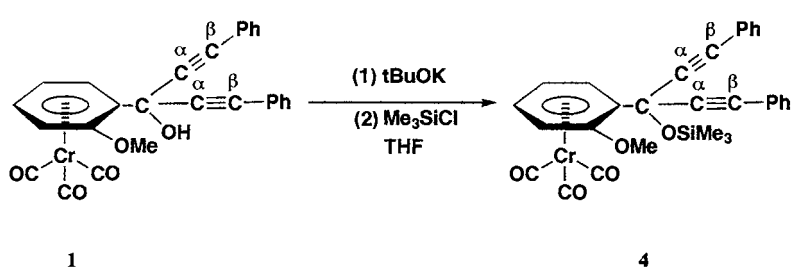
The structure of the major diastereoisomeric heterotrinuclear complex **7a** was determined unequivocally by single X-ray structural analysis (Fig. 1).

The relative configuration was identified as *S*R**. It seems reasonable for us to extend this stereochemical assignment to the other *ortho*-methoxy complexes and consequently to attribute for the major diastereoisomers **8a** and **9a** the *S*R** configuration. The assessment of this proposal is reinforced by the following facts: (1) chromatographic analysis (silica gel plates; eluent: ether–petroleum ether 1/3) gave a greater R_f value for the major diastereoisomers **7a, 8a, 9a** (*ortho*-methoxy series, Table 1). In the same conditions the *ortho*-methyl isomers **11a**–**11b** and **12a**–**12b** are inseparable; (2) for the *ortho*-methoxy series in the same NMR solvent ($CDCl_3$ or CD_3COCD_3) a chemical shift correlation is observed between the hydrogens of the alcohol function of each class of stereoisomers.

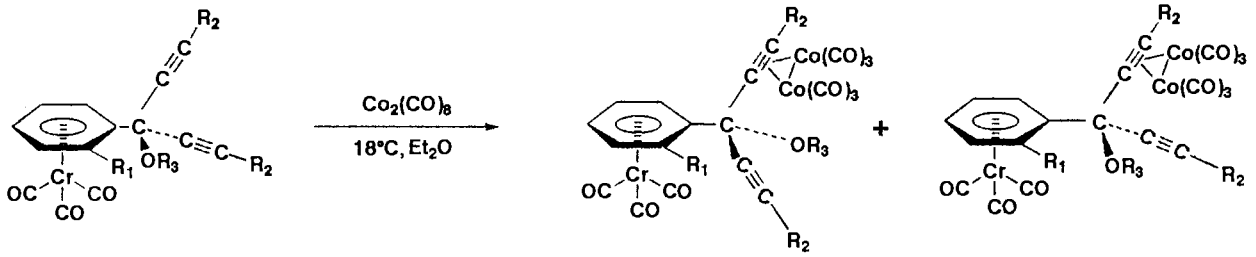
The low-field resonance of the hydroxyl hydrogen, found in $CDCl_3$, for the minor *ortho*-methoxy-isomers



Scheme 2.



Scheme 3.



			%	%
1 : R_1 = OMe	R_2 = Ph	R_3 = H	7a : 79	7b : 21
2 : R_1 = OMe	R_2 = $SiMe_3$	R_3 = H	8a : 80	8b : 20
3 : R_1 = OMe	R_2 = H	R_3 = H	9a : 68	9b : 32
4 : R_1 = OMe	R_2 = Ph	R_3 = $SiMe_3$	10a : 80	10b : 20
5 : R_1 = Me	R_2 = Ph	R_3 = H	11a : 65	11b : 35
6 : R_1 = Me	R_2 = $SiMe_3$	R_3 = H	12a : 60	12b : 40

Scheme 4.

7b and **8b** (Table 1) suggests the formation of an intramolecular hydrogen bond, probably with the oxygen of the methoxy group. The lack of significant chemical shift differences (δOH minor–δOH major, Table 1) observed for the *ortho*-methyl series confirms this view. On the other hand, the donor capacity of CD_3COCD_3 [13] allows the formation of an hydrogen bond with the hydroxyl hydrogen of the major isomers **7a**, **9a** (Table 1). As a consequence a low-field resonance is observed for the hydroxy protons and the chemical shift difference (δOH minor–δOH major) is inverse.

Finally for **10a**, the configuration reported in Scheme 4 was validated as follows: **10a** was reacted with NBu_4F at -40°C in CH_2Cl_2 to lead the hetero-trinuclear complex **7a** of known configuration together with the tricarbonylchromium complex **1** as the result of a decomplexation process by the fluoride anions [14].

Another important feature of the crystal structure data of **7a** is the location of the metal carbonyl fragments and of the oxygenated groups. In the crystal, to avoid severe steric interaction, the acetylenic cobalt carbonyl fragment lies far away from the tricarbonylchromium moiety. As a consequence the oxygenated groups (OR_3–OCH_3) are in a quasi *anti*-conformation.

Having in mind this information, the formation of the major diastereoisomer, for the *ortho*-methoxy complexes cases, is at best rationalized by the less strained transition state A in which the acetylenic cobalt carbonyl fragment lies on the *exo*-face of the arene tricarbonylchromium complex (Scheme 5). In the transition state similar to A, leading to the minor isomers, an unfavourable interaction involving the polar oxygenated groups appears. To minimize this interaction, the least sterically demanding linear acetylenic function is moved towards the chromiumtricarbonyl moiety by rotation around the C_{Ar}–C_1 bond (transition state B). When $R_2 = H$ the corresponding transition state is less strained and the percentage of the minor diastereoisomer **9b** rises slightly.

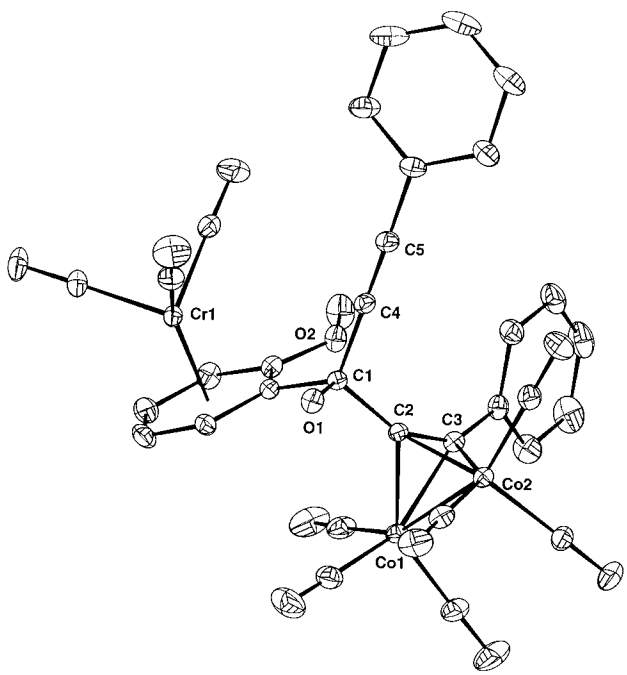
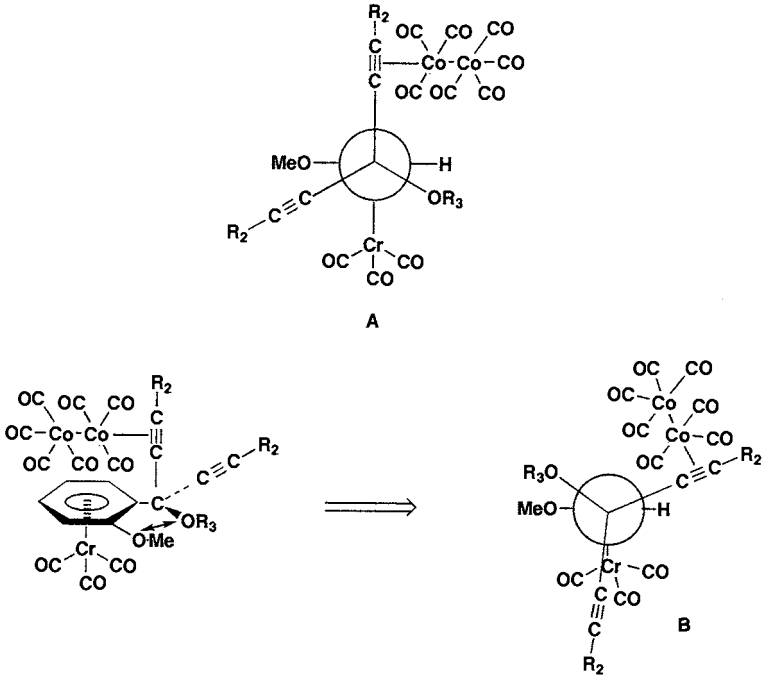
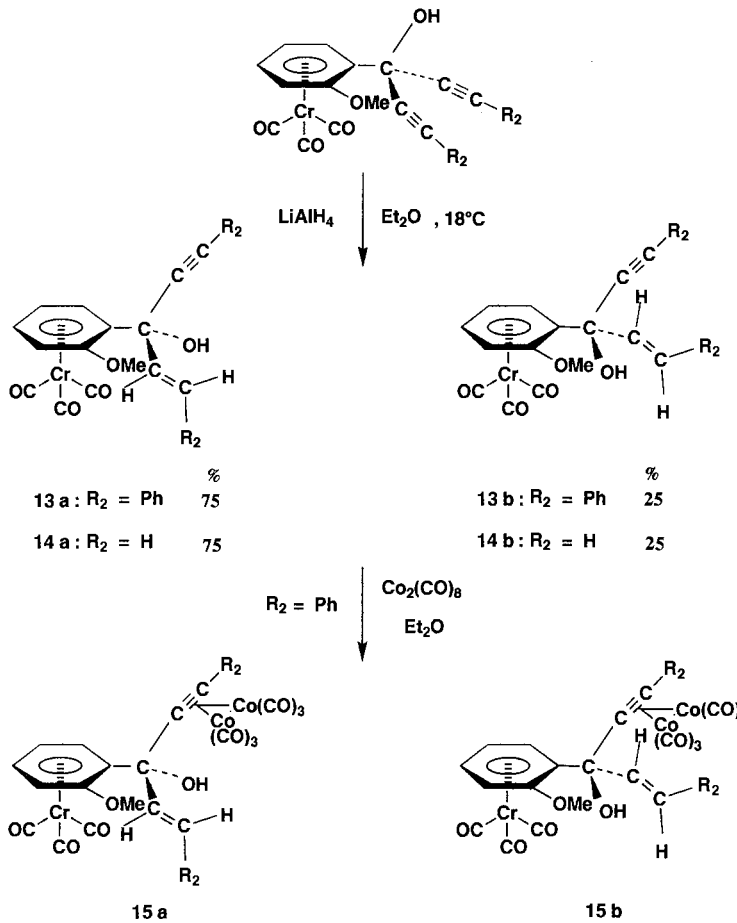


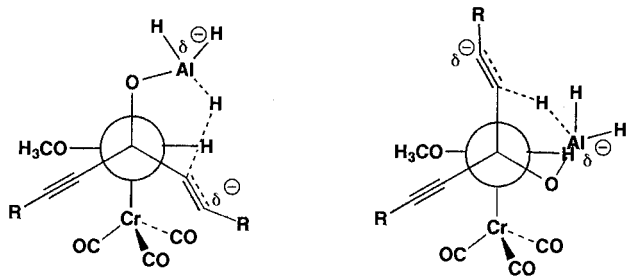
Fig. 1. Structure of **7a**.



Scheme 5.



Scheme 6.



Scheme 7.

For the *ortho*-methyl-complex case, in the lack of significant differences, related to those found for the *ortho*-methoxy series, the stereochemical assignment for **11a**–**12a**, **11b**–**12b** seems more difficult. However, assuming again an *exo* location of the acetylenic metal carbonyl fragment in the transition states, and the prominence of the unfavourable *ortho*-methyl–OH steric interaction over the ortho-methyl–R–C≡C-one [15] we suggest the configuration reported in Scheme 4 for **11a**–**12a** and **11b**–**12b**.

2.3. Diasteroselective $LiAlH_4$ reduction

We then examined the $LiAlH_4$ reduction.

Lithium aluminium hydride reduction of propargylic alcohols is a convenient route to allylic alcohols [12]. The mechanistic aspect of this reaction has received a great deal of attention. The reduction was known to proceed via specific hydride transfer from the aluminium bond to oxygen to the adjacent carbon of the acetylenic linkage [12].

In order to test the stereoselectivity of the reduction, complexes **1** and **3** were reacted with $LiAlH_4$ in ether solution to give after hydrolysis an unseparable mixture of the diastereoisomeric ene-yne complexes **13a**–**13b** (yield 42%, **13a**/**13b** 3/1) and **14a**/**14b** (yield 46%, **14a**–**14b** 3/1) (Scheme 6).

For **13a** and **13b** ^{1}H-NMR coupling constant values are consistent with a *cis* addition leading exclusively to the *trans* complexes [12].

The relative configuration of the diastereoisomers was determined as follows. The mixture of **13a**–**13b** was reacted with $Co_2(CO)_8$ to afford the diastereoisomeric hetero–trinuclear complexes **15a**–**15b** (Scheme 6). After separation by chromatography on silica gel plates, the ^{1}H-NMR of **15a** and **15b** was recorded (solvent $CDCl_3$).

Table 2
^{1}H-NMR chemical shifts of the hydroxyl hydrogen

No. alcohol	**7a**	**7b**	**15a**	**15b**
Solvent	$CDCl_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$
δ (OH) (ppm)	3.20	5.20	2.60	5.27

Assuming that **15a** and **15b** exist predominantly in the same favoured conformations than **7a** and **7b**, the chemical shift values of the alcohol hydrogen would be comparable for the two types of isomer. In perfect agreement with the prevision, similar O<u>H</u> chemical shift values were found for **15a** and **7a** and for **15b** and **7b** (Table 2).

Consequently we propose the *S*R** configuration for the major hetero–trinuclear en-yne complex **15a** and the *S*S** configuration for the tricarbonylchromium complex **13a**.

As noted above, the reduction of propargylic alcohols by $LiAlH_4$ involves in a first step the formation of an oxygen aluminium bond, followed by an intramolecular hydride transfer. On this basis the major formation of the *S*S** isomers **13a** and **14a** can be rationalized in terms of a cyclic transition state C (Scheme 7) in which the $-OAlH_3^-$ anionic group lies away from the tricarbonylchromium fragment, which prevents at best the unfavourable interactions with the *ortho*-methoxy group. In the transition state D which leads to the minor isomer, two unfavorable interactions occur on the one hand between the aluminium hydride and the phenyl $Cr(CO)_3$ groups and on the other hand between the partly negatively charged β carbon of the C≡C bond and the *ortho*-methoxy group.

3. Conclusions

Two diastereoselective reactions, induced by the chirality of *ortho*-substituted arene tricarbonylchromium

Table 1
^{1}H-NMR chemical shift of the hydroxyl hydrogen

No alcohol	**7a** [a]	**7a**	**7b**	**7b**	**8a**	**8b**	**9a**	**9b**	**11a**+**11b**	**12a**+**12b**
Solvent	$CDCl_3$	acetone-d_6	$CDCl_3$	acetone-d_6	$CDCl_3$	$CDCl_3$	acetone-d_6	acetone-d_6	$CDCl_3$	$CDCl_3$
δ (OH) (ppm)	3.20	6.59	5.20	5.69	3.00	5.05	6.20	5.39	3.31 3.26	3.11 3.05
R_f [b]	0.50		0.34		0.74	0.50	0.44	0.34		

[a] For the analogous complex (R_1 = H) δ (OH) $CDCl_3$ 3.26 ppm (M.-C. Sénéchal unpublished result).
[b] Silica gel 60; 0.25 mm plates; solvent 1:3 ether–petroleum ether.

complexes, involving diastereotopic acetylenic functions, have been reported. Good diastereoselectivity is obtained in the methoxy-*ortho* series for the cobalt carbonyl complexation and the $LiAlH_4$ reduction. The relative configuration of the diastereoisomeric products have been determined by the aid of X-ray structural analysis and ^{1}H-NMR.

As the diacetylenic tricarbonylchromium complexes could be obtained easily in optical active form, from the corresponding optically pure ester [16], the development of enantioselective synthesis based on this methodology is conceivable.

4. Experimental

All preparations were carried out under an atmosphere of dry nitrogen. Solvents were dried and distilled according to standard procedures. ^{1}H-NMR spectra were recorded in $CDCl_3$ or in acetone-d_6 on a Brucker A.M. 300 MHz spectrometer. Infrared spectra were recorded on a Perkin–Elmer Spectrum 1000 FTIR spectrophotometer using KBr plates. Mass spectra were recorded using a MS/MS Micromass Zab Sep TOF spectrometer.

Table 3
Interatomic distances (Å) for $C_{33}H_{18}O_{11}Co_2Cr$

Cr(1)–C(11)	1.827(3)	Cr(1)–C(12)	1.846(3)
Cr(1)–C(13)	1.839(3)	Cr(1)–C(21)	2.230
Cr(1)–C(22)	2.266(3)	Cr(1)–C(23)	2.225(3)
Cr(1)–C(24)	2.207(3)	Cr(1)–C(25)	2.230(3)
Cr(1)–C(26)	2.213(3)	Co(1)–Co(2)	2.4566(5)
Co(1)–C(2)	1.948(2)	Co(1)–C(3)	1.949(3)
Co(1)–C(14)	1.793(3)	Co(1)–C(15)	1.830(4)
Co(1)–C(16)	1.818(3)	Co(2)–C(2)	1.967(2)
Co(2)–C(3)	2.004(2)	Co(2)–C(17)	1.826(3)
Co(2)–C(18)	1.820(3)	Co(2)–C(19)	1.780(3)
O(1)–C(1)	1.420(3)	O(2)–C(22)	1.334(3)
O(2)–C(27)	1.429(4)	O(11)–C(11)	1.139(4)
O(12)–C(12)	1.139(5)	O(13)–C(13)	1.151(4)
O(14)–C(14)	1.132(5)	O(15)–C(15)	1.122(5)
O(16)–C(16)	1.119(4)	O(17)–C(17)	1.125(4)
O(18)–C(18)	1.124(4)	O(19)–C(19)	1.128(5)
C(1)–C(2)	1.515(3)	C(1)–C(4)	1.473(3)
C(1)–C(21)	1.534(3)	C(2)–C(3)	1.347(3)
C(3)–C(31)	1.460(4)	C(4)–C(5)	1.199(4)
C(5)–C(51)	1.431(4)	C(21)–C(22)	1.415(3)
C(21)–C(26)	1.421(3)	C(22)–C(23)	1.427(4)
C(23)–C(24)	1.386(5)	C(24)–C(25)	1.412(5)
C(25)–C(26)	1.394(4)	C(31)–C(32)	1.382(5)
C(31)–C(36)	1.383(4)	C(32)–C(33)	1.400(4)
C(33)–C(34)	1.360(7)	C(34)–C(35)	1.374(8)
C(35)–C(36)	1.398(6)	C(51)–C(52)	1.389(5)
C(51)–C(56)	1.391(5)	C(52)–C(53)	1.390(5)
C(53)–C(54)	1.375(8)	C(54)–C(55)	1.358(8)
C(55)–C(56)	1.392(5)		

Table 4
Bond angles (°) for $C_{33}H_{18}O_{11}Co_2Cr$

C(11)–Cr(1)–C(12)	87.0(2)	C(11)–Cr(1)–C(13)	90.1(2)
C(12)–Cr(1)–C(13)	89.7(2)	C(11)–Cr(1)–C(21)	107.0(1)
C(12)–Cr(1)–C(21)	95.6(1)	C(13)–Cr(1)–C(21)	162.3(1)
C(11)–Cr(1)–C(22)	86.8(1)	C(12)–Cr(1)–C(22)	125.7(1)
C(13)–Cr(1)–C(22)	144.2(1)	C(11)–Cr(1)–C(23)	94.8(1)
C(12)–Cr(1)–C(23)	162.2(1)	C(13)–Cr(1)–C(23)	108.0(1)
C(11)–Cr(1)–C(24)	125.7(2)	C(12)–Cr(1)–C(24)	147.1(2)
C(13)–Cr(1)–C(24)	87.6(2)	C(11)–Cr(1)–C(25)	161.1(1)
C(12)–Cr(1)–C(25)	110.9(1)	C(13)–Cr(1)–C(25)	95.7(1)
C(11)–Cr(1)–C(26)	143.5(1)	C(12)–Cr(1)–C(26)	89.4(1)
C(13)–Cr(1)–C(26)	126.2(1)		
Co(2)–Co(1)–C(2)	51.47(7)	Co(2)–Co(1)–C(3)	52.58(7)
C(2)–Co(1)–C(3)	40.4(1)	Co(2)–Co(1)–C(14)	150.9(1)
C(2)–Co(1)–C(14)	104.1(1)	C(3)–Co(1)–C(14)	99.0(1)
Co(2)–Co(1)–C(15)	100.6(1)	C(2)–Co(1)–C(15)	101.2(1)
C(3)–Co(1)–C(15)	140.7(1)	C(14)–Co(1)–C(15)	99.8(2)
Co(2)–Co(1)–C(16)	99.1(1)	C(2)–Co(1)–C(16)	144.4(1)
C(3)–Co(1)–C(16)	108.0(1)	C(14)–Co(1)–C(16)	95.8(2)
C(15)–Co(1)–C(16)	104.1(2)	Co(1)–Co(2)–C(2)	50.79(6)
Co(1)–Co(2)–C(3)	50.59(8)	C(2)–Co(2)–C(3)	39.6(1)
Co(1)–Co(2)–C(17)	97.8(1)	C(2)–Co(2)–C(17)	104.1(1)
C(3)–Co(2)–C(17)	140.6(1)	Co(1)–Co(2)–C(18)	97.6(1)
C(2)–Co(2)–C(18)	140.7(1)	C(3)–Co(2)–C(18)	104.1(1)
C(17)–Co(2)–C(18)	102.9(1)	Co(1)–Co(2)–C(19)	148.8(1)
C(2)–Co(2)–C(19)	100.8(1)	C(3)–Co(2)–C(19)	100.1(1)
C(17)–Co(2)–C(19)	102.5(2)	C(18)–Co(2)–C(19)	100.6(2)
C(22)–O(2)–C(27)	119.1(3)	O(1)–C(1)–C(2)	110.0(2)
O(1)–C(1)–C(4)	109.1(2)	C(2)–C(1)–C(4)	110.4(2)
O(1)–C(1)–C(21)	105.5(2)	C(2)–C(1)–C(21)	109.4(2)
C(4)–C(1)–C(21)	112.4(2)	Co(1)–C(2)–Co(2)	77.73(7)
Co(1)–C(2)–C(1)	132.7(2)	Co(2)–C(2)–C(1)	132.2(2)
Co(1)–C(2)–C(3)	69.8(1)	Co(2)–C(2)–C(3)	71.7(1)
C(1)–C(2)–C(3)	144.9(2)	Co(1)–C(3)–Co(2)	76.82(9)
Co(1)–C(3)–C(2)	69.7(1)	Co(2)–C(3)–C(2)	68.7(1)
Co(1)–C(3)–C(31)	135.9(2)	Co(2)–C(3)–C(31)	131.1(2)
C(2)–C(3)–C(31)	145.2(2)	C(1)–C(4)–C(5)	174.8(3)
C(4)–C(5)–C(51)	178.3(3)	Cr(1)–C(11)–O(11)	178.2(3)
Cr(1)–C(12)–O(12)	177.2(4)	Cr(1)–C(13)–O(13)	178.6(4)
Co(1)–C(14)–O(14)	176.5(4)	Co(1)–C(15)–O(15)	178.5(3)
Co(1)–C(16)–O(16)	178.8(4)	Co(2)–C(17)–O(17)	178.2(3)
Co(2)–C(18)–O(18)	179.0(4)	Co(2)–C(19)–O(19)	177.4(4)
C(1)–C(21)–C(22)	120.9(2)	C(1)–C(21)–C(26)	119.9(2)
C(22)–C(21)–C(26)	119.2(2)	O(2)–C(22)–C(21)	116.6(2)
O(2)–C(22)–C(23)	124.0(2)	C(21)–C(22)–C(23)	119.4(12)
C(22)–C(23)–C(24)	120.0(3)	C(23)–C(24)–C(25)	121.1(3)
C(24)–C(25)–C(26)	119.3(3)	C(21)–C(26)–C(25)	121.0(3)
C(3)–C(31)–C(32)	120.2(3)	C(3)–C(31)–C(36)	120.9(3)
C(32)–C(31)–C(36)	118.9(3)	C(31)–C(32)–C(33)	120.6(4)
C(32)–C(33)–C(34)	120.1(4)	C(33)–C(34)–C(35)	119.9(3)
C(34)–C(35)–C(36)	120.5(4)	C(31)–C(36)–C(35)	120.0(4)
C(5)–C(51)–C(52)	120.4(3)	C(5)–C(51)–C(56)	120.1(3)
C(52)–C(51)–C(56)	119.4(3)	C(51)–C(52)–C(53)	119.8(4)
C(52)–C(53)–C(54)	120.4(4)	C(53)–C(54)–C(55)	120.0(3)
C(54)–C(55)–C(56)	121.0(4)	C(51)–C(56)–C(55)	119.4(4)

4.1. Preparation of the diacetylenic tricarbonylchromium complexes

*4.1.1. General procedure for the preparation of the diynes **1**, **2**, **5**, **6***

A solution of the ester (5 mmol in 20 ml of THF)

was added at −40°C to a solution of the adequate lithium acetylide (12.5 mmol in 20 ml of THF). The reaction was warmed to room temperature (r.t.). The stirring was continued for 2 h. The reaction mixture was poured onto water. After extraction with ether, drying over $MgSO_4$ and evaporation of the solvent, chromatography was then performed on the residue using silica gel plates (eluent ether–petroleum ether).

*4.1.2. Preparation of the diyne **3***

Aqueous 1 M NaOH was added to a degassed methanolic solution of **2** (2.44 g, 5.4 mmol). Progress of the reaction was monitored by silica gel TLC plates. The reaction mixture was poured onto water and the organometallic complex extracted with ether. The organic layer was dried over $MgSO_4$. After evaporation of the solvent, chromatography was performed on the crude using silica gel plates (eluent ether–petroleum ether) to give the diyne **3** (1.44 g, 4.5 mmol).

*4.1.3. Preparation of the diyne **4***

The diyne **1** (0.474 g, 1 mmol) was dissolved in THF.

Table 5
Crystal data for $C_{33}H_{18}O_{11}Co_2Cr$

F_w	760.4
a (Å)	10.726(2)
b (Å)	13.572(2)
c (Å)	11.851(1)
α (°)	90.
β (°)	109.85(1)
γ (°)	90.
V (Å^3)	1622.6(4)
Z	2
Crystal system	Monoclinic
Space group	$P2_1$
Linear absorption coefficient μ (cm^{-1})	13.87
Density ρ (g cm^{-3})	1.56
Diffractometer	CAD4 0Enraf–Nonius
Radiation	Mo–K$_\alpha$ ($\lambda = 0.71069$ Å)
Scan type	$\omega/2\theta$
Scan range (°)	$0.8 + 0.345$ tgθ
θ Limits (°)	1–35
Temperature of measurement	r.t.
Octants collected	0,17; 0,21; −19,17
Nb of data collected	7665
Nb of unique data collected	7347
Nb of unique data used for refinement	5477 $(F_o)^2 > 3\sigma\ (F_o)^2$
R (int)	0.024
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.0379
$R_w = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma wF_o^2]^{1/2}$ [a]	0.0391
Absorption correction	No
Extinction parameter	903
Goodness-of-fit	0.998
Nb of variables	426
$\Delta\rho$ min (e Å^{-3})	−0.60
$\Delta\rho$ max (e Å^{-3})	0.40

[a] $w = w'[1 - ((\|F_o\| - \|F_c\|)/6\sigma\ (F_o))^2]^2$ with $w' = 1/\Sigma_r A_r T_r(X)$ with three coefficients, 9.02, −2.41 and 6.85 for a Chebychev Serie, for which X is F_o/F_o(max).

t-BuOK (0.224 g, 2 mmol) was added, and the solution was stirred at r.t. for 15 min. Me_3SiCl (0.326 g, 3 mmol) was then added. Progress of the reaction was monitored by silica gel TLC plates. The reaction mixture was poured onto water and the complex extracted with ether. The organic layer was dried over $MgSO_4$. After evaporation of the solvent chromatography was performed on the residue using silica gel plates (eluent ether–petroleum ether) to give **4** (0.402 g, 0.74 mmol).

*4.1.4. General procedure for the $Co_2(CO)_6$ complexation of the diynes **1**, **3**, **4**, **5**, **6**, **13a**, **13b***

A total of 4 mmol of $Co_2(CO)_8$ was added to a degased solution of diynes (2 mmol in 20 ml of ether) at r.t. After stirring for 2 h, the solvent was evaporated. Chromatography was performed on the residue using silica gel plates (eluent ether–petroleum ether) to give the expected cobalt carbonyl complexes.

*4.1.5. $LiAlH_4$ reduction of diynes **1** and **3***

The appropriate diyne alcohol and an excess of Li Al H_4 was stirred in ether at r.t. for 4 h. Hydrolysis was carried out by careful dropwise addition of H_2O. Then the organometallic complexes were extracted with ether. The ether solution was washed with water and dried over $MgSO_4$. After chromatography (silica gel plates, eluent ether–petroleum ether) the en-yne complexes were isolated as a yellow mixture of diastereoisomers. 0.474 g of complex **1** (1 mmol) gave 0.200 g of 1**3a** and **13b**. A total of 0.483 g of complex **3** (1.5 mmol) gave 0.223 g of **14a** and **14b**.

*4.1.6. Desilylation of the complex **10a***

Complex **10a** (0.240 g, 0.29 mmol) was dissolved in anhydrous CH_2Cl_2, and the resulting solution cooled to −40°C. A total of 76 mg (0.29 mmol) of solid TBAF [NBu_4F] was added. The solution was allowed to stir for 15 min. The reaction mixture was poured onto water, extracted with ether, and dried over $MgSO_4$. After evaporation of the solvent, chromatography was performed on the crude using silica gel plates (eluent ether–petroleum ether) to give the complex **7a** (70 mg, 32% Yield), the complex **1** (40 mg, 29% Yield) and a small portion of the unreacted complex **10a** (40 mg, 17% Yield).

4.2. X-ray crystallography (structure resolved by J. Vaisserman, Laboratoire de Chimie de Métaux de Transition, Université Pierre et Marie Curie, Paris, France)

Complex **7a** was crystallized from ether with petroleum 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 bond distances and bond angles are collected in Tables 3 and 4. The crystallographic data collection parameters appear in Table 5 and atomic positional parameters in Table 6.

4.3. Spectroscopic data for the new complexes

4.3.1. NMR, IR and analytical data for the new compounds

1 ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.56 (m, 4H, Ph); 7.35 (s, 6H, Ph); 6.45 (d, 1H, Bct); 5.64 (s, 1H, Bct); 5.08 (d, 1H, Bct); 4.85 (t, 1H, Bct); 4.01 (s, 1H, OH); 3.94 (s, 3H, OCH_3). IR (KBr) ν (cm^{-1}): ν (OH) 3524; ν (C≡O) 1963, 1881. MS m/z 474 M^+, 457 $(M–OH^-)^+$, 390 (M-3 CO)$^+$, 321 $(M–OH–Cr(CO)_3)^+$. Calc.: 474.0559. Found: 474.0585.

2 ^{1}H-NMR (acetone-d_6) δ (ppm): 6.45 (d, 1H, Bct); 5.87 (m, 2H, Bct + OH); 5.48 (d, 1H, Bct); 5.05 (t, 1H, Bct); 3.91 (s, 3H, OCH_3). ^{13}C NMR (acetone-d_6) δ (ppm): 234.01 (COBct); 143.72 ($COCH_3$); 105.15 (C≡CSi); 102.40 (CBct); 96.97 (CHBct); 89.37 (C≡CSi); 88.20 (CHBct); 84.33 (CHBct); 75.49 (CHBct); 63.30 (COH); 56.48 (OCH_3); −0.18 ($SiMe_3$); −0.23 ($SiMe_3$). IR (KBr) ν (cm^{-1}): ν (OH) 3530; ν (C≡O) 1971, 1886, 1874. MS m/z 466 M^+, 382 (M-3 CO)$^+$, 321 $(M–OH–Cr(CO)_3)^+$. Calc.: 466.0724. Found: 466.0726.

3 ^{1}H-NMR (acetone-d_6) δ (ppm): 6.47 (d, 1H, Bct); 6.02 (s, 1H, OH); 5.93 (t, 1H, Bct); 5.50 (d, 1H, Bct); 5.06 (t, 1H, Bct); 3.90 (s, 3H, OCH_3); 3.29 (s, 1H, acetylenic H); 3.23 (s, 1H, acetylenic H). ^{13}C-NMR (acetone-d_6) δ (ppm): 233.93 (COBct); 143.60 ($COCH_3$); 102.08 (CBct); 97.24 (CHBct); 96.77 (CHBct); 84.19 (CHBct); 83.71 (C≡CH); 75.34 (CHBct); 74.34 (C≡CH); 73.64 (C≡CH); 62.28 (COH); 56.66 (OCH_3). IR (KBr) ν (cm^{-1}): ν (OH) 3506, 3282; ν (C≡O) 1956, 1869. MS m/z 322 M^+, 305 $(M–OH^-)^+$, 266 $(M-2CO)^+$, 238 $(M-3CO)^+$. Calc.: 321.9933. Found: 321.9925.

4 ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.55 (m, 2H, Ph); 7.47 (m, 2H, Ph); 7.33 (m, 6H, Ph); 6.44 (d, 1H, Bct); 5.60 (t, 1H, Bct); 5,04 (d, 1H,Bct); 4.81 (t, 1H, Bct); 3.88 (s, 3H, OCH_3); 0,40 (s, 9H, $SiMe_3$). IR (KBr) ν (cm^{-1}): ν (OH) 3454; ν (C≡O) 1955, 1904, 1890. MS m/z 546 M^+, 462 $(M-3CO)^+$, 373 $(M-3CO-OSiMe_3)^+$, 321 $(M–Cr(CO)_3–OSiMe_3)^+$. Calc.: 546.0955. Found: 546.0969.

5 ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.52 (m, 4H, Ph); 7.36 (m, 6H, Ph); 6.43 (d, 1H, Bct); 5.52 (t, 1H, Bct); 5.07 (m, 2H, Bct); 3.13 (s, 1H, OH); 2.67 (s, 3H, CH_3). IR (KBr) ν (cm^{-1}): ν (OH) 3431; ν (C≡O) 1965, 1947, 1885. MS m/z 458 M^+, 441 $(M–OH^-)^+$, 374 $(M-3CO)^+$, 305 $(M–OH–Cr(CO)_3)^+$. Calc.: 458.0610. Found: 458.0630.

6 ^{1}H-NMR (acetone-d_6) δ (ppm): 6.45 (d, 1H, Bct); 6.36 (s, 1H, OH); 5.70 (t, 1H, Bct); 5.31 (d + t, 2H, Bct); 2.61 (s, 3H, CH_3); 0.20 (s, 9H, $SiMe_3$); 0.17 (s, 9H, $SiMe_3$). ^{13}C-NMR (acetone-d_6) δ (ppm): 234.13 (COBct); 112.29 (C≡CSi); 111.62 (CMe); 105.20 (CBct); 97.14 (CHBct); 96.02 (CHBct); 94.13 (CHBct); 90.58 (C≡CSi); 89.81 (C≡CSi); 88.32 (CHBct); 63.60 (COH); 20.06 (CH_3); −0.24 ($SiMe_3$); −0.38 ($SiMe_3$). IR (KBr) ν (cm^{-1}): ν (OH) 3413; ν (C≡O) 1958, 1899, 1881. MS m/z 442 M^+, 366 $(M-3CO)^+$, 297 $(M–OH–Cr(CO)_3)^+$. Calc.: 450.0775. Found: 450.0781.

7a ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.74 (m, 2H, Ph); 7.47 (m, 2H, Ph); 7.33 (m, 3H, Ph); 7.31 (m, 3H, Ph); 6.40 (d, 1H, Bct); 5.60 (t, 1H, Bct); 4.94 (d, 1H,Bct); 4.87 (t, 1H, Bct); 3.48 (s, 3H, OCH_3); 3.21 (s, 1H, OH). ^{13}C-NMR ($CDCl_3$) δ (ppm): 232.84 (COBct); 199.02 (COCo); 141.55 ($COCH_3$); 138.03 (C Ph); 131.74 (CH Ph); 129.79

Table 6
Fractional atomic coordinates for $C_{33}H_{18}O_{11}Co_2Cr$

Atom	x/a	y/b	z/c	U_{eq}
Cr(1)	0.44886(4)	1.03522(4)	0.12717(4)	0.0351
Co(1)	0.99650(3)	0.95495(4)	0.33338(3)	0.0356
Co(2)	0.99933(3)	0.77928(4)	0.28434(3)	0.0340
O(1)	0.7160(2)	0.8667(2)	0.0673(2)	0.0390
O(2)	0.6463(2)	0.9390(2)	0.3829(2)	0.0430
O(11)	0.2931(3)	0.9102(3)	0.2360(3)	0.0724
O(12)	0.3519(4)	0.9006(3)	−0.0838(3)	0.0819
O(13)	0.2161(3)	1.1675(3)	0.0175(4)	0.0696
O(14)	0.8922(3)	1.1161(3)	0.4390(4)	0.0739
O(15)	0.9908(4)	1.0441(3)	0.1045(3)	0.0790
O(16)	1.2721(3)	0.9752(3)	0.4944(3)	0.0772
O(17)	1.0289(3)	0.8048(3)	0.0474(2)	0.0653
O(18)	1.2722(3)	0.7373(3)	0.4419(3)	0.0679
O(19)	0.8790(4)	0.5858(2)	0.2713(4)	0.0777
C(1)	0.7099(2)	0.8734 (2)	0.1849 (2)	0.0305
C(2)	0.8478(2)	0.8639(2)	0.2768(2)	0.0302
C(3)	0.9176(2)	0.8462(2)	0.3929(2)	0.0347
C(4)	0.6231(2)	0.7947(2)	0.2016(2)	0.0361
C(5)	0.5530(3)	0.7273(2)	0.2070(3)	0.0408
C(11)	0.3515(3)	0.9594(3)	0.1940(3)	0.0468
C(12)	0.3897(3)	0.9537(3)	−0.0051(3)	0.0520
C(13)	0.3049(3)	1.1159(3)	0.0604(3)	0.0512
C(14)	0.9328(3)	1.0557(3)	0.3953(4)	0.0506
C(15)	0.9944(4)	1.0109(3)	0.1923(3)	0.0529
C(16)	1.1673(3)	0.9682(3)	0.4322(3)	0.0526
C(17)	1.0164(3)	0.7937(3)	0.1371(3)	0.0452
C(18)	1.1681(3)	0.7526(3)	0.3812(3)	0.0478
C(19)	0.9262(3)	0.6604(2)	0.2740(3)	0.0511
C(21)	0.6553(2)	0.9765(2)	0.1932(2)	0.0325
C(22)	0.6244(2)	1.0054(2)	0.2954(2)	0.0370
C(23)	0.5738(3)	1.1020(2)	0.3001(3)	0.0456
C(24)	0.5622(4)	1.1683(2)	0.2082(4)	0.0513
C(25)	0.5988(4)	1.1419(2)	0.1085(3)	0.0483
C(26)	0.6429(3)	1.0464(2)	0.1007(2)	0.0396
C(27)	0.6111(5)	0.9623(4)	0.4858(3)	0.0625
C(31)	0.9099(3)	0.8168(2)	0.5089(2)	0.0390
C(32)	0.8113(4)	0.7534(3)	0.5144(3)	0.0497
C(33)	0.8028(5)	0.7251(3)	0.6252(4)	0.0594
C(34)	0.8927(6)	0.7594(3)	0.7289(3)	0.0625
C(35)	0.9917(6)	0.8221(4)	0.7248(3)	0.0698
C(36)	1.0010(4)	0.8510(3)	0.6148(3)	0.0574
C(51)	0.4678(3)	0.6469(2)	0.2097(3)	0.0417
C(52)	0.3316(4)	0.6605(3)	0.1741(4)	0.0571
C(53)	0.2495(4)	0.5807(4)	0.1719(5)	0.0641
C(54)	0.3023(6)	0.4884(3)	0.2044(4)	0.0622
C(55)	0.4356(6)	0.4749(3)	0.2398(4)	0.0667
C(56)	0.5205(4)	0.5532(3)	0.2428(4)	0.0562

(CH Ph); 128.75 (CH Ph); 128.46 (CH Ph); 128.34 (CH Ph); 127.61 (CH Ph); 122.25 (C Ph); 103.55 (CBct); 102.24 (C ≡ C Ph); 95.00 (CHBct); 94.52 (CHBct); 91.79 (C ≡ C Ph); 90.52 (C ≡ C Ph); 86.18 (C ≡ C Ph); 83.48 (CHBct); 72.85 (CHBct); 70.21 (COH); 54.97 (OCH_3). IR (KBr) ν (cm^{-1}): ν (OH) 3544; ν (C≡O) (Co) 2093, 2035, 2026 ν (C≡O) (Cr) 1961, 1890, 1848. MS m/z 760 M^+, 743 $(M-OH^-)^+$, 592 $(M-6CO)^+$, 564 $(M-7CO)^+$, 508 $(M-9CO)^+$, 456 $[M-Cr(CO)_3-6CO]^+$. Calc.: 759.8918. Found: 759.8926.

7b ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.74 (m, 2H, Ph); 7.34 (m, 8H, Ph); 6.35 (d, 1H, Bct); 5.61 (t, 1H, Bct); 5.21 (s, 1H, OH); 4.96 (d, 1H, Bct); 4.88 (t, 1H, Bct); 3.64 (s, 3H, OCH_3). ^{13}C-NMR ($CDCl_3$) δ (ppm): 231.97 (COBct); 199.06 (COCo); 140.27 (COMe); 137.96 (C Ph); 132.08 (CH Ph); 129.94 (CH Ph); 128.99 (CH Ph); 128.72 (CH Ph); 128.24 (CH Ph); 127.86 (CH Ph); 121.63 (C Ph); 101.57 (CBct); 102.48 (C≡C Ph); 101.57 (CBct); 96.50 (CHBct); 94.94 (CHBct); 93.69 (C≡C Ph); 88.44 (C≡C Ph); 87.61 (C≡C Ph); 77.03 (COH); 72.14 (CHBct); 55.44 (OCH_3). IR (KBr) ν (cm^{-1}): ν (OH) 3544; ν (C≡O) (Co) 2094, 2057, 2020; ν (C≡O) (Cr) 1957, 1890, 1873. MS m/z 760 M^+, 743 $(M-OH^-)^+$, 592 $(M-6CO)^+$, 564 $(M-7CO)^+$, 508 $(M-9CO)^+$, 456 $[M-Cr(CO)_3-6CO]^+$ Calc.: 759.8918. Found: 759.8895.

8a ^{1}H-NMR ($CDCl_3$) δ (ppm): 6.23 (d, 1H, Bct); 5.59 (t, 1H, Bct); 5.02 (d, 1H, Bct); 4.87 (t, 1H, Bct); 3.81 (s, 3H, OCH_3); 3.00 (s, 1H, OH); 0.30 (s, 9H, $SiMe_3$); 0.18 (s, 9H, $SiMe_3$). ^{13}C NMR ($CDCl_3$) δ (ppm): 232.75 (COBct); 199.80 (COCo); 141.28 (COCH3); 115.58 (C≡CSi); 105.40 (CBct); 104.02 (C≡CSi); 94.93 (CHBct); 94.37 (CHBct); 90.70 (C≡CSi); 83.74 (CHBct); 79.57 (C≡CSi); 72.93 (CHBct); 70.08 (COH); 55.16 (OCH_3); 0.76 ($SiMe_3$); −0.54 ($SiMe_3$). IR (KBr) ν (cm^{-1}): ν (OH) 3582; ν (C≡O) (Co) 2091, 2054, 2026; ν (C≡O) (Cr) 1952, 1881, 1868. MS m/z 752 M^+, 735 $(M-OH^-)^+$, 584 $(M-6CO)^+$, 556 $(M-7CO)^+$, 528 $(M-8CO)^+$, 500 $(M-9CO)^+$, 448 $[M-Cr(CO)_3-6CO]^+$ Calc.: 751.9083. Found: 751.9033.

8b ^{1}H-NMR ($CDCl_3$) δ (ppm): 6.22 (d, 1H, Bct); 5.56 (t, 1H, Bct); 5.05 (s, 1H, OH); 4.92 (t, 1H, Bct); 4.89 (d, 1H, Bct); 3.72 (s, 3H, OCH_3); 0.33 (s, 9H, $SiMe_3$); 0.20 (s, 9H, $SiMe_3$). ^{13}C-NMR ($CDCl_3$) δ (ppm): 231.73 (COBct); 199.88 (CO Co); 139.89 ($COCH_3$); 117.03 (C≡CSi); 104.83 (CBct); 101.82 (C≡CSi); 95.81 (CHBct); 93.72 (CHBct); 91.88 (C≡CSi); 83.72 (CHBct); 80.55 (C≡CSi); 77.02 (COH); 71.93 (CHBct); 55.69 (OCH_3); 0.86 ($SiMe_3$); −0.63 (SiMe3). IR (KBr) ν (cm^{-1}): ν (OH) 3500; ν (C≡O) (Co) 2091, 2053, 2017; ν (C≡O) (Cr) 1969, 1888. MS m/z 752 M^+, 735 $(M-OH^-)^+$, 584 $(M-6CO)^+$, 556 $(M-7CO)^+$, 528 $(M-8CO)^+$, 500 $(M-9CO)^+$, 448 $[M-Cr(CO)_3-6CO]^+$ Calc.: 751.9083. Found: 751.9078.

9a ^{1}H-NMR (acetone-d_6) δ (ppm): 6.46 (s, 2H, Bct + acetylenic H); 6.21 (s, 1H, OH); 5.87 (t, 1H,Bct); 5.47 (d, 1H, Bct); 5.09 (t, 1H, Bct); 3.93 (s, 3H, OCH_3); 3.23 (s, 1H, acetylenic H); 3.23 (s, 1H, acetylenic H). ^{13}C-NMR (acetone-d_6) δ (ppm): 234.31 (COBct); 200.72 (COCo); 143.11 ($COCH_3$); 105.47 (Cbct); 104.12 (C≡CH); 97.11 (CHBct); 96.04 (CHBct); 85.90 (C≡CH); 84.76 (CHBct); 75.29 (CHBct); 75.08 (C≡CH); 74.42 (C≡CH); 69.52 (COH); 56.20 (OCH_3). IR (KBr) ν (cm^{-1}): ν (OH) 3401, 3297; ν C≡O (Co) 2102, 2041, 2017; ν (C≡O) (Cr) 1961, 1894, 1874. MS m/z 608 M^+, 591 $(M-OH^-)^+$, 468 $(M-5CO)^+$, 440 $(M-6CO)^+$, 384 $(M-8CO)^+$, 356 $(M-9CO)^+$, 304 $[M-Cr(CO)_3-6CO]^+$ Calc.: 607.8292. Found: 607.8249.

9b ^{1}H-NMR (acetone-d_6) δ (ppm): 6.52 (s, 2H, Bct + complexed acetylenic H); 5.93 (t, 1H, Bct); 5.53 (d, 1H, Bct); 5.39 (s, 1H, OH); 5.16 (t, 1H, Bct); 4.01 (s, 3H, OCH_3) 3.53 (s, 1H, acetylenic H). ^{13}C-NMR (acetone-d_6) δ (ppm): 233.89 (COBct); 200.48 (COCo); 142.63 ($COCH_3$); 104.05 (CBct); 102.25 (C≡CH); 98.18 (CHBct); 96.73 (CHBct); 85.30 (CHBct); 84.43 (C≡CH); 76.95 (CHBct); 76.25 (C≡CH); 75.29 (COH); 75.20 (C≡CH); 56.87 (OCH_3). IR (KBr) ν (cm^{-1}): ν (OH) 3518, 3317; ν (C≡O) (Co) 2097, 2025, 2017; ν (C≡O) (Cr) 1961, 1907, 1885.

10a ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.58 (m, 4H, Ph); 7.38 (m, 3H, Ph); 7.26 (m, 3H, Ph); 6.18 (d, 1H,Bct); 5.51 (t, 1H, Bct); 4.88 (t, 1H, Bct); 4.76 (d, 1H, Bct); 3.31 (s, 3H, OCH_3); 0.39 (s, 9H, $OSiMe_3$). IR (KBr) ν (cm^{-1}): ν (C≡O) (Co) 2092, 2055, 2034; ν (C≡O) (Cr) 1965, 1886, 1859. MS m/z 832 M^+, 692 $(M-5CO)^+$, 636 $(M-7CO)^+$, 580 $(M-9CO)^+$, 528 $[M-Cr(CO)_3-6CO]^+$ Calc.: 831.9313. Found: 831.9313.

10b ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.58 (m, 4H, Ph); 7.34 (m, 6H, Ph); 6,30 (d, 1H, Bct) 5.60 (t, 1H, Bct); 4.86 (d, 1H, Bct); 4.68 (t, 1H, Bct); 3.66 (s, 3H, OCH_3); 0,31 (s, 9H, $OSiMe_3$). IR (KBr) ν (cm^{-1}): ν (C≡O) (Co) 2094, 2055, 2033; ν (C≡O) (Cr) 1962, 1890, 1877.

11a + 11b ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.62 (m, 2H, Ph); 7.50 (m, 1H, Ph); 7.35 (m, 7H, Ph); 6.30 (d, 1H,Bct); 6.15 (d, 1H, Bct); 5.49 (t, 2H, Bct); 5.17 (m, 2H, Bct); 4.97 (m, 2H, Bct); 3.31 (s, 1H, OH); 3.27 (s, 1H, OH); 2.45 (s, 3H, CH_3); 2.38 (s, 3H, CH_3). IR (KBr) ν (cm^{-1}): ν (OH) 3418; ν (C≡O) (Co) 2093, 2062, 2049; ν (C≡O) (Cr) 1957, 1886. MS m/z 744 M^+, 727 $(M-OH^-)^+$, 604 $(M-5CO)^+$, 576 $(M-6CO)^+$, 496 $[M-Cr(CO)_3-4CO]^+$, 440 $[M-Cr(CO)_3-6CO]^+$ Calc.: 743.8969. Found: 743.8940.

12a + 12b ^{1}H-NMR ($CDCl_3$) δ (ppm): 6.14 (d, 1H, Bct); 5.94 (d, 1H, Bct); 5.48 (t, 1H, Bct); 5.42 (t, 1H, Bct); 5.22 (t, 1H, Bct); 5.15 (t, 1H, Bct); 5.07 (d, 1H, Bct) 5.02 (d, 1H, Bct); 3.11 (s, 1H, OH); 3.05 (s, 1H, OH); 2.67 (s, 3H, CH_3); 2.56 (s, 3H, CH_3); 0.33 (s, 9H, $SiMe_3$); 0.19 (s, 9H, $SiMe_3$). IR (KBr) ν (cm^{-1}): ν (OH) 3560; ν (C≡O) (Co) 2091, 2053, 2025; ν (C≡O) (Cr) 1960, 1894, 1872. MS m/z 736 M^+, 719 $(M-OH^-)^+$, 596 $(M-5CO)^+$, 568 $(M-6CO)^+$, 496 $[M-Cr(CO)_3-4CO]^+$, 484 $(M-9CO)^+$, 432 $[M-Cr(CO)_3-6CO]^+$ Calc.: 743.8969. Found: 743.8940.

13a + 13b ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.53 (m, 4H,

Ph); 7.32 (m, 6H, Ph); 7.11 (d, 1H minor, =CH $J = 16$ Hz; 7.01 (d, 1H minor, =CH $J = 16$ Hz); 6.57 (d, 1H major, =CH $J = 16$ Hz); 6.55 (d, 1H major, =CH $J = 16$ Hz); 6.28 (d, 1H, Bct); 6.26 (d, 1H, Bct); 6.10 (d, 1H, Bct); 6.09 (d, 1H, Bct); 5.64 (t, 2H, Bct); 5.04 (d, 2H, Bct); 4.81 (t, 2H, Bct); 3.89 (s, 3H minor, OCH3); 3.86 (s, 3H major, OCH3); 3.80 (s, 1H minor, OH); 3.70 (s, 1Hmajor, OH). IR (KBr) ν (cm^{-1}): ν (OH) 3475; ν (C≡O) (Cr) 1960, 1894, 1867. MS m/z 476 M^+, 459 $(M-OH^-)^+$, 392 $(M-3CO)^+$, 323 $[M-Cr(CO)_3-OH]^+$ Calc.: 476.0716. Found: 476.0712.

14a + 14b ^{1}H-NMR ($CDCl_3$) δ (ppm): 6.18 (dd, 1H major, =CH $J = 18$ Hz $J = 10$ Hz); 6.17 (d, 1H major, Bct); 6.14 (dd, 1H minor, =CH $J = 18$ Hz $J = 10$ Hz); 5.96 (t, 1H major, Bct); 5.77 (d, 1H major, =CH2 $J = 19$ Hz); 5.63 (d, 1H minor, =CH2 $J = 18$ Hz); 5.61 (t, 1H major, Bct); 5.61 (t 1H major, Bct); 5.42 (d, 1H minor, =CH2 $J = 10$ Hz); 5.32 (d, 1H major, =CH2 $J = 10$ Hz); 5.02 (d, 1H minor, Bct); 5.00 (d, 1H major, Bct); 4.78 (t, 1H major, Bct); 4.77 (t, 1H minor, Bct); 3.86 (s, 3H minor, OCH3); 3.83 (s, 3H major, OCH3); 3.76 (s, 1H minor, OH); 3.52 (s, 1H major, OH); 2.83 (s, 1H major, C≡H); 2.79 (s, 1H minor, C≡H)). IR (KBr) ν (cm^{-1}): ν (OH) 3513, 3293; ν (C≡O) (Cr) 1959, 1872. MS m/z 324 M^+, 307 $(M-OH^-)^+$, 240 $(M-3CO)^+$, 171 $[M-Cr(CO)_3-OH]^+$ Calc.: 324.0090. Found: 324.0086.

15a ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.37 (m, 11H, Ph=CH); 7.00 (d, 1H, =CH $J = 16$ Hz); 6.51 (d, 1H, Bct); 5.58 (t, 1H, Bct); 4.85 (dd, 2H, Bct); 3.18 (s, 3H, OCH_3); 2.60 (s, 1H, OH). IR (KBr) ν (cm^{-1}): ν (OH) 3540; ν (C≡O) (Co) 2091, 2055, 2032; ν (C≡O) (Cr) 1965, 1890, 1862. MS m/z 762 M^+, 745 $(M-OH^-)^+$, 594 $(M-6CO)^+$, 510 $(M-9CO)^+$, 458 $(M-9CO-Cr)^+$, Calc.: 761.9075. Found: 761.9076.

15b ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.36 (m, 11H, Ph=CH); 6.60 (d, 1H, =CH $J = 1.6$ Hz); 5.72 (d, 1H, Bct); 5.34 (t, 1H, Bct); 5.28 (d, 1H, OH $J = 1.65$ Hz); 4.88 (d, 1H, Bct); 4.76 (t, 1H, Bct); 3.39 (s, 3H, OCH_3). IR (KBr) ν (cm^{-1}): ν (OH) 3508; ν (C≡O) (Co) 2090, 2054, 2022; ν (C≡O) (Cr) 1957, 1881, 1873.

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