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Study of the reactivity of the carbon–carbon triple bond in $(CO)_5M{=}C(OEt)(C{\equiv}CPh)$ complexes ($M = Cr$ or W) towards $[PPh_4][HFe_3(CO)_{11}]$ or $[Co_2(CO)_8]$: a ligand transfer reaction (Fe) or thermally induced build up of heterotrimetallic clusters (Co) bridged by the carbyne ligands C–C(OEt)=CPh–C(O)– or C–CPh=C(OEt)–C(O)–

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Abstract

Complexes $[(CO)_5M{=}C(OEt)(C{\equiv}CPh)]$ ($M = Cr$ (**1a**), W (**1b**)) react with $[PPh_4][HFe_3(CO)_{11}]$ to give $[PPh_4][Fe_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C(OEt){=}C{=}CHPh]$ by a ligand transfer reaction. Complexes **1a** and **1b** react with octacarbonyldicobalt to give $[\{(CO)_5M{=}C(OEt)C{\equiv}CPh\}Co_2(CO)_6]$ ($M = Cr$ (**3a**) or W (**3b**)), **3a** being characterized by an X-ray structure determination. In boiling hexane, **3a** and **3b** rearrange to the clusters $[MCo_2(CO)_7(\mu\text{-}CO)_2\{\mu_3\text{-}\eta^4\text{-}CC(OEt){=}CPhC(O)\}]$ ($M = Cr$ (**4a**) or W (**4b**)) partially characterized by an X-ray structure determination for **4a** and their isomers $[MCo_2(CO)_7(\mu\text{-}CO)_2\{\mu_3\text{-}\eta^4\text{-}CCPh{=}C(OEt)C(O)\}]$ ($M = Cr$ (**5a**) or W (**5b**)) spectroscopically characterized.

Key words: Iron; Cobalt; Chromium; Tungsten

1. Introduction

Since their first synthesis in 1972 [1], $[(CO)_5M{=}C(OEt)(C{\equiv}CPh)]$ ($M = Cr$, **1a**; $M = W$, **1b**) or their derivatives with different substituents on carbon atoms, the reactivity of the carbon–carbon triple bond towards secondary amines [1,2], alcohols [3] or towards cycloaddition reactions with diazoalcanes [4] or activated olefins [5] have been studied.

At the beginning of the present work, the complexing properties of the carbon–carbon triple bond had not been explored, but in 1992 a number of papers appeared where the complexation of the triple bond by octacarbonyldicobalt was studied [6,7]. This prompted us to report our results concerning the reactivity of the phenylethynyl carbene ligand towards $[PPh_4][HFe_3(CO)_{11}]$ and $[Co_2(CO)_8]$. This study has been undertaken to check whether the carbon–carbon triple bond shows the same reactivity towards the iron cluster [8] as do alkynes and whether the alkynyl is able to build up new heterometallic clusters.

With the iron cluster we actually observed a ligand-transfer reaction leading to $[PPh_4][Fe_3(CO)_9\{\mu_3\text{-}\eta^3\text{-}C(OEt){=}C{=}CHPh\}]$ (**2**) with elimination of $[M(CO)_6]$, while with octacarbonyldicobalt, we observed first a

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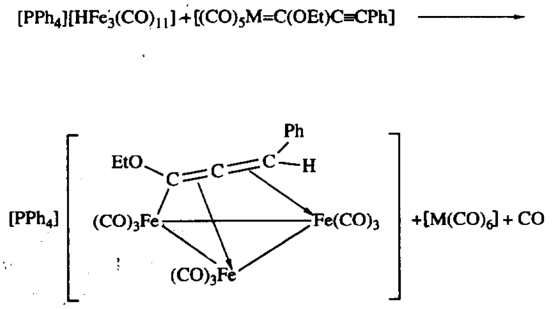
complexation of the triple bond, consistent with recent published results [6,7] and then its thermal rearrangement under smooth conditions (boiling hexane) of the resulting trinuclear complex leading to the ene-one carbyne ligand, $C{-}C(OEt){=}CPh{-}CO$ stabilized by a MCo_2 cluster, which we characterized partially by an X-ray structure determination in the case of chromium. Isomeric clusters containing the $C{-}CPh{=}C(OEt){-}CO{-}$ carbyne ligand were also detected spectroscopically.

2. Results and discussion

2.1. Reaction of $[(CO)_5M{=}C(OEt)(C{\equiv}CPh)]$ (1a, 1b) with $[PPh_4][HFe_3(CO)_{11}]$

An equimolecular mixture of **1a** or **1b** and $[PPh_4][HFe_3(CO)_{11}]$ reacts smoothly at room temperature to give a mixture of $[M(CO)_6]$ and a new complex **2** which can be isolated by fractional crystallization. IR spectroscopy shows terminal carbonyl groups while ^1H NMR spectroscopy shows resonance assigned to a CH group at 4.04 ppm. The structure of **2** is confirmed by the ^{13}C NMR data which compare well with those of the $[PPh_4][Fe_3(CO)_9\{\mu_3\text{-}\eta^3\text{-}C(OEt){=}C{=}CHR\}]$ (R = $C(O)CH_3$ or $C(O)OCH_3$) which were obtained by reduction of $[Fe_3(CO)_9(\mu_3\text{-}COEt)(\mu_3\text{-}CCH_2R)]$ [9]. Resonances at 197.3, 141.3, and 44.3 ppm attributed to the *C*(OEt), C(OEt)=*C*= and *C*HPh atoms, respectively, have values very similar to the 220.1, 146.1 and 38.1 ppm observed for the same groups in $[PPh_4][Fe_3(CO)_9\{\mu_3\text{-}\eta^3\text{-}C(OEt){=}C{=}CHR\}]$ [7]. We propose a similar structure for **2** with a trinuclear iron cluster stabilized by a $C(OEt){=}C{=}CHPh$ $\mu_3\text{-}\eta^3$-bound allenyl group. The reaction is summarized in eqn. (1).



(1)

The formation of **2** results from the insertion of the carbon–carbon triple bond into the Fe–H bond of the iron cluster, a common reaction of the alkynes with this cluster [8], and from the transfer of the carbene ligand onto the iron framework, the CO evolved regenerating the $[M(CO)_6]$ complexes.

2.2. Reaction of $[(CO)_5M{=}C(OEt)(C{\equiv}CPh)]$ (1a, 1b) with $[Co_2(CO)_8]$

Complexes **1a** or **1b** react quickly at room temperature with one equivalent of $[Co_2(CO)_8]$ to give $[\{(CO)_5M{=}C(OEt)C{\equiv}CPh\}CO_2(CO)_6]$ (**3a**, M = Cr or **3b**, M = W) in nearly quantitative yield. The IR spectra of the two products are very similar in the ν(CO) stretching region, and appear to be the superposition of the IR spectra of $[(RC{\equiv}CR)Co_2(CO)_6]$ and $[(CO)_5M{=}C(OEt){-}C{\equiv}CPh]$. Comparison of ^{13}C NMR data of **1a**, **1b** with **3a** and **3b** shows that complexation of the triple bond induces a shift of the carbene resonance towards lower field (about 20 ppm) and lowers the chemical shift difference between the two carbon atoms of the triple bond.

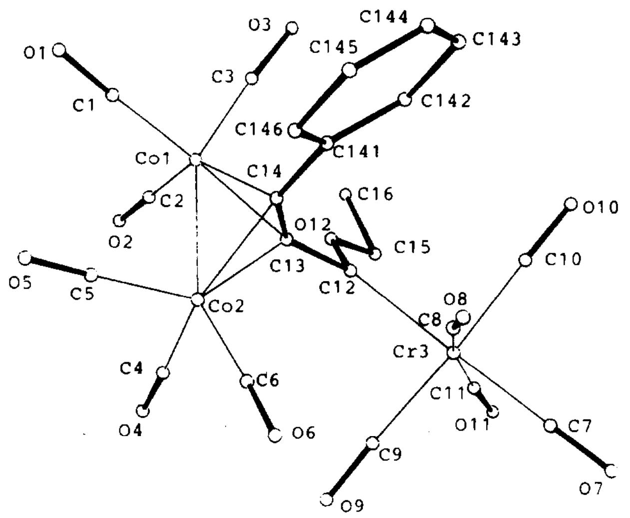


Fig. 1. Structure of $[\{(CO)_5Cr{=}C(OEt)C{\equiv}CPh\}Co_2(CO)_6]$ (**3a**) showing the atomic numbering scheme.

Complex **3a** has been characterized by an X-ray diffraction study and it compares well with the recently published structure of the related $[\{(CO)_5Cr{=}C(OMe){-}C{\equiv}CPh\}Co_2(CO)_6]$ [6]. The atomic numbering scheme is shown in Fig. 1 and bond lengths and angles of interest are in Table 1. Table 2 shows the final atomic coordinates. As expected, the $[Co_2(CO)_6]$ unit is bonded to the C(13)–C(14) triple bond and bond lengths and bond angles for this part of the molecule are as usual for complexes $[(RC{\equiv}CR)Co_2(CO)_6]$ [10]. Comparison with the structure of **1a** [11] shows that the complexation of the triple bond has not induced significant changes in the chromium sphere of coordination, except for lengthening of the triple bond. Indeed, the Cr(3)–C(12) distance (2.05(1) Å) is similar to the distance found in **1a** (2.00(2) Å). The most significant change concerns the steric influence of the $Co_2(CO)_6$ group which induces bending of the Cr(3)–C(8)–O(8) and Cr(3)–C(11)–O(11) moieties.

Compounds **3a** and **3b** were heated under reflux in hexane with the expectation of forming mixed Group 6-cobalt clusters. A rapid change from red brown to dark green occurred, and IR spectroscopy showed that

TABLE 1. Selected bond lengths (Å) and angles (°) for $[(CO)_5Cr{=}C(OEt)C{\equiv}CPh]{-}Co_2(CO)_6$ (**3a**)

Co(1)–Co(2)	2.463(3)	Co(2)–C(4)	1.82(2)
Co(1)–C(1)	1.81(2)	Co(2)–C(5)	1.79(1)
Co(1)–C(2)	1.80(2)	Co(2)–C(6)	1.84(2)
Co(1)–C(3)	1.73(2)	Co(2)–C(13)	1.95(1)
Co(1)–C(13)	1.93(2)	Co(2)–C(14)	1.95(1)
Co(1)–C(14)	1.96(1)	C(13)–C(14)	1.32(2)
C(14)–C(141)	1.48(2)	C(12)–C(13)	1.47(2)
C(12)–O(12)	1.34(2)	C(15)–O(12)	1.46(2)
C(15)–C(16)	1.52(2)	C(12)–Cr(3)	2.05(1)
Cr(3)–C(7)	1.88(2)	Cr(3)–C(8)	1.84(1)
Cr(3)–C(9)	1.91(2)	Cr(3)–C(10)	1.85(2)
Cr(3)–C(11)	1.86(2)		
Cr(3)–C(12)–O(12)	129(1)	Cr(3)–C(12)–C(13)	126(1)
O(12)–C(12)–C(13)	104(1)	C(12)–C(13)–Co(2)	132(1)
C(12)–C(13)–C(14)	142(1)	C(13)–C(14)–Co(1)	69(1)
Co(2)–C(13)–C(14)	70(1)	Co(1)–C(13)–Co(2)	78.7(6)
C(14)–C(13)–Co(1)	71(1)	C(13)–C(14)–Co(2)	70(1)
C(13)–Co(2)–C(14)	39(1)	C(12)–C(13)–Co(1)	134.5(1)
C(13)–Co(2)–Co(1)	50.3(4)	Co(1)–C(14)–Co(2)	78.1(5)
C(13)–Co(1)–C(14)	39.6(6)	C(14)–Co(2)–Co(1)	51.1(4)
Co(1)–C(1)–O(1)	177(1)	Cr(3)–C(7)–O(7)	179(1)
Co(1)–C(2)–O(2)	178(2)	Cr(3)–C(8)–O(8)	171(1)
Co(1)–C(3)–O(3)	175(2)	Cr(3)–C(9)–O(9)	175(1)
Co(2)–C(4)–O(4)	176(1)	Cr(3)–C(10)–O(10)	178(1)
Co(2)–C(5)–O(5)	176(1)	Cr(3)–C(11)–O(11)	173(2)
Co(2)–C(6)–O(6)	177(1)		

the starting complexes had disappeared. In the first experiments, purification of products was carried out by chromatography on Florisil. This allowed the isolation in low yields of products **4a** and **4b**, which have similar IR properties.

The infrared spectra in the ν(CO) region indicate the presence of terminal and bridging carbonyl groups and the pattern of these spectra suggests cluster formation. Moreover, a weak absorption around 1675 cm^{-1} is consistent with the presence of a ketonic group. ^1H NMR spectroscopy shows the presence of ethoxy and phenyl groups while the ^{13}C NMR spectra are not very informative, except for a resonance at 313.6 ppm for **4a** and 288.1 ppm for **4b** which could indicate a carbyne ligand [12].

We have attempted to carry out an X-ray diffraction study of **4a** but the crystals were not of sufficient quality to obtain reliable bond length and angle data [13*]. Nevertheless the overall geometry of the molecule corresponds to $[Co_2Cr(CO)_7(\mu\text{-}CO)_2\{\mu_3\text{-}\eta^4\text{-}(C{-}C(OEt){=}CPh{-}C(O))\}]$ and is shown in Fig. 2. It consists of a $CrCo_2$ triangle, each cobalt being bonded to two terminal carbonyl groups, and the chromium atom to three terminal carbonyl groups. Each Co–Cr bond is bridged by a carbonyl group. The complex organic ligand can be described as an ene-one carbyne $C{-}C(OEt){=}C(Ph){-}C(O){-}$ resulting from CO fixation on the β carbon of the triple bond and formally from the migration of the ethoxy group to the α carbon atom. The carbyne atom is bonded to the three metals and the carbon–carbon double bond is π-bonded to Co(2), the ketonic group being σ-bonded to Co(1).

Examination of the crystalline product by ^1H and ^{13}C NMR spectroscopy before chromatography shows that two compounds are actually present, even though the IR spectra of the mixture are not very different from the pure **4a** or **4b** (some shoulders are apparent on the main bands). ^1H NMR spectra give evidence of the presence of an additional ethoxy group in 3 : 1 and 1 : 2 ratios for **5a** and **5b**, respectively. The ^{13}C NMR

TABLE 2. Atomic coordinates ($\times 10^5$) and thermal parameters as $U_{eq} = (U_1 \times U_2 \times U_3)^{1/3}$ for $[\{(CO)_5Cr{=}C(OEt)C{\equiv}CPh\}]Co_2(CO)_6]$ (**3a**)

Atom	x	y	z	U_{eq}
Co(1)	39081(25)	2200(13)	9579(7)	46(1)
Co(2)	38557(26)	12475(13)	15192(7)	45(1)
Cr(3)	−2748(25)	18328(13)	11694(8)	47(1)
O(1)	60148(147)	−7995(63)	13168(44)	96(6)
O(2)	51976(160)	10307(83)	2011(47)	138(8)
O(3)	23144(141)	−8608(79)	4525(43)	101(7)
O(4)	47237(150)	25214(79)	9413(43)	123(7)
O(5)	63858(137)	7558(66)	19442(38)	81(6)
O(6)	26996(137)	20141(62)	23217(36)	90(6)
O(7)	−25935(137)	26438(67)	16474(36)	86(6)
O(8)	−314(121)	11320(59)	20966(34)	78(5)
O(9)	17305(134)	30743(64)	13940(55)	122(7)
O(10)	−21931(128)	5913(74)	8858(45)	105(6)
O(11)	−12830(170)	27635(81)	3814(45)	140(8)
O(12)	15551(86)	10893(52)	4413(31)	51(4)
C(1)	52049(172)	−3930(82)	11890(54)	55(6)
C(2)	46849(175)	7113(95)	4870(60)	68(7)
C(3)	29987(177)	−4430(114)	6497(59)	76(9)
C(4)	43893(157)	20495(83)	11767(56)	63(7)
C(5)	54371(188)	9532(91)	17689(56)	59(7)
C(6)	31039(166)	17192(81)	20162(54)	55(7)
C(7)	−17043(173)	23414(82)	14636(60)	59(7)
C(8)	−343(156)	13478(78)	17261(48)	51(6)
C(9)	10102(185)	25939(89)	13259(59)	70(7)
C(10)	−14345(173)	10657(95)	9925(55)	64(7)
C(11)	−8239(186)	23952(93)	6693(59)	78(8)
C(12)	12960(150)	12332(78)	8816(44)	40(5)
C(13)	24015(159)	8592(83)	11311(45)	44(6)
C(14)	26435(130)	3853(76)	14670(45)	34(5)
C(15)	7122(153)	13650(86)	663(45)	63(7)
C(16)	11597(175)	9215(91)	−3503(45)	72(7)
C(141)	19363(160)	−1691(77)	17566(49)	39(5)
C(142)	7549(171)	−4945(86)	16025(49)	56(7)
C(143)	828(191)	−10319(89)	18720(76)	78(9)
C(144)	6752(290)	−12312(115)	22907(79)	104(12)
C(145)	17773(240)	−9130(126)	24272(75)	93(10)
C(146)	24808(170)	−3771(95)	21760(53)	59(7)

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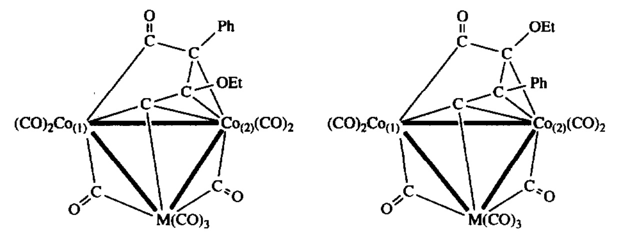
* Reference number with asterisk indicates a note in the list of references.



M = Cr (4a)
W (4b)

M = Cr (5a)
W (5b)

Fig. 2. Structure of $[Co_2Cr(CO)_7(\mu\text{-}CO)_2\{\mu_3\text{-}\eta^4(C\text{-}C(OEt){=}CPh\text{-}C(O))\}]$ (**4a**) as determined by X-ray analysis and proposed structure for $[Co_2M(CO)_7(\mu\text{-}CO)_2\{(\mu_3\text{-}\eta^4(C\text{-}CPh{=}C(OEt)\text{-}C(O))\}]$ (M = Cr (**5a**) or W (**5b**).

spectrum of the mixture confirms the presence of two products, **5a** and **5b**, new resonances being specifically observed at 289.3 ppm (**5a**) and 263.4 ppm (**5b**). These observations suggest a mixture of isomers formed during the reaction, **5a** and **5b** being decomposed during chromatography. The great similarity of spectroscopic data suggests that the second isomer differs by the positions of the substituents on the bridging organic group and they should contain the moiety C–C-(Ph)=C(OEt)–C(O)– shown in Fig. 2.

It is difficult to propose a precise mechanism for this rearrangement but the two isomers suggest an intramolecular interaction of the Cr–carbene with the coordinated triple bond, and successive rearrangement and CO insertion reactions.

3. Experimental section

3.1. General

All reactions were performed under dinitrogen with use of standard Schlenk techniques. IR spectra were recorded on a Perkin-Elmer 225 spectrometer. NMR spectra were recorded on Bruker AC 200 (^1H) and WM 250 (^{13}C) instruments. Elemental analyses were performed in our laboratory. Complexes $[(CO)_5M{=}C(OEt)(C{\equiv}CPh)]$ (**1a, 1b**) were prepared according to published procedures [1] and $[PPh_4][HFe_3(CO)_{11}]$ was prepared by cation exchange of $[NEt_4][HFe_3(CO)_{11}]$ [14] by $[PPh_4]Br$.

3.2. Synthesis of $[PPh_4][Fe_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C(OEt){=}C{=}CHPh)]$ (2)

To 1 g of $[PPh_4][HFe_3(CO)_{11}]$ dissolved in dichloromethane was added 0.45 g of $[(CO)_5Cr{=}C(OEt)(C{\equiv}CPh)]$ and the solution was stirred for 17 h. The solution was then evaporated to dryness under vacuum for 2 h in order to eliminate most of the $[Cr(CO)_6]$ formed and the residue was dissolved in the minimum amount of methanol. Cooling to −20°C induced the crystallization of 0.6 g of **2** as dark brown crystals (55%). IR ν(CO) (CH_2Cl_2): 2040m, 1970s, 1945sh, 1925sh cm^{-1}. ^1H NMR ($(CD_3)_2CO$) except phenyl resonances: 4.21 (q, $J = 7.1$ Hz, OCH_2); 4.04 (CH); 1.40 (t, $J = 7.1$ Hz, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) except phenyl resonances: 219.8, 219.2, 215.2 (CO); 197.3 (*C*(OEt)); 141.3 (C(OEt)=*C*=); 66.8 (OCH_2); 44.3 (=CHPh); 14.8 (CH_3) ppm. Anal. Found: C, 57.35; H, 3.89. $C_{44}H_{31}Fe_3O_{10}P$ calcd.: C, 57.55; H, 3.40%.

3.3. Synthesis of $[\{(CO)_5M{=}C(OEt)C{\equiv}CPh\}Co_2(CO)_6]$ (3a, M = Cr; 3b, M = W)

An equimolecular mixture of $[Co_2(CO)_8]$ and $[(CO)_5M{=}C(OEt)(C{\equiv}CPh)]$ was stirred in hexane at room temperature. Rapid CO evolution was observed and the solution was stirred for 1 h, then evaporated to dryness under vacuum. Redissolution in a minimum of hexane and cooling to −20°C gave **3a** or **3b** as dark brown crystals in 60–70% yield.

3a: IR ν(CO) (hexane): 2095m, 2060vs, 2040s, 2020m, 1950vs cm^{-1}. ^1H NMR (C_6D_6) except phenyl resonances: 4.72 (q, $J = 7$ Hz, OCH_2); 1.20 (t, $J = 7$ Hz, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) except phenyl resonances: 332.1 (=*C*(OEt)(CCPh); 223.4, 216.5, 198.7 (CO); 100.8, 97.3 (CC); 77.8 (OCH_2); 14.8 (CH_3) ppm. Anal. Found: C, 41.25; H, 1.83. $C_{22}H_{10}Co_2CrO_{12}$ calcd.: C, 41.54; H, 1.58%.

3b: IR ν(CO) (hexane): 2092m, 2060vs, 2038s, 2032s, 2020m, 1952vs, 1933s cm^{-1}. ^1H NMR (C_6D_6) except phenyl resonances: 4.57 (q, $J = 7$ Hz, OCH_2); 1.19 (t, $J = 7$ Hz, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) except phenyl resonances: 306.8 (JWC = 96 Hz) (=*C*(OEt) (CCPh); 202.7 (JWC = 117 Hz); 197.5 (JWC = 127 Hz); 198.7 (CO); 102.5, 100.3 (CC); 80.1 (OCH_2); 14.6 (CH_3) ppm. Anal. Found: C, 34.66; H, 1.52. $C_{22}H_{10}Co_2O_{12}W$ calcd.: C, 34.41; H, 1.31%.

3.4. Synthesis of $[MCo_2(CO)_7(\mu\text{-}CO)_2\{\mu_3\text{-}\eta^4(C\text{-}C(OEt){=}CPh\text{-}C(O)\}]$ (4a, M = Cr; 4b, M = W) and $[MCo_2(CO)_7(\mu\text{-}CO)_2\{\mu_3\text{-}\eta^4(C - CPh{=}C(OEt) - C(O)\}]$ (5a, M = Cr; 5b, M = W)

Complex **3a** or **3b** (0.5 g) heated under reflux in hexane for 1 h. During this time the solution turned green. At the end of the reaction the solution was evaporated to dryness and was treated in two ways: (i) the residue was chromatographed on Florisil and eluted with a 1:1 mixture of hexane and toluene, allowing the isolation of **4a** (20% yield) and **4b** (25% yield) as dark green crystals, or (ii) the hexane solution was filtered through Celite to prevent decomposition to the metals and the solution was concentrated and cooled to −20°C leading to a mixture of **4a** and **5a** (48% yield) or **4b** and **5b** (60% yield).

4a: IR ν(CO) (hexane): 2084m, 2049vs, 2035vs, 2024s, 2012s, 2003m, 1899m, 1893m, 1674w cm^{-1}. ^{1}H NMR (C_6D_6) except phenyl resonances: 3.68 (m, OCH_2); 1.19 (t, $J = 7$ Hz, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) except phenyl resonances: 313.6 (*C*C(OEt)); 221.6, 220.4 (CO), 210.2 (C=O), 142.2 (C(OEt)), 109.3 (C(Ph)), 72.3 (OCH_2), 15.5 (CH_3) ppm. Anal. Found: C, 41.33; H, 1.59. $C_{21}H_{10}Co_2CrO_{11}$ calcd.: C, 41.47; H, 1.66%.

4b: IR ν(CO) (hexane): 2088m, 2052vs, 2032vs, 2020m, 2010s, 1998w, 1915m, 1675w cm^{-1}. ^{1}H NMR (C_6D_6) except phenyl resonances: 3.64 (m, OCH_2); 1.20 (t, $J = 7$ Hz, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) except phenyl resonances: 288.2 (*C*C(OEt)); 208.5 (C=O); 201.5, 198.7, 196.3 (CO); 140.8 (C(OEt)); 103.7 (C(Ph)); 71.9 (OCH_2); 15.3 (CH_3) ppm. Anal. Found: C, 34.22; H, 1.49. $C_{21}H_{10}Co_2O_{11}W$ calcd.: C, 34.08; H, 1.36%.

5a: ^{1}H NMR (C_6D_6) except phenyl resonances: 4.45 (m, OCH_2); 1.02 (t, $J = 7$ Hz, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$ except phenyl resonances: 289.3 (*C*C(Ph)); 221.6, 220.4 (CO); 204 (C=O); 172.6 (C(OEt)); 70.6 (OCH_2); 66.4 (C(Ph)); 15.3 (CH_3) ppm.

5b: ^{1}H NMR (C_6D_6) except phenyl resonances: 4.57 (m, OCH_2); 1.03 (t, $J = 7$ Hz, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) except phenyl resonances: 263.4 (*C*C(Ph)); 202.7 (C=O); 201.3, 198.8 (CO); 170.4 (C(OEt)); 69.2 (OCH_2); 62.8 (C(Ph)); 14 (CH_3) ppm.

3.5. *Crystal structure determination of* $[\{(CO)_5Cr{=}C(OEt)C{\equiv}CPh\}Co_2(CO)_6]$

Crystal data. $C_{22}H_{10}Co_2CrO_{12}$, M = 636.17, orthorhombic, a = 9.796(1), b = 17.841(1), c = 29.302(4) Å, V = 5121(1) Å^3 (by least-squares refinement on diffractometer angles for 25 automatically-centred reflections, Cu-Kα), space group *Pbca*, $Z = 8$, $D_c = 1.65$ g cm^{-3}, μ(Cu-Kα) = 145.9 cm^{-1}, $T = 298$ K.

Data collection and processing. Phillips PW-100 diffractometer, ω–2θ scan technique, graphite-monochromated Cu Kα radiation; 4914 independent reflections measured ($2 \leq \theta \leq 65°$), 1397 of which were assumed as observed ($I > 2\sigma$) and absorption corrections were made [15]. No significant decay was observed.

Structure analysis and refinement. The structure was solved by a combination of Patterson and direct methods [16–18], and subsequent difference Fourier synthesis. Atomic scattering factors were taken from the usual tabulations [19]. Anomalous dispersion terms for Cr, Co and O were included in F_c [19]. An empirical weighting scheme was applied so as to give no trends in $\langle w\Delta^2F\rangle$ *vs.* $\langle |F_o| \rangle$ and $\langle \sin\theta/\lambda \rangle$ [20]. Final R and R_w values were 0.059 and 0.062, respectively.

Tables of thermal parameters, complete lists of bond lengths and angles and list of structure factors are available from the authors or from the Cambridge Crystallographic Data Centre.

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