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(η^6-Phenyl)Cr(CO)$_3$- and (η^6-phenyl)Co$_4$(CO)$_9$-substituted metallocenylcarbinols of the iron subgroup: synthesis, structure and hydrogen bonding

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Abstract

The synthesis of α-metallocenylcarbinols (M = Fe, Ru, Os) with bulky organometallic substituents R in the carbinol group ($R_1 = (\eta^6$-phenyl)Cr(CO)$_3$, $R_2 = (\eta^6$-phenyl)Co$_4$CO$_9$) is reported. The steric hindrances caused by these R are shown to prevent the usual association of carbinols via intermolecular hydrogen bonds of the OH $\cdots$ O type. In the crystal, chelate cycles with intramolecular hydrogen bonds of the OH $\cdots$ M type are formed. The results of an X-ray diffraction study are in good agreement with the IR spectroscopic data, providing evidence of an additional weak OH $\cdots$ OC interaction present in R_1-substituted carbinols. In solution, no molecules with free (i.e. not bonded via intramolecular hydrogen bonds) OH groups are found. The relative stability of such chelate cycles is discussed.

Introduction

It has previously been reported [1,2] that α-metallocenylcarbinols can form two types of chelate cycles with intramolecular hydrogen bonds involving either the cyclopentadienyl ring (OH $\cdots$ π) or the metal atom (OH $\cdots$ M). In dilute solution, molecules with intramolecular H-bonds are in equilibrium with molecules containing free OH groups [2]. In the solid state, depending on the nature of the metal and the substituents at the carbinol group, intramolecular hydrogen bonds with chelate cycles via the metal either retain or are partially or completely replaced by intermolecular H-bonds of the OH $\cdots$ O type [3,4] *.

The equilibrium position between molecules with free and bonded OH groups (in CCl_4 solution) is highly dependent on the shape and size of the substituent. Thus, the introduction of planar aryl substituents leads to an equilibrium shift towards free OH groups. The value of the equilibrium constant (K_{eq}) decreases along a series which is mainly controlled by the size rather than the electronic properties of

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* H-Complexes of an unusual type, (OH $\cdots$ π)(Mes), have also been found [3].

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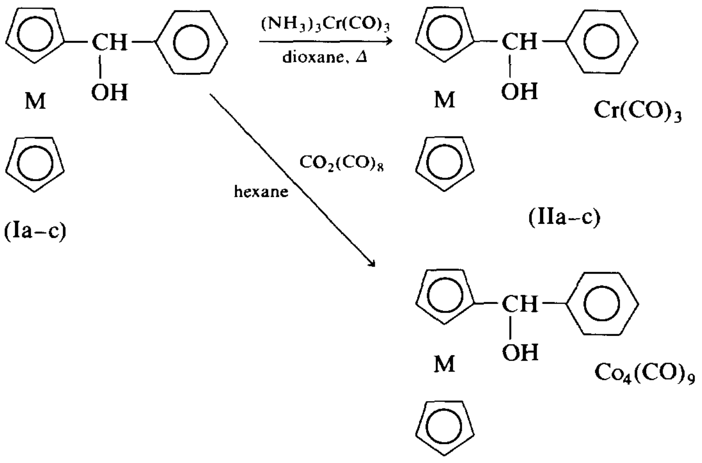
the substituents: $CH_3 > C_6H_5 > C_6F_5 >$ Mes [1,3]. The influence of a bulky ^{t}Bu substituent is quite different. Thus, upon substitution of R = Me by ^{t}Bu in Fc-CHROH, equilibrium is totally shifted towards the molecules with bonded OH groups; as a result, the spectrum shows only the $\nu(OH \cdots Fe)$ band, i.e. the K_{eq} value for the Me substituent is far lower than for ^{t}Bu [7].

In this connection, it seemed worthwhile to examine how the equilibrium is influenced by substituents whose size is substantially increased owing to coordination of the aryl group with the metallocarbonyl fragment. As substituents R, arenetricarbonylchromium and arenetetracobaltnonacarbonyl π-complexes were chosen. Of considerable interest was the possibility of forming a competitive hydrogen bond with metal atoms included in the substituent (Cr, Co). Also, we were curious to determine whether these bulky substituents hinder the association of molecules, i.e. whether the chelate cycles closed by the $OH \cdots M$ intramolecular H-bonds are retained in the solid state or are replaced by intermolecular hydrogen bonding.

The compounds necessary for the investigation have not been reported in the literature. These were synthesized according to the scheme:



(Ia–c)

(IIa–c)

(IIIa–c)

(M = Fe (a), Ru (b), Os (c))

Compounds IIa–c were prepared by a published procedure [5] which is usually used for the synthesis of tricarbonyl(arene)chromiums; tetracobaltnonacarbonyl complexes (III) were obtained as described in [6] (yields, melting points and elemental data are collected in Tab. 1). All the compounds obtained are high-melting solids, which are air-stable in the solid state (clusters IIIa–c should be kept in a refrigerator) and decompose slowly in solution.

The structure of the compounds in the solid state and in solutions of CCl_4 and hexane was examined by IR spectroscopy in the region of hydroxyl and carbonyl stretching vibrations. An X-ray structure determination was performed on IIIa.

Discussion

1. IR spectra

The spectra of dilute CCl_4 solutions of IIa–c and IIIa,b do not show bands for the free OH groups which for the starting carbinols, Ia–c, occur at 3612–3615 cm^{-1}.

Table 1

Properties of the compounds obtained

Compound	Yield (%)	M.p. (°C)	Analyses Found (calcd.) (%)		Molecular formula
			C	H	
IIa	82	153–157 (dec.)	55.61 (56.10)	3.78 (3.77)	$C_{20}H_{16}CrFeO_4$
IIIa	44	Decomp. without melt.	40.09 (40.04)	2.28 (2.07)	$C_{26}H_{16}Co_4FeO_{10}$
IIb	50	160–162 (dec.) 125–130	50.97 (37.84)	3.67 (1.95)	$C_{20}H_{16}Co_4O_{10}Ru$
IIc	55	160–165 (dec.)	42.91 (42.70)	3.08 (2.87)	$C_{20}H_{16}CrO_4Os$ [a]
IIIc	13	Decomp. without melt. 85–95	34.46 (34.15)	2.20 (1.76)	$C_{26}H_{16}Co_4O_{10}Os$ [b]

[a] (%) Cr 9.44 (9.24), (%) Os 33.80/(33.81). [b] (%) Os 21.19 (20.80).

The spectra exhibit only one band (3570–3470 cm^{-1}) for OH groups bonded via intramolecular hydrogen bonds (Tab. 2). Hence, on coordination of bulky metal-containing moieties such as $Cr(CO)_3$ and $Co_4(CO)_9$ with the phenyl substituent at the carbinol C atom, the equilibrium shifts totally towards the molecules involving intramolecular H-bonds; the effect of these moieties is similar to that of ^tBu groups.

In the case of ruthenocenyl- and osmocenylcarbinols, the character of the intramolecular hydrogen bonds formed is easy to analyse.

For the carbinols IIb,c, IIIb, the position of the bands for the bonded OH groups shows only a slight difference from that of ν(bonded OH) for the starting compounds with Ph-substituents at the carbinol group, namely, from $\nu(OH \cdots Ru)$ and $\nu(OH \cdots Os)$ for Ib,c, respectively. Substitution of one bulky substituent (IIb) by another (IIIb) has no effect. Consequently, there can be no question that chelate cycles of one type, those closed by $OH \cdots M$ hydrogen bonds, are formed.

A more complicated situation is observed for ferrocenylcarbinols, where rather weak intramolecular hydrogen bonds of the $OH \cdots Fe$ and $OH \cdots \pi$ types are able to compete [1]. In the starting ferrocenophenylcarbinol Ia both H-bond types are present. However, acccording to [1], as the size of the substitution at the carbinol group increases (R = Mes, ^tBu), only one type of intramolecular H-bond is formed in solution, that of $OH \cdots Fe$. These data led us to conclude that in the carbinols under investigation (IIa, IIIa), which contain very bulky substituents R, the same type of intramolecular hydrogen bond is preserved, namely, the $OH \cdots Fe$ type. This suggestion is confirmed by the X-ray data for IIIa, which show that the OH-group is rotated towards the iron atom (see the next section). As ν(OH) frequencies for solution and crystal are similar, it might be inferred that the same situation is observed in solution, while other types of intramolecular hydrogen bond ($OH \cdots \pi$ and $OH \cdots Co$) are not realized.

It has previously been established [7] that in tricarbonyl(hydroxyindane)chromiums an intramolecular hydrogen bond between hydroxyl and the chromium atom is present. With this in mind and taking into account that, with the formation of such H-bonds, the shift in values for the ν(free OH) bands turned out to be only slightly lower than in the case of an intramolecular H-bond with the iron atom [7],

Table 2

IR spectral data, ν(OH) and $\Delta\nu(1/2)$ cm^{-1}, for McCHOHR-type compounds

R M	$C_6H_5Cr(CO)_3$ (II)				$C_6H_5Co_4(CO)_9$ (III)				C_5H_5 (I) [1–4]				Assignment [a]
	Nujol		CCl_4		Nujol		CCl_4		Nujol		CCl_4		
	νOH	$\Delta\nu(1/2)$	νOH	$\Delta\nu(1/2)$	νOH	$\Delta\nu(1/2)$	νOH	$\Delta\nu(1/2)$	νOH	$\Delta\nu(1/2)$	νOH	$\Delta\nu(1/2)$	
Fe(a)									3460	70			νOH ··· O(1)
	3562	30	3576	64	3565	20	3575	50					νOH ··· Fe(2)
											3560sh 3570	[b]	νOH ··· π(2)
											3612		ν free OH
Ru(b)									3415	110			νOH ··· O
	3500	60	3500	110	3505	30	3500	130			3491	90	νOH ··· Ru(2)
											3615		ν free OH
Os(c)					–	–	–	–	3390	180			νOH ··· O(1)
	3470	90	3472	130	–	–	–	–			3461	108	νOH ··· Os(2)
					–	–	–	–			3615		ν free OH

[a] 1, intermolecular hydrogen bond; 2, intramolecular hydrogen bond. [b] In cyclohexane these bands are separated [1].

we were led to examine the possibility of competition between intramolecular hydrogen bonds of the OH ··· Cr and OH ··· Fe types in compound IIa. The spectra of a model compound in which the ferrocenyl fragment was replaced by the phenyl species were studied. In the spectrum of $C_6H_5CHOHC_6H_5Cr(CO)_3$ the only band for the free OH groups was observed at 3620 cm^{-1}. The absence of an intramolecular H-bond in the model compound indicates that the $Cr(CO)_3$ arrangement is not able to compete, and, moreover, that the band at 3576 cm^{-1} in the spectrum of IIa belongs to an intramolecular hydrogen bond of the OH ··· Fe rather than the OH ··· Cr type.

As already mentioned, an X-ray investigation of IIIa has revealed that in the solid state the chelate cycles with an OH ··· Fe bond are preserved and there is no self-association of the OH ··· O type. Similar spectroscopic features for IIIa and the other compounds (IIa–c, IIIb) (namely, the similar values of ν(HO) in the spectra of solutions and solids and an increase in the band halfwidths on going from solution to crystal) suggest that preservation of intramolecular H-bonds of the OH ··· M type is common for metallocenylcarbinols in the solid state.

Thus, all the studied α-metallocenylphenylcarbinols and ferrocenyl-t-butylcarbinol in the solid state are associated owing to usual intermolecular hydrogen bonds of the OH ··· O type ([3,4] and Tab. 2), whereas the synthesized compounds with bulkier organometallic substituents involve OH ··· M intramolecular hydrogen bonds (M = Fe, Ru, Os) in the crystal. The absence of selfassociation can reasonably be ascribed to increased steric hindrances induced by such substituents. In the spectra of solutions, the bands for molecules with free OH groups are not seen. The relative stability of chelate cycles with OH ··· M bonds is the same for carbinols containing arene $Cr(CO)_3$ and arene $Co_4(CO)_9$ substituents. As in the case of the starting compounds, on increasing the size and basicity of the metal atom, the relative stability of the intramolecular H-bond increases in the order Fe < Ru < Os.

Additional information on the structure of the carbinols in solution and in the crystal was provided by an analysis of the spectra in the metallocarbonyl region (ν(CO)). The spectra of solutions of α-metallocenylcarbinols with arenetricarbonyl chromium substituent R (IIa–c) exhibit two intense bands, ν(CO), at 1980–1975 and 1911–1906 cm^{-1} (Tab. 3). The close positions of the maxima for these bands and bands attributed to the A and E modes of arenetricarbonylchromiums [8,9] indicate the preservation of C_{3v} symmetry of the $Cr(CO)_3$ group in IIa–c.

In the spectra of solutions of metallocenylcarbinols IIIa,b, one observes five bands whose occurrence is close to the frequencies shown in the spectra of (arene)$Co_4(CO)_9$ [10] (Tab. 3). Hence, the symmetry of the $Co_4(CO)_9$ moiety in compounds IIIa,b also remains the same. The assignment of the bands is presented in Tab. 3.

A pronounced difference was observed between the spectra of compounds IIa–c, IIIa,b and the relevant metallocarbonyl-arene π-complexes in the solid state. In addition to the E-mode band splitting which is normally observed for such complexes, new absorption bands appear at 1950–1960 cm^{-1} for IIa–c and at 1980–1984 and 1860–1862 cm^{-1} for IIIa,b, respectively. It should be mentioned that, according to the X-ray data, the hydrogen atom of the OH group in compound IIIa is in contact with the oxygen atom of the CO ligand of the adjacent molecule. Such an interaction can explain the appearance of an additional band in the spectrum of this compound in the crystal. The close positions of the new bands in the spectra of all

Table 3

IR spectral data for compounds of the type McCHOHR ($R = C_6H_5M_n(CO)_m$) and $C_6H_5M_n(CO)_m$ in the ν(CO) range

N	$M_n(CO)_m$	FeCHOHR		RcCHOHR		OcCHOHR		$C_6H_6M_n(CO)_m$ [a]		Assignment
		Nujol	C_6H_{12}	Nujol	C_6H_{12}	Nujol	C_6H_{12}	Nujol	C_6H_{12}	
I	$Cr(CO)_3$	1976s	1980s	1978s	1976s	1978s	1975s	1971s	1985s	ν(CO) (A^1)
		1956m		1959m		1960m				
		1884sh		1886sh						
		1870vs	1911s		1906s	1888vs	1910s	1874sh		
				1877vs				1860s	1915	ν(CO) (E)
II	$Co_4(CO)_9$	2075s	2071s	2074s	2075s	–	–	2070s	2075s	$\nu_1(A_1)$
		2030s	2030s	2032s	2034vs	–	–	2032s	2031vs	$\nu_3(E)$
		2025s		2024s				2021s		
		2005s	2010s	2007s	2014m	–	–	2010s	2013s	$\nu_2(A_1)$
		1996s	1998s	1996m	2000m	–	–	1993s	2000s	$\nu_4(E)$
		1980s		1984s		–	–			
		1860m		1860s		–	–			
		1808s	1832s	1808vs	1825vs	–	–	1802vs	1829s	ν(E) bridge

[a] The data and assignment for $C_6H_6Cr(CO)_3$ are taken from [8,9], those for $C_6H_6Co_4(CO)_9$ from [10].

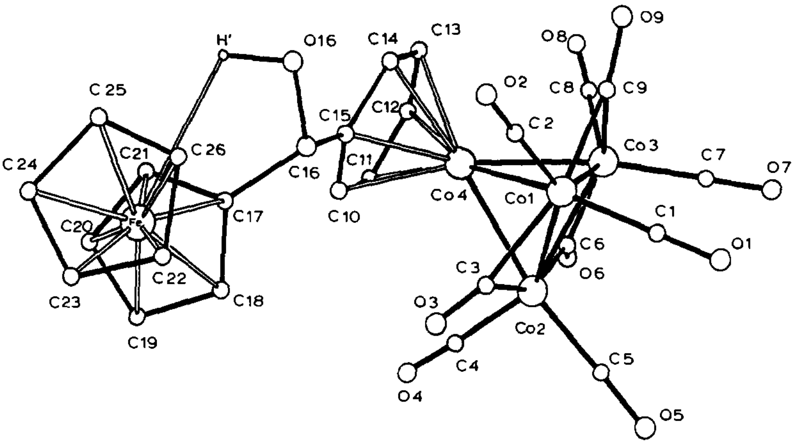


Fig. 1. Molecule IIIa (hydrogen atoms, except for those in hydroxyl groups, are not depicted).

metallocenylcarbinols studied allow on to suppose that the origin of these bands is identical and is connected with weak molecular interactions of the type OH ··· OC.

2. *X-ray investigation*

The structural features of molecule IIIa have been elucidated by an X-ray diffraction study. The structure of the molecule is shown in Fig. 1.

Selected bond lengths and bond angles are listed in Tab. 4. Molecule IIIa occupies a general position in the crystal. Atomic coordinates and complete tables of geometrical parameters for IIIa are deposited at the Cambridge Crystallographic database.

Molecule IIIa includes a tetrahedral cluster fragment (η^6-arene)$Co_4(CO)_9$ which is structurally analogous to the dodecacarbonyltetracobalt cluster, $Co_4(CO)_{12}$ (IV), [11,12]. This cluster fragment may be formed from IV on replacing three terminal CO-groups at the apical Co(4) atom by the η^6-arene ligand with the overall ligand arrangement being preserved. The remaining coordination environment of the Co_4 metallic core in IIIa involves three μ-CO and six terminal CO-ligands (of these, three are equatorial and three are apical). The angular parameters of the ligand environment at the triangular base Co(1)Co(2)Co(3) for the clusters of a given type are presented in Fig. 2. The closest structural analogues of IIIa are the arene-nonacarbonyltetracobalt clusters (η^6-C_6H_6)$Co_4(CO)_9$ (V) and (η^6-$C_6H_4Me_2$)$Co_4(CO)_9$ (VI) [13]. As in structures V and VI, the tetrahedral Co_4 metallic core undergoes pronounced trigonal-pyramidal distortions, viz. the average bond length between the base metals (2.454 Å) is almost 0.04 Å shorter than the mean distance between the Co–Co bonds and the apical Co(4) atom (2.490).

In Tab. 5 are shown the relevant interligand angles for IIIa and its closest structural analogues (Fig. 2). Since a disordered structure such as $Co_4(CO)_{12}$ is determined with greater errors, Tab. 5 also includes the data for its structural analogue, the cluster $Rh_4(\mu\text{-}CO)_3(CO)_9$, whose geometry has been determined more accurately. The angles at the apexes of the tetrahedral metallic core testify to the stability of the ligand environment in the clusters under consideration.

Table 4

Bond lengths (Å) and bond angles (degrees) in IIIa

Bond lengths			
Co(1)-Co(2)	2.455(1)	Co(4)-C(12)	2.143(7)
Co(1)-Co(3)	2.445(1)	Co(4)-C(13)	2.121(8)
Co(2)-Co(3)	2.463(1)	Co(4)-C(14)	2.130(7)
Co(1)-Co(4)	2.481(1)	Co(4)-C(15)	2.192(7)
Co(2)-Co(4)	2.472(1)	Fe-C(17)	2.040(6)
Co(3)-Co(4)	2.517(1)	Fe-C(18)	2.040(7)
Co(1)-C(1)	1.800(8)	Fe-C(19)	2.020(7)
Co(1)-C(2)	1.785(7)	Fe-C(20)	2.039(8)
Co(1)-C(3)	1.925(7)	Fe-C(21)	2.047(7)
Co(2)-C(3)	1.928(6)	Fe-C(22)	2.038(8)
Co(2)-C(4)	1.771(8)	Fe-C(23)	2.035(7)
Co(2)-C(5)	1.794(8)	Fe-C(24)	2.051(7)
Co(2)-C(6)	1.927(6)	Fe-C(25)	2.027(8)
Co(3)-C(6)	1.915(7)	Fe-C(26)	2.031(8)
Co(3)-C(7)	1.806(8)	C(15)-C(16)	1.538(9)
Co(3)-C(8)	1.793(8)	C(16)-C(17)	1.493(9)
Co(3)-C(9)	1.915(7)	C(16)-O(16)	1.423(9)
Co(1)-C(9)	1.918(7)	O(16)-H^1	1.1(1)
Co(4)-C(10)	2.150(7)	Fe···H^1	2.9(1)
Co(4)-C(11)	2.132(7)	Fe···O(16)	3.466(5)
Bond angles			
Co(4)-Co(1)-C(2)	100.0(2)	Co(2)-Co(1)-C(1)	102.5(2)
Co(4)-Co(2)-C(4)	92.6(2)	Co(3)-Co(1)-C(1)	103.7(2)
Co(4)-Co(3)-C(8)	92.1(2)	Co(3)-Co(2)-C(5)	101.6(3)
Co(2)-Co(1)-C(2)	144.1(2)	Co(1)-Co(2)-C(5)	106.8(2)
Co(3)-Co(1)-C(2)	139.6(2)	Co(1)-Co(3)-C(7)	107.7(2)
Co(3)-Co(2)-C(4)	135.9(2)	Co(2)-Co(3)-C(7)	109.2(2)
Co(1)-Co(2)-C(4)	139.5(3)	C(1)-Co(1)-C(2)	99.3(3)
Co(1)-Co(3)-C(8)	137.9(2)	C(4)-Co(2)-C(5)	99.6(3)
Co(2)-Co(3)-C(8)	134.5(2)	C(7)-Co(3)-C(8)	102.1(3)

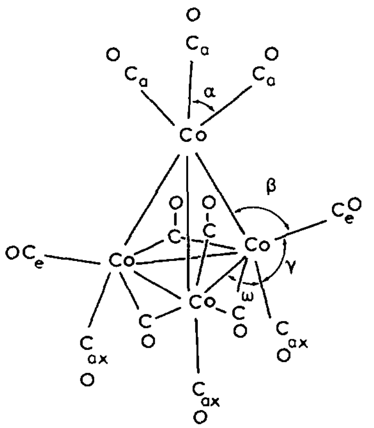


Fig. 2. Molecular structure of $Co_4(CO)_9(\mu\text{-}CO)_3$. Selected interligand angles and orientations of the terminal CO-ligands are denoted as a, apical; e-equatorial; and ax, axial.

Table 5

Angles (degrees) in clusters IIIa, IV–VII

		β	γ	δ	ω	References
I $Co_4(CO)_9$-(η^6-C_6H_5CHOHFe)	IIIa	92.1–100.0	99.3–102.1	134.5–144.1	102.5–111.1	[a]
II $Co_4(CO)_{12}$	IV	102	105	136	105	[2]
III (η^6-C_6H_6)$Co_4(CO)_9$	V	98.9	99.6	140.3–142.0	103.6–105.0	[4]
IV (η^6-$C_6H_4Me_2$)$Co_4(CO)_9$-	VI	97.9–101.9	97.7–100.4	138.4–142.7	101.3–107.5	[4]
$Ph_4(CO)_{12}$	VII	95.0	98.0			[2]

[a] Present work.

Replacement of the three terminal carbonyl ligands in the apical position of $Co_4(CO)_{12}$ by the η^6-arene ligand leads to a decrease in Tolman's conic angle for the CoL fragment (from 115° for $L = (CO)_3$ to 105–110° for $L = \eta^6$-C_6H_6, see [14]). Relaxation of steric tensions in the coordination environment of cluster I is manifested by a small decrease (3°) of the tilting angle β of the terminal equatorial CO ligands from the corresponding Co–Co bonds between the apical and basal cobalt atoms, and also by an analogous increase (of 1° on average) in the "scissor" angles OC–M–CO (γ) between the equatorial and axial CO ligands as compared to the structure of $Rh_4(CO)_{12}$. The presence of a bulky ferrocenylcarbinol substituent in the arene ligand of IIIa causes far more pronounced variations in the β angles for different metal atoms at the cluster base. An equatorial carbonyl ligand C(2)O(2) which is close to the carbinol moiety (the pseudotorsion angle C(2)Co(1) ··· C(15) C(16) is equal to −35.6(7)°; the intramolecular contact C(2) ··· C(16), 3.41 Å, corresponds to the double Van der Waals radius of a carbon atom) is displaced from the relevant Co(1)–CO(4) bond to a greater extent than other equatorial CO ligands. The difference between the β angles in IIIa is ca. 8°, whereas for clusters IV and V, which have no bulky substituents in the arene fragment, this value does not exceed 4°.

An average-squares plane of the η^6-arene ring is almost parallel to the base plane of the cluster Co(1)Co(2)Co(3) (the dihedral angle is 1.2°). In the arene ligand the C(15) *ipso*-atom is displaced by 0.037 Å from the average-squares plane defined by the other five cyclic atoms (deviations of the latter atoms from this plane are within 0.009 Å) towards the side opposite the Co(4) atom. Ferrocenyl and OH substituents are located on the opposite side of the arene ligand plane with respect to the cluster nucleus $Co_4(CO)_9$; an average-squares plane of the five-membered cycle C(17)–C(21) in the ferrocene nucleus is oriented perpendicular to the arene plane (the dihedral angle is 86.8°).

The H^1 atom attached to the O(16) hydroxyl atom is oriented towards the iron atom. The intramolecular Fe–H^1 contact is 2.9(1) Å, the non-bonding distance Fe ··· O(16) is 3.466(5) Å, and the Fe–H–O(16) angle is 113(8)°. The torsion angle C(15)C(16)O(16)H^1 is 26°. The observed OH group orientation may be regarded as evidence for the presence of a weak hydrogen bond of the O–H^1 ··· Fe type in IIIa. This type of bond has also been suggested for the structures of $C_5H_5FeC_5H_4C(OH)$-(PhC_4O_2) (where the Fe ··· O distance is 3.57 Å) [15], $C_5H_5RhC_7H_5C(OH)Me$ (where the Rh ··· O distance is 3.49 Å) [16] and [η^5-$C_5H_4(CH_2)_3$]Fe[η^5-

$C_6H_3C(OH)PhEt]$ (where the Fe · · · O distance is 3.45 Å) [17]. In addition to its interaction with the Fe atom, the H^1 atom participates in the H^1 · · · O(9A) contact (2.16(13) Å) with the CO oxygen atom of the adjacent molecule A (generated from the basic one by an inversion centre); the O(16) · · · O(9A) distance is 2.932(9) Å. The other intermolecular contacts in structure IIIa correspond to normal Van der Waals interactions.

Thus, the results of X-ray and spectroscopic studies on the tetracobaltnonacarbonyl arene π-complex of ferrocenylcarbonyl suggest the existance of a weak intramolecular hydrogen bond of the OH · · · Fe type and an additional intermolecular OH · · · OC interaction in the crystal.

Experimental

IR spectra were measured with Specord M-80 and IR-75 spectrophotometers in Nujol and solutions of CCl_4 (in the ν(OH) range, $c = 2.5 \times 10^{-3}$ mol/l, $d = 2$ cm) and cyclohexane (in the ν(CO) range, $c = 2.5 \times 10^{-2}$ mol/l, $d = 0.01$ cm).

The unit cell parameters of crystals of IIIa and the intensities of 2839 independent reflections were measured with an automatic Syntex $P2_1$ diffractometer (−120 °C, graphite monochromated Mo-K_α radiation, $\theta/2\theta$ scan technique, $2\theta \leqslant 48°$, 2753 observed reflections with $I > 2\sigma(I)$). Crystals of IIIa are monoclinic; $a = 15.367(5)$, $b = 11.613(3)$, $c = 15.452(4)$ Å, $\beta = 108.76(2)°$, space group $P2_1/n$, $Z = 4$.

The structure was solved by a direct method using the MULTAN program) and refined by the block-diagonal least-squares method in an isotropic approximation to $R = 0.070$. A correction for absorption (μ(Mo-K_α) = 32.00 cm^{-1}) was performed by the DIFABS procedure. The final anisotropic refinement of all non-hydrogen atoms, including all hydrogen atoms (located from a difference Fourier synthesis) as fixed contributions, converged to $R = 0.036$ and $R_w = 0.040$ for 2690 reflections with $I > 3\sigma(I)$. All calculations were carried out on an Eclipse S/200 computer using INEXTL programs [18].

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