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Organometallic cluster complexes with face-capping arene ligands, 9[1]. Hydrogenation of the side-chain in [{(C_5H_5)Co}$_3$(μ_3-alkenylbenzene)]: synthesis and structure of the cluster complexes [{(C_5H_5)Co}$_3$(μ_3-η^2:η^2:η^2-C_6H_5–CHR^1–CH_2R^2)][2]

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Abstract

Catalytic hydrogenation (1 bar H_2, 20°C, Pd/C catalyst) of the C=C double bond in the side-chain of the *facial* alkenylbenzene ligands of the cluster complexes [{(C_5H_5)Co}$_3${μ_3-C_6H_5(CR^1)(CHR^2)}] **2b**–**c** gave the derivatives [{(C_5H_5)Co}$_3${μ_3-C_6H_5(CHR^1)(CH_2R^2)}] **3b**–**d** in high yield (**b**, $R^1 = CH_3$, $R^2 = H$; **c**, $R^1 = H$, $R^2 = Ph$; **d**, $R^1 = Ph$, $R^2 = H$). The X-ray crystal and molecular structures of **3c** and **3d** were determined. In both derivatives a *facial* μ_3-η^2:η^2:η^2 coordination of one phenyl ring to the tricobalt cluster was found. Only one of two possible diastereomeric conformers is present in the crystals of **3d**. The expanded μ_3-phenyl rings show a small but statistically significant Kekulé-type (trigonal) distortion. In solution hindered rotation of the μ_3-arenes on top of the [(C_5H_5)Co]$_3$ clusters is observed by NMR spectroscopy. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Arene Clusters; Cyclopentadienyl; Cobalt

1. Introduction

The organometallic cluster complexes [{(C_5H_5)M}$_3$(μ_3-η^2:η^2:η^2-arene)] (M = Co, Rh) are kinetically very stable molecules [2]. It has recently been shown that the rhodium derivatives can be synthesised by stepwise addition of (C_5H_5)Rh fragments (photogenerated from [(C_5H_5)Rh(C_2H_4)$_2$]) directly to the six-membered ring of the arene (typically benzene or hexamethylbenzene) [3]. Such a straightforward synthetic route is impracticable for the tricobalt analogues. Some time ago, we reported the facile formation of [{(C_5H_5)Co}$_3$(μ_3-η^2:η^2:η^2-β-methylstyrene)] **2a** from [(C_5H_5)Co(C_2H_4)$_2$] **1** and β-methylstyrene or allylbenzene [4]. Not even traces of arene cluster complexes were formed under the same reaction conditions with benzene or alkylbenzenes as the aromatic substrates. Obviously, the unsaturated side chain plays a crucial role during the assemblage of the trimetal cluster [5]. Indeed, a considerable number of cluster complexes **2** have been prepared in like manner from **1** and a variety of 1-alkenylbenzenes [6,7].

A number of features of the solid state structures, dynamic behaviour and reactivity of **2** appear to be influenced by the unsaturated substituent. Crystallographic studies on a number of derivatives **2** showed a small Kekulé-type distortion of the μ_3-arene rings [2,8]. Electronic conjugation between the ring and side-chain may have a non-negligible effect on the alternating longer and shorter endocyclic C–C bonds. The steric bulk of the substituent, which is of course a function of the hybridisation (connectivity) of the α-C, is expected to influence the dynamic behaviour of the arene cluster.

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[1] For part 8 see ref. [1].

[2] Dedicated to Professor Brian Johnson on the occasion of his 60th birthday.

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Table 1
^{1}H-NMR spectroscopic data (δ in C_6D_6) for complexes **3b–d**

Complex	C_5H_5	μ_3-Phenyl	Side chain
3b[a]	4.72 (s, 15H)	4.20 (m, 2H), 4.40 (m, 3H)	1.09 (d, 6H, CH_3), 2.15 (sept, 1H, CH)
3c[b]	4.68 (s, 15H)	4.23 (m, 5H)	2.24 (t, 2H, CH_2), 2.98 (t, 2H, CH_2), 7.1–7.3 (m, Ph)[c]
3d[a]	4.72 (s, 15H)	4.21 (m, 3H, *m*-H, *p*-H) 4.53 (d, 1H, *o*-H), 4.61 (d, 1H, *o*-H)	1.25 (d, 3H, CH_3), 3.46 (q, 1H, H–C_α), 7.1–7.2 (m, *p*-H)[c], 7.30 (t, 2H, *m*-H), 7.47 (d, 2H, *o*-H)

[a] 333 K. [b] 313 K. [c] Overlap with solvent resonances.

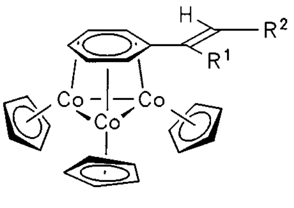
Finally, an olefinic side-chain offers additional functionality, which may mask the reactivity of the *facial* arene ligand itself [1]. These problems prompted us to look into the synthesis of μ_3-arene tricobalt derivatives without a C=C double bond in the α-position to the face-capping arene ring.

In this paper we report on the catalytic hydrogenation of the unsaturated side-chain in some cluster complexes **2** to give the target molecules **3** which are not accessible via the direct route utilising $(C_5H_5)Co$ fragments and the arene ligand. Catalytic hydrogenation of $[\{(C_5H_5)Co\}_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}\beta\text{-methylstyrene})]$ **2a** to give the *n*-propyl derivative **3a** has already been briefly described in an earlier paper ([6]a). However, since due to the poor quality of the crystalline material an X-ray crystal structure analysis could not be carried out, no details of the structure of this complex are known.

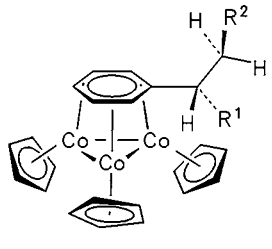
2. Results

2.1. Syntheses

Toluene solutions of the complexes **2b** ($R^1 = CH_3$, $R^2 = H$), **2c** ($R^1 = H$, $R^2 = Ph$) and **2d** ($R^1 = Ph$, $R^2 = H$) were treated with dihydrogen (1 bar) in the presence of a Pd/charcoal catalyst. After reaction times between several hours (**2b**, **2d**) and more than a week (**2c**) the educts had been quantitatively converted into the complexes **3b** ($R^1 = CH_3$, $R^2 = H$), **3c** ($R^1 = H$, $R^2 = Ph$) and **3d** ($R^1 = Ph$, $R^2 = H$), respectively. The products were isolated as dark brown crystalline solids in 50–95% yield.



	R^1	R
2a	H	CH_3
2b	CH_3	H
2c	H	Ph
2d	Ph	H



	R^1	R
3a	H	CH_3
3b	CH_3	H
3c	H	Ph
3d	Ph	H

2.2. Spectroscopic investigations

The proton and carbon resonances of the μ_3-phenyl rings in **3b**–**d** are shifted to high field with respect to those of the uncoordinated phenyl groups (Tables 1 and 2). Hence, two sets of four C resonances each (3 CH, 1 C) are observed for the 1,2-diphenylethane (dibenzyl) ligand in **3c**. The isopropylbenzene ligand in **3b** also gives four signals for the *facial* phenyl ring. In contrast, six ^{13}C resonances can be assigned to the cluster coordinated phenyl ring in the 1,1-diphenylethane derivative **3d**, in addition to the four signals at lower field, which are due to the uncoordinated phenyl ring of this ligand. The methyl hydrogens of the isopropyl substituent in **3b** appear as a broad resonance at room temperature (r.t.), accompanied by a sharp septet due to the methyne proton. On cooling to 235 K, the broad feature splits into two sharp doublets, without any noticeable change of the septet resonance. At 333 K, a sharp doublet/septet pattern is observed. At ambient temperature, the ^{1}H-NMR spectrum of **3c** shows two separate pseudotriplets ($\Delta\delta \approx 0.7$) for the two methylene groups of the 1,2-diphenylethane ligand.

The three cyclopentadienyl ligands in **3b**–**d** give rise to only one slightly broadened singlet both in the ^{1}H- ($\delta \approx 4.7$) and ^{13}C-NMR spectra ($\delta \approx 82$) at r.t. These resonances sharpen when the samples are warmed to 330 K.

2.3. Crystal structure analyses

Single crystal X-ray structure determinations were carried out with **3c** and **3d**. Both complexes crystallise monoclinic in non-centrosymmetric space groups (**3c** $P2_1$, **3d** *Cc*). Important bond lengths and angles are given in Table 3. Views of the molecules are presented in Figs. 1 and 2. Only one of the two possible diastereomers is present as a racemic mixture in the crystals of **3d** (Fig. 1). Complex **3c** crystallised enantiomerically pure (Fig. 2). The crystal packing of **3c** and **3d** has been examined in detail; the results are described elsewhere [9].

Table 2
^{13}C-NMR spectroscopic data[a] (δ in C_6D_6) for complexes **3b–d**

Complex	C_5H_5	μ_3-Phenyl		C_α	C_β	Phenyl	
		CH	C_{ipso}			CH	C_{ipso}
3b[b]	82.5	39.8[c], 40.8[c], 41.9[c]	63.5	38.6[c]	24.0		
3c[d]	82.5	39.3, 40.5, 44.6	60.7	39.7[e]	45.2[e]	126.1, 128.6, 129.0	142.8
3d[f]	82.6	39.5[c], 41.0[c], 41.2[c], 45.0, 49.3	65.8	39.0[c]	21.1	126.2, 127.4, 128.6	149.2

[a] Assignment was supported by determination of signal multiplicities using the DEPT and J-modulated spin–echo techniques. [b] 333 K. [c] μ_3-Phenyl CH or C_αH. [d] 313 K. [e] C_α or C_β. [f] 298 K.

In both complexes, the diphenylethane ligand is bound to a $[(C_5H_5)Co]_3$ cluster in the μ_3-η^2:η^2:η^2 coordination mode via one of the phenyl rings. The μ_3-phenyl rings are essentially planar (root mean square deviation of the C atoms from the best plane: 0.015 (**3c**) and 0.004 (**3d**)) and are expanded considerably compared to the uncoordinated phenyl groups. A staggered conformation is adopted by the ca. coplanar Co_3 and C_6 rings. There is a slight alternation of the endocyclic C–C bond lengths within the μ_3-phenyl rings, which is however not significant in all the cases (the differences in length, Δd(CC), of adjacent bonds are one to nine times larger than the esds of the individual bond distances). In all cases, the bonds ‘on top’ of a metal atom are nominally shorter than the two adjacent bonds, which are ‘in between’ the metals.

The substituents on the μ_3-phenyl rings are displaced from the C_6-plane in the direction away from the Co_3-cluster. This distortion is most obvious with the α-C atoms of the side chains (0.623(7) (**3c**) and 0.544(7) (**3d**), corresponding to bond angles of 24 and 20°, respectively), but is also noticeable with the H atoms, which are less accurately localised (0.2–0.4 Å off the C_6-plane).

Table 3
Selected bond lengths (Å) and angles (°) for complexes **3c** and **3d**

	3c	**3d**
Co(1)–Co(2)	2.5319(14)	2.5014(11)
Co(1)–Co(3)	2.4905(14)	2.4895(12)
Co(2)–Co(3)	2.4970(14)	2.5218(11)
Co(1)–C(1)	2.041(5)	2.069(4)
Co(1)–C(2)	2.027(5)	2.011(5)
Co(2)–C(3)	2.038(6)	2.021(5)
Co(2)–C(4)	2.018(6)	2.022(5)
Co(3)–C(5)	2.037(5)	2.023(5)
Co(3)–C(6)	2.028(6)	2.021(5)
C(1)–C(2)	1.406(7)	1.416(7)
C(1)–C(6)	1.449(8)	1.443(6)
C(2)–C(3)	1.438(8)	1.437(7)
C(3)–C(4)	1.412(8)	1.412(7)
C(4)–C(5)	1.446(9)	1.434(8)
C(5)–C(6)	1.427(8)	1.405(7)
C(1)–C(13)	1.511(8)	1.524(6)
C(13)–C(14)	1.547(8)	1.542(7)
C(13)–C(7)		1.526(6)
C(14)–C(7)	1.507(8)	

3. Discussion

3.1. Syntheses and structures

In previous work, we noted that **2a** was rather inert to a number of conventional addition reagents aimed at the olefinic functionality [5]. In contrast to this behaviour, hydrogenation of the C=C double bonds in the side chains of **2** occurs under conditions which are similar to those needed for the free ligands. The observed considerable difference of the rates of this reac-

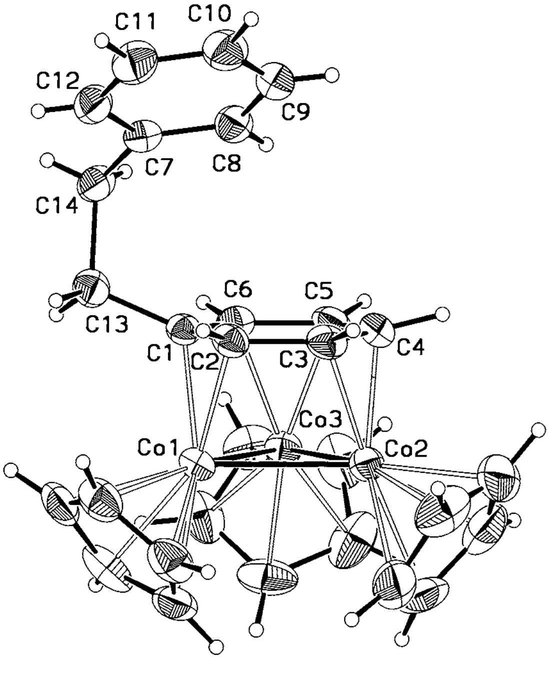


Fig. 1. Molecular structure of **3c**. Displacement ellipsoids are at the 30% level.

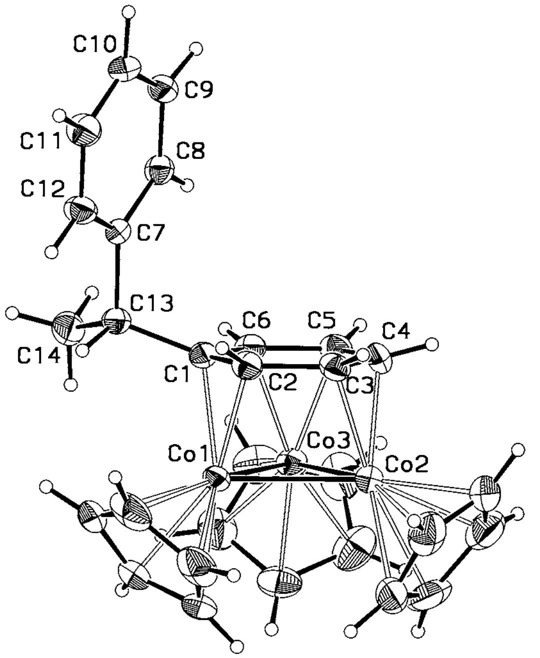


Fig. 2. Molecular structure of **3d**. Displacement ellipsoids are at the 30% level.

tion for the two isomeric substrates **2c** and **2d** (and also between **2b** and **2c**) also parallels the behaviour of the free ligands. The commonly observed less facile hydrogenation of internal compared to terminal alkenes merely is an example of deactivation of the C–C π-bond with increasing degree of substitution [10]. This effect should be even more pronounced with the very bulky $[(C_5H_5)Co]_3(\mu_3$-phenyl) substituent.

Interestingly, hydrogenation of the side chains in some derivatives of **2** was observed on several other occasions where it had not initially been expected. The side-chain hydrogenated alkylbenzene complexes **3a** and **3d** were the only isolatable products of the reactions of the alkenylbenzene derivatives **2a** and **2d**, respectively, with dimethylphenylsilane in the presence of AIBN or H_2PtCl_6 [5]. Apparently, hydrogenation is preferred to hydrosilation in these systems. Likewise, **3d** was observed along with free 1,1-diphenylethane and **2d** in a 1:1:1 ratio when ca. equimolar mixtures of **2d** and CF_3COOH were allowed to stand for 24 h [1]. The cluster stabilised carbonium ion $[\{(C_5H_5)Co\}_3(\mu_3\text{-}C_6H_5CMe_2)]^+$, obtained by protonation of the methylene group in **2b**, also decomposed within weeks at -20°C to give a 3:1 mixture of **2b** and **3b** [1]. As an explanation for the latter two observations, reaction with hydrogen 'in statu nascendi', generated from oxidation [1] of some cobalt containing species by the acid, can be envisaged.

The $[(C_5H_5)Co]_3(\mu_3$-phenyl) cores of the cluster complexes **3c** and **3d** have very similar geometries. The staggered arrangement of the Co_3 and C_6 rings, corresponding to a μ_3-η^2:η^2:η^2 coordination, is typical for arene ligands capping a triangular face of a metal cluster [7,11]. Minor deviations from the ideal staggered geometry, which occur in some derivatives with bulky substituents, can be explained with steric repulsion between the substituents on the μ_3-arene and the other ligands on the metal cluster. For example, in the complex $[(\mu_3\text{-H})\{(C_5H_5)Co\}_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$-1,1-diphenylethane)$]^+$ $[\mathbf{3d}+\mathrm{H}]^+$, the protonation product of **3d**, the μ_3-arene is rotated by a few degrees within the plane parallel to the Co_3-triangle, away from the ideal staggered conformation [1]. From the behaviour in solution, where full rotation of the μ_3-arenes is generally observed [2,8], it is obvious that the intrinsic rotational barrier is relatively small. In **3d**, steric repulsions between the substituents on the α-carbon atom C13 and the cyclopentadienyl rings are minimised in the conformation which is actually found in the crystal (Fig. 2). Here, the methyl group $(C14)H_3$ nicely fits in between the cyclopentadienyl ligands on cobalt atoms Co1 and Co3, even with a nearly perfect staggered arrangement of the Co_3 and C_6 rings. However, in the complex $[\mathbf{3d}+\mathrm{H}]^+$ steric strain is imposed on the $[(C_5H_5)Co]_3$ (μ_3-phenyl) unit by the face capping hydrido ligand, which pushes the C_5H_5 groups apart, into the direction of the μ_3-phenyl, and causes the observed deviation from the ideal geometry. With the α-carbon atom C13 being secondary rather than *tertiary*, steric congestion in **3c** is even less severe than in **3d**.

A collection of data relating to the endocyclic C–C bond lengths in the two different types of phenyl groups in **3c** and **3d** is compiled in Table 4. Relevant data for **2d** and $[\mathbf{3d}+\mathrm{H}]^+$ are also included for comparison. An expansion of the metal coordinated arene rings compared to the free phenyl groups is obvious. This lengthening on coordination of the C–C bonds is fairly independent of the particular complex in Table 4 and even of the type of metal cluster (similar effects are found in the second-row metal (Rh) cyclopentadienyl and second- (Ru) or third-row metal (Os) carbonyl cluster complexes [2,11]).

The presence and significance of a true Kekulé-type (trigonal) distortion of the μ_3-C6 rings is much more difficult to assess. In our theoretical study of the hypothetical $[\{(C_5H_5)Co\}_3(\mu_3\text{-}C_6H_6)]$ we have pointed out that such a distortion is the consequence of a reduction of symmetry of the C_6-ligand (from 6-fold in free benzene to 3-fold in the μ_3-coordination site), which triggers a mixing of benzene HOMO and LUMO, in phase with the metal orbitals [12]. As a consequence, a stronger interaction of the arene with the metal cluster is expected to induce a stronger distortion of the C_6-ligand. This explains the general trend that arenes bonded to metal clusters composed of second- or third-row transition metals tend to show a more pronounced alternation of endocyclic bond lengths than that which is found in the first-row (cobalt) cluster complexes. The bending of the substituents out of the plane of the *facial* arene ligand away from the metal cluster can also be related to an optimisation of overlap between the metal cluster and arene π-orbitals [12].

The presence of a second, non-coordinated phenyl ring in **3c** and **3d** offers the possibility to further assess the significance of the Kekulé-type distortion observed in the *facial* phenyl ligands. In the previously published structure of **2d**, complications caused by the conjugation of the two phenyl rings with the C=C double bond in the side chain could not be ruled out completely [5]. This problem is not present with the complexes of type **3**. Inspection of Table 4 reveals that those three C–C bonds within the μ_3-arene ligands which come to lie on top of the cobalt atoms are consistently shorter than the other set of three bonds, which fall in between the metals. The difference is however small and not even significant for some individual pairs of adjacent bonds (Table 3).

As can be seen from Tables 3 and 4, there are some pairs of C–C bonds within the free phenyl groups in **2d**, **3c**, **3d** and [**3d**$+$H]$^+$ which are significantly different in length by as much as seven times the esd. In principle, in a benzene derivative any substituent is expected to have some influence on the geometry of the benzene ring to which it is attached. This problem has been addressed by systematic studies [13]. The effects of alkyl substituents on endocyclic bond lengths were found to be considerably less pronounced and more prone to errors than those on bond angles. In any case they should be comparable for both types of phenyl rings (μ_3 cluster coordinated and free), and vary in a systematic way around the C_6 ring [13].

Table 4
Selected distances (Å) relating to the geometry of the phenyl rings in complexes **3c**, **3d**, [**3c**$+$H]$^+$ and **2d**

	3c	**3d**	[**3d**$+$H]$^{+}$[a]	**2d**[b]
μ_3-η^2:η^2:η^2-C_6H_5R				
d_{mean}(CC, short)[c]	1.419(8)	1.411(4)	1.411(8)	1.418(6)
Δ_{max}[d(CC, short)][d]	0.021	0.011	0.020	0.014
d_{mean}(CC, long)[e]	1.440(9)	1.438(4)	1.442(9)	1.449(3)
Δ_{max}[d(CC, long)][f]	0.021	0.010	0.021	0.006
Δ_{mean}[d(CC, short–long)][g]	0.021(10)	0.027(6)	0.031(8)	0.031(6)
Δ_{min}[d(CC, short–long)][h]	0.009	0.020	0.022	0.021
Δ_{max}[d(CC, short–long)][i]	0.041	0.039	0.043	0.041
C_6H_5R				
d_{mean}(CC)[j]	1.377(11)	1.382(5)	1.375(16)	1.387(18)
Δ_{max}[d(CC)][k]	0.014	0.029	0.054	0.057
Δ_{mean}[d(CC)][l]	0.014(8)	0.005(2)	0.020(13)	0.021(14)

[a] Ref. [1]. [b] Ref. ([6]a). [c] Mean of the lengths of the three C–C bonds 'on top' of the metal atoms with standard deviation in parentheses. [d] Largest difference of the lengths of any two in the set of three C–C bonds 'on top' of the metal atoms. [e] Same as [c] but for the bonds 'in between' the metal atoms. [f] Same as [d] but for the bonds 'in between' the metal atoms. [g] Mean difference of the lengths of adjacent C–C bonds with standard deviation in parentheses. [h] smallest difference between the lengths of any two adjacent C–C bonds. [i] Same as [h] but largest difference. [j] Same as [c] and [d] but for all six C–C bonds. [k] Same as [d] and [f] but for any two C–C bonds. [l] Same as [g] but for all C–C bonds.

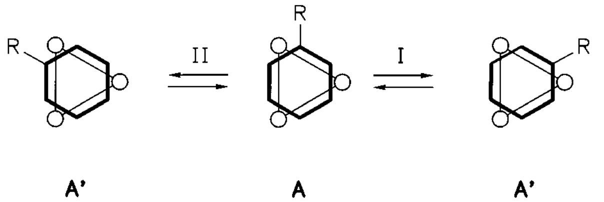
In the structures of **3c** and **3d** there is no obvious regularity in the observed pattern of bond lengths within the free phenyl groups. This contrasts the more regular pattern of alternating longer and shorter bonds in the cluster coordinated phenyl rings. The geometry of the free phenyl rings, as obtained from the refinement of our X-ray diffraction data at ambient temperature, is more likely to be influenced by systematic errors than that of the metal coordinated rings. The former are less restricted to undergo librational motion in the crystal than the latter, which are tightly bound to the metal cluster frame. Indeed, inspection of the Hirshfeld $\Delta_{A,B}$ values [14] indicates considerable motion of the free phenyl groups relative to the rest of the molecules [15]. In effect, the above arguments attach a higher significance to the observed distortion of the face-capping arene rings than to that of the phenyl substituents in the side-chains. A similar case can be put forward for complex **2d**.

The length of the central bond C13–C14 of the 1,2-diphenylethane ligand in **3c** compares well with that of the C13–C14 bond of the 1,1-isomer in **3d** (Table 3) and with results [16] obtained by ab initio MO-calculations on dibenzyl. An apparent discrepancy with the values reported for free 1,2-diphenylethane (1.48–1.517 Å) results from experimental artifacts, due to a particular torsional vibration of the molecules in crystalline dibenzyl [16,17].

3.2. Dynamic stereochemistry

The NMR spectroscopic data of **3b** and **c** compare well with those of other derivatives. In particular, the proton and carbon chemical shifts of the *facial* μ_3-phenyl groups are similar in **2** and **3**. As in the free ligands, there is an α-effect [18] of the substituents on the chemical shifts of the *ipso* C atoms. These resonate at a lower field than the CH resonances. The magnitude of this shift ($\Delta\delta = 10$–20 ppm) is independent of the hybridisation (sp^2 in **2**, sp^3 in **3**) of the α-C.

In the solid state, the three cyclopentadienyl cobalt units which form the cluster backbone of our complexes are rendered inequivalent by the presence of the substituent on the *facial* arene ligands. The presence of only one singlet for all the protons (and carbons,

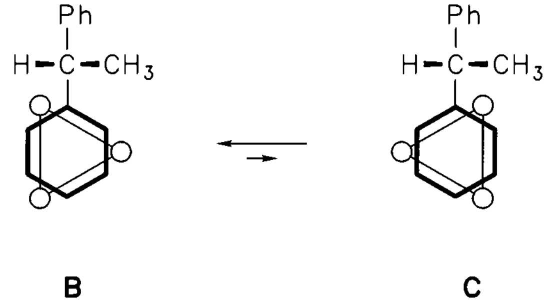


Scheme 1.

respectively) of the three cyclopentadienyl ligands in the ^{1}H- and ^{13}C-NMR spectra is indicative of a dynamic process which equilibrates the three cyclopentadienyl ligands in solution [19]. A rotation of the μ_3-arene in the plane parallel to the Co_3 triangle is consistent with all the experimental data, as will be illustrated in detail below.

Any derivative $[\{(C_5H_5)Co\}_3(\mu_3\text{-}C_6H_5R)]$ with a monosubstituted *facial* arene ligand is intrinsically chiral in the staggered $(\eta^2{:}\eta^2{:}\eta^2)$ conformation. This does not only lead to inequivalence of the three $(C_5H_5)Co$ groups and of all five CH units of the μ_3-phenyl nucleus, but also makes the two methyl groups of the prochiral isopropyl substituent in **3b** diastereotopic. The latter is quite obvious in the low temperature proton spectra of this complex. A 60° rotation of the arene (**A** → **A**′, e.g. process I in Scheme 1) causes inversion of chirality. Such a movement pairwise equilibrates the sets *ortho* and *meta* CH-groups of the μ_3-phenyl ligand as well as the methyl resonances in **3b** [20], but it is not sufficient to average the chemical shifts of all three $(C_5H_5)Co$ groups (only two of these are interchanged). However, starting from **A**, **A**′ can be reached by a second process (II in Scheme 1), which has the same effect on the μ_3-phenyl ring and on the methyl substituents but interchanges a different set of two out of the three $(C_5H_5)Co$ groups. Thus, any combination of the dynamic processes I and II will reproduce the experimental spectra at the high temperature limit, provided that both are fast on the NMR time scale. In effect, this corresponds to a full (360°) rotation of the *facial* arene ligand.

The stereochemical situation is somewhat different in **3d**, due to the asymmetry of the α-carbon atom C13. In this complex, the two staggered conformations **B** and **C** (Scheme 2) are diastereomers, each of which may be a pair of enantiomers. A fast rotation of the μ_3-arene interconverts the diastereomers and equilibrates the three $(C_5H_5)Co$ groups. It does, however, not lead to equivalence of the two *ortho* and the two *meta* CH-units of the μ_3-phenyl ligand. In the proton spectra, the two pseudo-doublets for the *ortho* protons of the μ_3-phenyl group are clearly separated (Table 1). Furthermore, all five carbon resonances (4 CH, 1 C) for the μ_3-phenyl ligand are resolved even at the high temperature limit, in complete agreement with the above arguments.



Scheme 2.

4. Conclusions

(1) Starting with the free arenes, the tricobalt cluster complexes of the type $[\{(C_5H_5)Co\}_3(\mu_3\text{-arene})]$ can only be synthesised with alkenylbenzenes as the *facial* ligands. We have shown in this paper that the C=C double bond in the side chain is by no means required for such complexes to be stable once they have been formed. This supports our view of a crucial involvement of the alkenyl substituent in intermediate steps during the assembly of the metal cluster [5].

(2) The structure of the $[(C_5H_5)Co]_3(\mu_3\text{-arene})$ cluster core is very similar in the complexes **2** (with alkenylbenzenes as *facial* ligands) and **3** (with alkylbenzenes as *facial* ligands). A detailed comparison of the geometries of the free and Co_3 face-capping phenyl groups attaches statistical significance to the small Kekulé-type distortion of the latter ligands. The influence of the unsaturation within the side chain on the structure of the μ_3-phenyl ring is considered negligible.

(3) Hydrogenation of the side-chains in **2** may be used to synthesise derivatives which are particularly suited to test and define the interesting dynamic stereochemistry of *facial* arene coordination.

5. Experimental section

5.1. General procedures

All operations were carried out under an atmosphere of purified nitrogen or argon (BASF R3-11 catalyst) using Schlenk techniques. Solvents were dried by conventional methods. Alumina used as a stationary phase for column chromatography was first heated to 180–200°C under vacuum for several days, then treated with 5% deoxygenated water and stored under nitrogen. The cluster complexes **2b**–**d** were prepared by published methods ([6]a). NMR spectra were obtained on a Bruker AC 200 instrument (200.1 MHz for ^{1}H, 50.3 MHz for ^{13}C). ^{1}H and ^{13}C chemical shifts are reported versus TMS and were determined by reference to internal TMS or residual solvent peaks. To assign the carbon resonances, their multiplicities were determined using the DEPT or *J*-modulated spin–echo techniques. Mass spectra were measured in the electron impact ionisation mode (EI) at 70 eV on Finnegan MAT 8230 and MAT CH7 spectrometers. Elemental analyses were performed locally by the microanalytical laboratory of the organisch-chemisches Institut der Universität Heidelberg and by Mikroanalytisches Labor Beller, Göttingen.

5.2. General procedure for hydrogenations

In a 500 ml flask a ca. 1 mmol sample of **2** is dissolved in 50–150 ml of toluene. After addition of 30–50 mg Pd on charcoal (10% Pd) the mixture is frozen with liquid nitrogen. The flask is evacuated, filled with hydrogen and warmed to r.t. The mixture is mechanically agitated until hydrogenation is complete (checked by ^{1}H-NMR of samples taken periodically). The catalyst is then removed by filtration (G4 frit). The filtrate is concentrated to a small volume and chromatographed on alumina (2.5 × 20 cm, eluent toluene/petroleum ether 1:1). The product **3** is crystallised from the eluate at −20°C.

5.2.1. [{(C_5H_5)Co}$_3$(μ_3-η^2:η^2:η^2-iso-propylbenzene)] (3b)

Using 1.48 g (3.02 mmol) of **2b**, a 750 mg yield (51%) of **3b** was obtained as dark brown microcrystals (reaction time 24 h). M.p. 155°C. MS (EI) *m*/*z* (relative intensity): 492 (23, M^+), 372 (15, $[(CpCo)_3]^+$), 371 (18, $[(CpCo)_3-H]^+$), 370 (100, $[(CpCo)_3-2H]^+$), 311 (13), 310 (18), 247 (17, $[(CpCo)_2-H]^+$), 189 (43, $[Cp_2Co]^+$), 149 (17), 124 (13, $[CpCo]^+$), 120 (17, L^+), 119 (42, $[L-H]^+$), 105 (45, $[L-CH_3]^+$), 91 (26, $[PhCH_2]^+$), 77 (12, Ph^+), 71 (20), 59 (6, Co^+), 57 (37), 43 (40), 41 (32); (L = *iso*-propylbenzene). Anal. Calc. (found): C, 58.54 (58.30); H, 5.53 (5.45).

5.2.2. [{(C_5H_5)Co}$_3$(μ_3-η^2:η^2:η^2-1,2-diphenylethane)] (3c)

Using 660 mg (1.19 mmol) of **2c**, a 560 mg yield (85%) of **3c** was obtained as black crystals (reaction time 10 days). M.p. 156°C. MS (EI) *m*/*z* (relative intensity): 554 (14, M^+), 370 (45, $[(CpCo)_3-2H]^+$), 365 (12), 247 (20, $[(CpCo)_2-H]^+$), 241 (47), 189 (97, $[Cp_2Co]^+$), 182 (8, L^+), 150 (17), 124 (47, $[CpCo]^+$), 91 (100, $[PhCH_2]^+$), 65 (12, Cp^+), 59 (24, Co^+), 39 (18, $[C_3H_3]^+$); (L = 1,2-diphenylethane). Anal. Calc. (found): C, 62.83 (62.76); H, 5.27 (5.24).

5.2.3. [{(C_5H_5)Co}$_3$(μ_3-η^2:η^2:η^2-1,1-diphenylethane)] (3d)

Using 590 mg (1.07 mmol) of **2d**, a 550 mg yield (93%) of **3d** was obtained as black crystals (reaction time 16 h). M.p. 151°C. MS (EI) *m*/*z* (relative intensity): 554 (21, M^+), 371 (11, $[(CpCo)_3-H]^+$), 370 (64, $[(CpCo)_3-2H]^+$), 365 (26), 247 (12, $[(CpCo)_2-H]^+$), 189 (100, $[Cp_2Co]^+$), 182 (28, L^+), 168 (11), 167 (77, $[L-CH_3]^+$), 165 (16), 124 (28, $[CpCo]^+$), 59 (18, Co^+); (L = 1,1-diphenylethane). Anal. Calc. (found): C, 62.83 (62.16); H, 5.27 (5.07).

5.3. Crystal structure determinations

Single crystals were grown from toluene/petroleum ether solutions at 5 to −20°C. Intensity data were collected on a Siemens Stoe AED2 four circle diffractometer at ambient temperature and corrected for Lorentz, polarisation and absorption effects (Table 5). The structures were solved by direct methods, and refined by full-matrix least-squares based on F^2 using all measured unique reflections. All non-H atoms were given anisotropic displacement parameters. The H atoms on the μ_3-phenyl rings and on C13 (complex **3d** only) were located in difference Fourier syntheses and refined with isotropic displacement parameters. All other H atoms

Table 5
Details of the crystal structure determinations of complexes **3c** and **3d**

	3c	**3d**
Formula	$C_{29}H_{29}Co_3$	$C_{29}H_{29}Co_3$
Mol. wt.	554.35	554.35
Crystal size (mm)	0.12 0.40 0.65	0.10 0.20 0.75
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	*Cc*
a (Å)	8.853(4)	17.358(5)
b (Å)	9.460(5)	14.766(4)
c (Å)	13.858(7)	9.296(3)
β (°)	90.56(3)	105.77(3)
V (Å^3)	1160.5(10)	2293.0(12)
Z	2	4
$D_{calc.}$ (g cm^{-3})	1.586	1.606
F(000)	568	1136
μ(Mo–K$_\alpha$) (mm^{-1})	2.13	2.16
X-radiation, λ (Å)	Mo–K$_\alpha$, graphite monochromated, 0.71069	
Data collection temperature (K)	ambient	
$2\theta_{max}$ (°)	62	60
hkl-range	−12/12, 0/13, 0/20	−24/23, 0/20, 0/13
Reflections measured	3902	3333
Unique	3902	3333
Observed [$I \geq 2\sigma(I)$]	2170	2053
Absorption correction	Empirical, ψ-scans	Empirical, ψ-scans
Parameters refined	345	334
GOF	0.945	0.927
R (obs. reflections only)	0.038	0.030
wR_2 (all reflections)[a]	0.090	0.069
A, *B*	0.038, 0	0.029, 0
P	[Max(F_o^2, 0)+$2F_c^2$]/3	[Max(F_o^2, 0)+$2F_c^2$]/3

[a] $w = 1/[\sigma^2(F_o^2)+(AP)^2+BP]$.

were inserted in calculated positions (see Section 6). The absolute structure could be determined for both crystals by means of the Flack *x*-parameter, which was close to zero (0.011(27) for **3c**, $-0.021(19)$ for **3d**). The calculations were performed using the programs SHELXS-86 and SHELXL-97 [21]. Graphical representations were drawn with ORTEP-II [22].

6. Supplementary material available

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100813. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: teched@chemcrys.cam.ac.uk).

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