

Organometallic cluster complexes with face-capping arene ligands, **10**. A study of the influence of substituents on the synthesis of organometallic cluster complexes of the type $[\{(C_5H_5)Co\}_3(\mu_3-\eta^2:\eta^2:\eta^2\text{-alkenylarene})]^1$

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Abstract

The cluster complexes $[\{(C_5H_5)Co\}_3(\mu^3-\eta^2:\eta^2:\eta^2\text{-arene})]$ **5a–c** (arene = methyl- β -methylstyrene), **6** (arene = 3,5-dimethyl- β -methylstyrene), **7** (arene = *o*-methylstilbene), **8b,c** (arene = fluoro- β -methylstyrene) and **9a** (arene = 2-phenylbut-2-ene) have been prepared from the alkenylbenzene or corresponding allylbenzene derivatives and $[(C_5H_5)Co(C_2H_4)_2]$ **1** or $[(C_5H_5)Co(C_6Me_6)]$ **2**. Yields were found to depend on the arene ligands; they were generally lower than those obtained with less highly substituted derivatives. With *o*-, *m*- and *p*-methylallylbenzene and **1** the corresponding μ_3 -arene cluster complexes $[\{(C_5H_5)Co\}_3(\mu_3-\eta^2:\eta^2:\eta^2\text{-arene})]$ **5a–c** (arene = *o*-, *m*- and *p*-methyl- β -methylstyrene, respectively) were formed in 5, 60 and 5% yield. In contrast, *o*-, *m*- and *p*-fluoroallylbenzene did not react with **1**. After treatment of these arenes with **2**, $[\{(C_5H_5)Co\}_3(\mu^3-\eta^2:\eta^2:\eta^2\text{-arene})]$ **8b** and **8c** (arene = *m*- and *p*-fluoro- β -methylstyrene) were obtained in 37 and 30% yield. The crystal and molecular structures of **8c** and **9a** have been established by single crystal X-ray diffraction. Variable temperature NMR studies showed **5b** and **8b** to be mixtures of two exchanging diastereomers. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Arene clusters; Cyclopentadienyl; Cobalt

1. Introduction

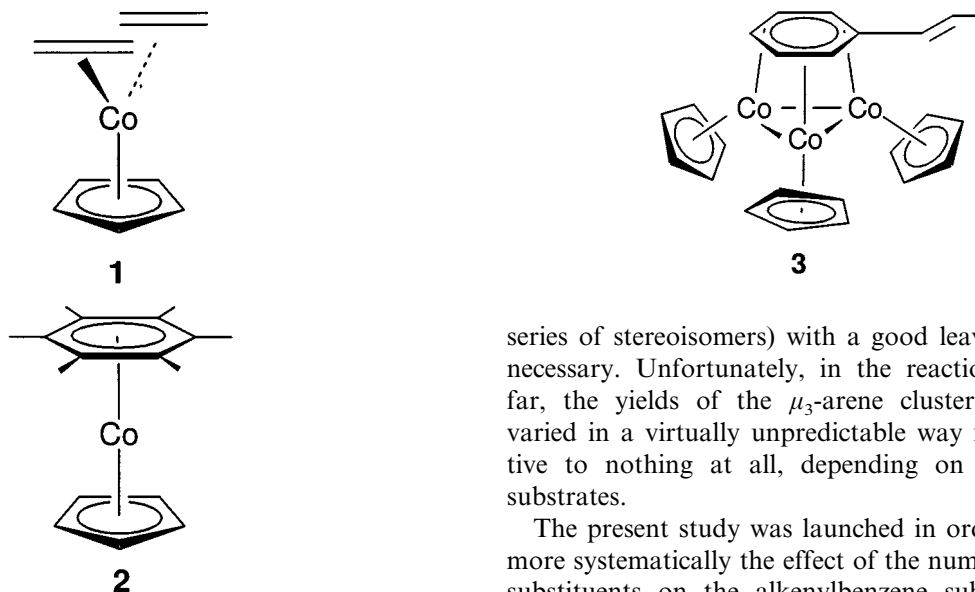
The face-capping (facial) bonding mode of benzene to a molecular metal cluster has been established only a little more than 10 years ago [2]. Since then, cluster complexes with facial arene ligands continue to receive considerable attention [3]. We reported on the synthesis of cluster complexes of the type $[\{(C_5H_5)Co\}_3(\mu_3-\eta^2:\eta^2:\eta^2\text{-arene})]$ from reactive sources of the $(C_5H_5)Co$ fragment, such as $[(C_5H_5)Co(C_2H_4)_2]$ **1** and $[(C_5H_5)Co(C_6Me_6)]$ **2**, and certain substituted benzene

derivatives with unsaturated side chains [4]. This general route employs ligand assisted cluster formation from mononuclear metal containing fragments ‘on site’ of an alkenylbenzene ligand [5].

Only cluster derivatives **A** with a carbon–carbon double bond in conjugation to the μ_3 -arene ring are accessible directly. This appears to be a fairly stringent limitation of our synthetic method. However, the alkenyl substituent in **A** may be hydrogenated without destruction of the cluster complex, thus opening a route to a wider range of derivatives **B** with fully or partially saturated substituents on the facial arene ligand ([1], [4]b). Furthermore, the synthesis of **A** does not depend on the availability of the 1-alkenylbenzene ligand. The latter substrates may be replaced by any suitable phenyl substituted alkene which, in the presence of the $(C_5H_5)Co$ reagents used to assemble the metal cluster, is

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¹ Dedicated to the memory of Dr Laszlo Zsolnai (deceased April 26, 1998).



converted into the corresponding 1-alkenylbenzene derivative. For example, treatment of allylbenzene with **1** gave the cluster complex $[\{(C_5H_5)Co\}_3(\mu_3\text{-}\beta\text{-methylstyrene})]$ **3** just as the analogous reaction with β -methylstyrene itself ([4]a). This rearrangement of the ligand (i.e. the shift of the double bond within the side chain into the position in conjugation to the phenyl) is catalytic and smoothly proceeds at a lower temperature than the assembly of the metal cluster. Consequently, the same yields of **3** were obtained with both β -methylstyrene and allylbenzene as the substrate ([4]b). Rearrangement of 4-phenylbut-1-ene, where the carbon-carbon double bond is separated from the phenyl by two methylene groups, followed by formation of $[\{(C_5H_5)Co\}_3(\mu_3\text{-}\beta\text{-ethylstyrene})]$ has also been demonstrated ([4]b).

We became interested in the synthesis of complexes of type **A** and/or **B** with a particular number and arrangement of substituents on the arene nucleus and on the side chain mainly for two reasons. First, our quantitative investigations of the intramolecular dynamics of these cluster complexes demanded a series of derivatives with particular molecular symmetry, ranging from asymmetric to quite symmetric [6]. Second, for a study of the regiochemistry of nucleophilic substitution on the facial arene ligands, ([4]e) derivatives (preferably

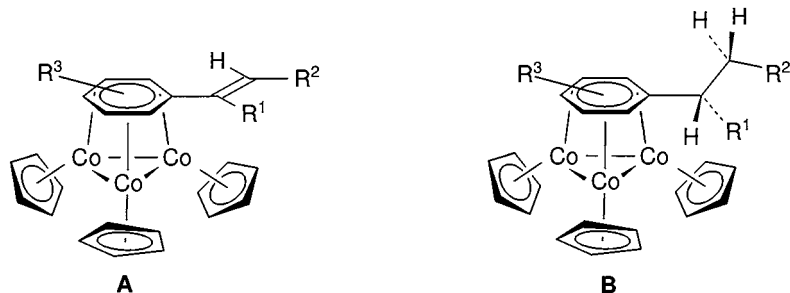
series of stereoisomers) with a good leaving group are necessary. Unfortunately, in the reactions studied so far, the yields of the μ_3 -arene cluster complexes **A** varied in a virtually unpredictable way from quantitative to nothing at all, depending on the particular substrates.

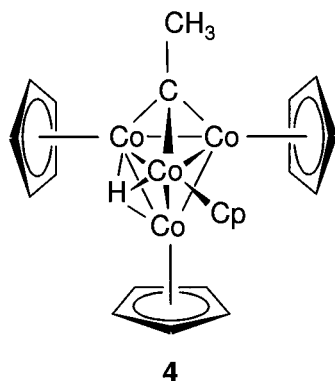
The present study was launched in order to evaluate more systematically the effect of the number and site of substituents on the alkenylbenzene substrate on the formation of the μ_3 -arene cluster complexes **A**, and to provide specific derivatives for kinetic and reactivity studies.

2. Results

2.1. General preparation

Reactions were carried out with either **1** or **2** as the source of $(C_5H_5)Co$ fragments. Usually an excess of the $(C_5H_5)Co$ reagent was used. Reactions with **1** were carried out in petroleum ether solution. Samples were taken periodically from the reaction mixtures and analysed by 1H -NMR spectroscopy. In order to suppress the formation of $[H\{(C_5H_5)Co\}_4(CCH_3)]$ **4** [7], the thermal decomposition product of **1** and the control of the temperature had to be meticulously maintained during the reactions with **1**. Reaction mixtures involving allylbenzene derivatives were first allowed to stand at ambient temperature until rearrangement to give the styrene derivatives was complete. The solutions were then stirred at 40–45°C for 3–4 h. If no formation of **4** was noted during this period, the reaction was brought to completion by heating to about 60°C. Otherwise, the temperature was immediately lowered by 5–10°C, and the reaction was allowed to proceed at that temperature





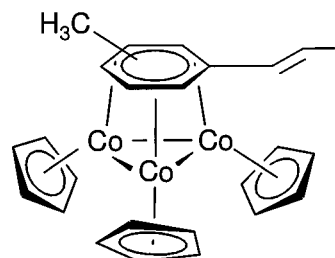
until all of **1** had been consumed. The μ_3 -arene cluster complexes, which are only moderately soluble in non-polar solvents, usually precipitated from the reaction mixtures. Complex **2** was used in thf solution; monitoring of the reaction by NMR spectroscopy was not feasible due to the paramagnetism of **2**. Removal of hexamethylbenzene proved to be a major obstacle during work-up of the crude products obtained with **2**. Typically, the bulk of this material was sublimed off the product mixture under vacuum, or removed by washing with cold hexane.

Final purification of the products—except the complexes containing fluoroarenes—was effected by column chromatography on deactivated alumina. This technique was indispensable when the arene clusters had to be separated from **4**, which is nearly always formed in variable amounts during the reactions with the ethylene complex **1**.

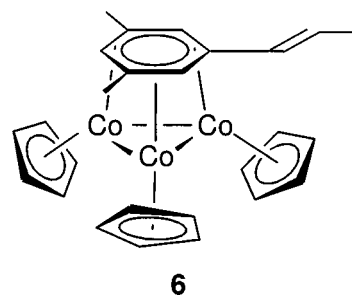
2.2. Ring substituted derivatives

2.2.1. Ring (methyl) substituted β -methylstyrene derivatives

Reactions were carried out with **1** and *o*-, *m*- and *p*-methyl-allylbenzene, respectively. Appreciable amounts of the expected μ_3 -arene cluster product, $[(C_5H_5)Co]_3\{\mu_3-(methyl-\beta-methylstyrene)\}$ **5**, were only formed with the *meta* isomer of the arene ligand. The product **5b** was isolated in 60% yield. With the *ortho* and *para* substituted ligands, only a little of the corresponding μ_3 -arene cluster complexes was formed. Separation from the main product **4** was only possible



5a (*ortho*), **5b** (*meta*), **5c** (*para*)



by means of repeated chromatography, which caused considerable product losses. Hence, only very small samples of pure **5a** and **5c** were finally isolated.

2.2.2. 3,5-Dimethyl- β -methylstyrene

This ligand was also generated in situ from the corresponding allyl derivative in the presence of **1**. The μ_3 -arene cluster complex **6** was formed in small amounts (yield ca. 5%), utilising **1** as the source of $(C_5H_5)Co$ fragments. Due to the formation of large amounts of **4**, complex **6** could not be obtained in pure form.

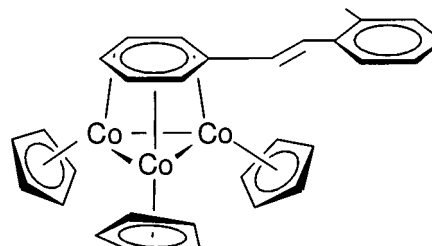
2.2.3. *o*-Methylstilbene

[1-(*o*-methylphenyl)-2-phenylethene]

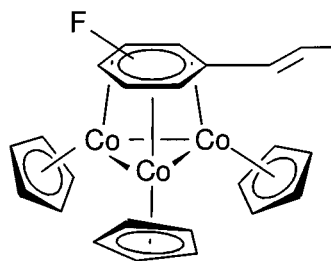
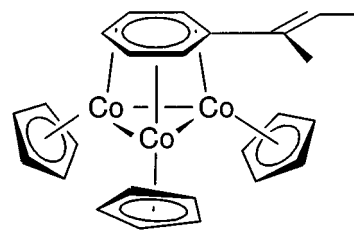
Reaction of this ligand with **1** gave a single trinuclear product, **7**, in 20–50% yield. In this complex, the tricobalt cluster is attached to the *monosubstituted* arene (phenyl) ring of the ligand. No traces were detected of the other possible coordination isomer, **7'**, with the *o*-tolyl ring system of the ligand in the facial coordination.

2.2.4. Ring (fluorine) substituted β -methylstyrene derivatives

In the reactions with fluoro-allylbenzene ligands great care had to be taken to exclude even minor bromo-fluorobenzene impurities. Contaminated ligands (< 99.9% pure) led to catalytic decomposition of the $(C_5H_5)Co$ reagents. Even with highly pure ligands, no arene cluster complexes were obtained from either of *o*-, *m*- and *p*-fluoro-allylbenzene and **1**. With the more reactive reagent **2** the products **8b** and **8c** with facial fluoro- β -methylstyrene ligands were formed in moderate yields (30 and 37%, respectively). No arene cluster was formed from *o*-fluoro-allylbenzene and **2**.



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**8b** (*meta*), **8c** (*para*)**9a**

2.2.5. 1-(*p*-Fluorophenyl)-1-phenylethene

This ligand did not give an arene cluster complex when treated with **2**.

2.3. Side-chain substituted complexes

2.3.1. 1,1-Diphenylpropene and 1,2-diphenylpropene

The preparation of the complex **10a** in 38% yield from 1,1-diphenylpropene and **2** was described previously ([4]b). In marked contrast, no μ_3 -arene cluster complex could be obtained from 1,2-diphenylpropene and **1** or **2**.

2.3.2. 2-Phenylbut-2-ene and 1-phenyl-iso-butene

When these ligands were treated with **2** under identical conditions, an arene cluster (**9a**) was only obtained with the *n*-butene derivative. Complex **9a** was isolated in 43% yield.

2.4. Spectroscopic investigations

The most characteristic feature of the ^1H - and ^{13}C -

NMR spectra of all the μ_3 -arene cluster derivatives described in this investigation is a singlet resonance for all the cyclopentadienyl protons and carbon atoms, respectively, regardless of the complexity of the facial arene ligand (Tables 1 and 2). At room temperature these resonances are broad in some cases but sharpen when the samples are heated to about 50°C. With respect to the free ligands the resonances of the cluster coordinated arene rings are shifted to high field [$\delta(^1\text{H}) = 4.0\dots 4.7$, $\delta(^{13}\text{C}) = 30\dots 56$, $\delta(^{19}\text{F}) = -148\dots -146$]. In most cases, the number of carbon resonances for these rings corresponds to the full symmetry of the free ligands (i.e. for monosubstituted arenes: 3 CH + 1 C; for 1,2-(*ortho*-) and 1,3-(*meta*-) disubstituted arenes: 4 CH + 2 C; for 1,4-(*para*-) disubstituted arenes: 2 CH + 2 C).

The proton spectra of **5b**, **7**, **8b** and **8c** were investigated in the temperature range 170–320 K. With all complexes, the singlet resonance due to the cyclopentadienyl rings broadens on cooling and finally splits into several sharp components. Complexes **7** and **8c** (Fig. 1) showed only three cyclopentadienyl resonances below

Table 1

^1H -NMR spectroscopic data (δ) for the complexes [$\{(\text{C}_5\text{H}_5)\text{Co}\}_3\{\mu_3\text{-R}(\text{C}_6\text{H}_4)\text{CH}=\text{CHCH}_3\}$] **5a–5c** (R = Me) and **8b,c** (R = F)

	R	C_5H_5	μ_3 -arene	R	H- α	H- β	CH_3
5a ^a	CH ₃ -2	4.83	4.36 (m), 4.73 (m)	1.98	6.41 (dq)	5.63 (dq)	1.71 (dd)
5b ^b	CH ₃ -3	4.69	4.20 (m), 4.46 (m)	1.77	5.85 (dq)	5.53 (dq)	1.63 (dd)
5c ^b	CH ₃ -4	4.82	4.36 (m), 4.49 (m)	1.84	5.86 (dq)	5.59 (dq)	1.66 (dd)
8b ^b	F-3	4.65	3.98 (m), 4.28 (m), 4.48 (m), 4.81 (m)		5.74 (dq)	5.47 (dq)	1.57 (dd)
8c ^c	F-4	4.67	4.23 (m), 4.51 (m)		5.74 (dq)	5.49 (dq)	1.59 (dd)

^a In CD_2Cl_2 .

^b In C_6D_6 .

^c In $[\text{D}_8]$ -toluene.

Table 2

^1H -NMR spectroscopic data (δ) for the complexes [$\{(\text{C}_5\text{H}_5)\text{Co}\}_3\{\mu_3\text{-C}_6\text{H}_5\text{C}(\text{R})=\text{CHR}'\}$] **9a** (R = R' = CH₃), **10a** ([4]b) (R = Ph, R' = CH₃) and **7** (R = H, R' = $\text{C}_6\text{H}_4\text{Me}-2$)

	R	R'	C_5H_5	μ_3 -arene	R	H- β	R'
9a ^{ab}	CH ₃	CH ₃	4.68	4.29 (m)	1.56	5.79 (q)	1.54 (d)
10a ^a	Ph	CH ₃	4.69	4.27 (m), 4.63 (m)	7.1–7.3	5.89 (q)	1.52 (d)
7	H	$\text{C}_6\text{H}_4\text{Me}-2$	4.68(br)	4.27 (m), 4.7 (m)	6.61 (d) ^c	6.79 (d) ^c	7.05 (m), 7.59(m) 2.23 (s, CH ₃)

^a In C_6D_6 .

^b Temperature, 320 K.

^c Assignment to H- α or H- β tentative.

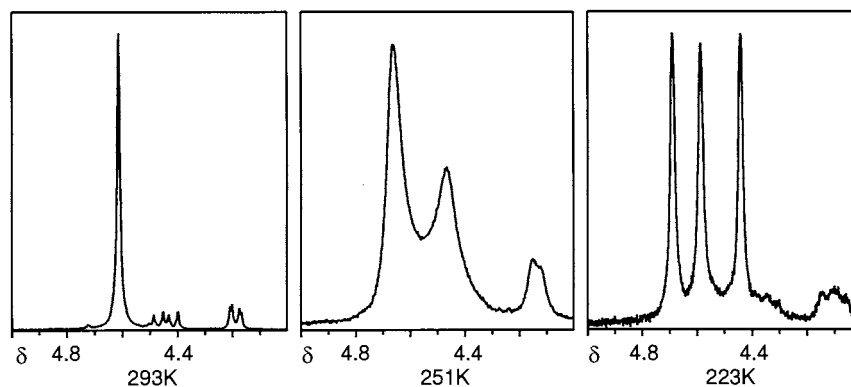


Fig. 1. Temperature dependent $^1\text{H-NMR}$ spectra of **8c**. Only the region of the C_5H_5 and arene ring proton resonances is shown.

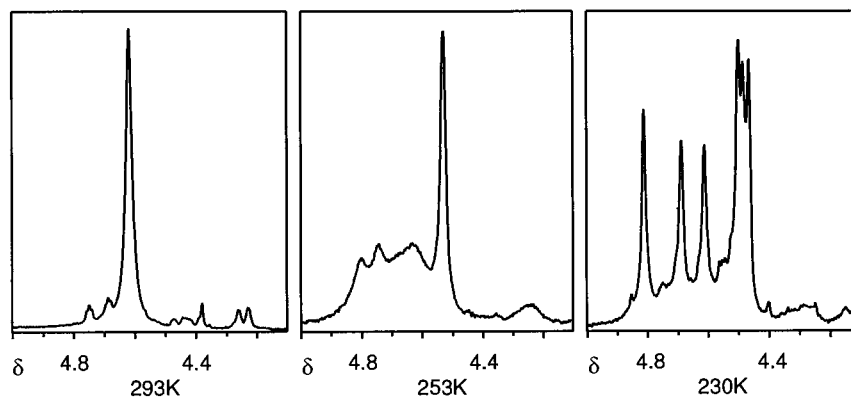


Fig. 2. Temperature dependent $^1\text{H-NMR}$ spectra of **8b**. Only the region of the C_5H_5 resonances and arene ring proton resonances is shown.

about 230 K. In contrast, for **5b** and **8b**, two sets of three cyclopentadienyl signals were observed at low temperature (Fig. 2). In the case of **5b**, a limiting low temperature spectrum could not be obtained; most of the other proton resonances of this complex were still broad even at 170 K.

2.5. Crystal structure analyses

Single crystal structure determinations were carried

out with complexes **8c** and **9a**. Important bond lengths and angles are given in Table 3. Views of the molecules are presented in Figs. 3 and 4. The molecules of both **8c** and **9a** are chiral. Complex **8c** crystallises as racemic mixture. The crystals of **9a** contain only one enantiomeric form (Fig. 4).

In both complexes the arene ligand attains the $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$ coordination mode to the $[(\text{C}_5\text{H}_5)\text{Co}]_3$ cluster, with a staggered arrangement of the C_6 and Co_3 rings. There is a noticeable alternation of endocyclic carbon–

Table 3

^{13}C - and ^{19}F -NMR spectroscopic data^a (δ , in C_6D_6 , 50 MHz) for the complexes $[(\text{C}_5\text{H}_5)\text{Co}]_3\{\mu_3\text{-R}(\text{C}_6\text{H}_4)\text{CH}=\text{CHCH}_3\}$ **5a,b** (R = Me) and **8b,c** (R = F)

	R	C_5H_5	$\mu_3\text{-arene}$		$\text{C-}\alpha$	$\text{C-}\beta$	R	CH_3
			CH	C_{ipso}				
5a	$\text{CH}_3\text{-}2$	83.1	37.9, 39.5, 39.8, 45.5	56.2, 58.2	136.2	118.8	25.5	18.7
5b	$\text{CH}_3\text{-}3$	83.0	37.7, 41.2, 45.7, 47.0	55.1, 55.9	139.4	116.0	28.0	18.3
8b^b	F-3	83.3 ^{c,d}	33 ^c , 34.8, 40.3	e, f	137.5	117.9	-145.8 ^g	18.1
8c	F-4	83.4	31.3, 37.6 ^c	54.8 ^f	139.5	116.7	-148.4 ^g	18.2

^a Assignment was supported by determination of signal multiplicities using the DEPT and J -modulated spin-echo techniques.

^b In CD_2Cl_2 , 126 MHz.

^c Broad resonance.

^d Sharp at 50 MHz.

^e Region around $\delta = 54$ obscured by solvent resonances.

^f Not detected.

^g $\delta(^{19}\text{F})$, 84.3 MHz.

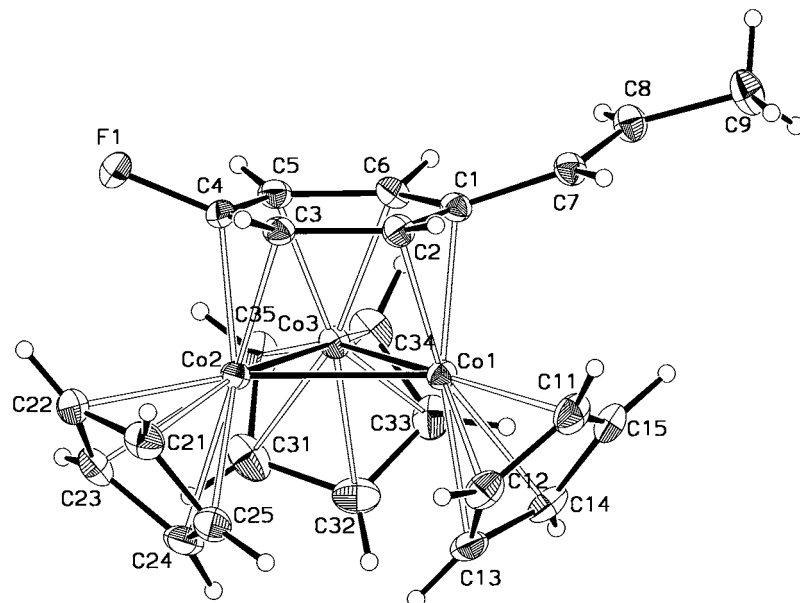


Fig. 3. Molecular structure of **8c**. Displacement ellipsoids are at the 30% level.

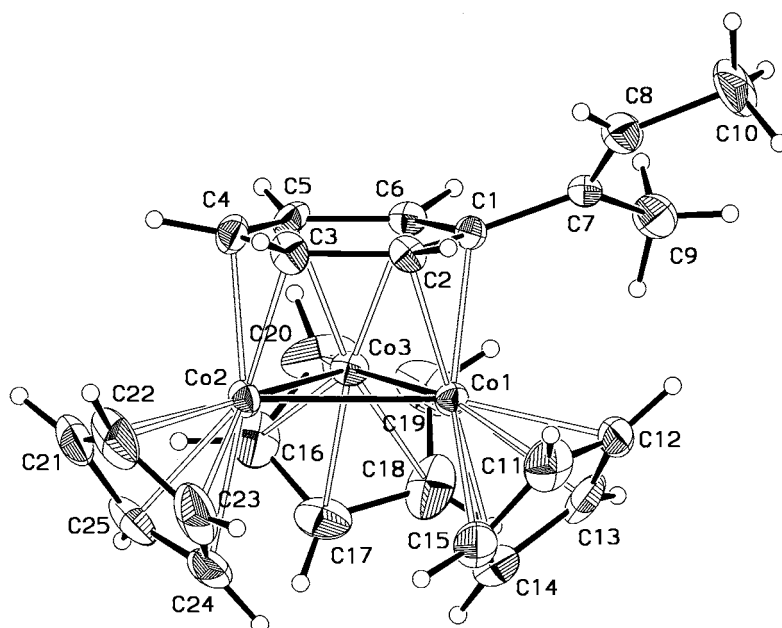
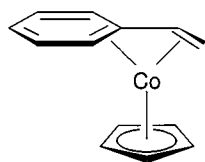


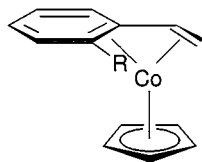
Fig. 4. Molecular structure of **9a**. Displacement ellipsoids are at the 30% level.

carbon bond lengths in the μ_3 -ligands, with the bonds 'on top' of the cobalt atoms being consistently shorter than the others. The differences $\Delta d(\text{CC})$ between adjacent endocyclic bonds range from a minimum of 0.003 Å to a maximum of 0.042 Å in **8c**, and from 0.004 to 0.06 Å in **9a**, respectively (Table 5). A slight distortion

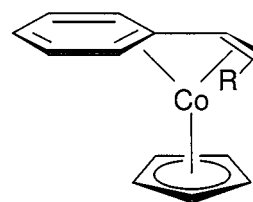
from planarity of the μ_3 -arenes is apparent with the *ipso* carbon atoms C1, which bear the alkenyl side chain. These atoms are displaced from the plane of the other ring atoms (largest deviation of C2 through C6 from



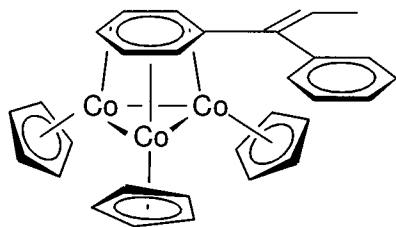
C



D



E



10a

this plane: 0.008 Å in **8c**, 0.01 Å in **9a**) by about 0.055 Å, away from the tricobalt cluster. The alkenyl side chains are planar, and are at an angle to the μ_3 -arene (16.8(1)° in **8c** and 39.6(2)° in **9a**).

All substituents on the μ_3 -arenes are displaced from the best plane through the C₆-ring, away from the Co₃-triangle. This distortion is most obvious with the α -carbon atoms of the side chains [0.466(5) Å (**8c**) and 0.52(1) Å (**9a**)] and the fluorine atom [0.562(4) Å], corresponding to bend angles of 21, 18 and 24°, respectively. It is also noticeable with the hydrogen atoms, which are less accurately localised (0.2–0.3 Å off the C₆-plane).

3. Discussion

On previous occasions we noted that the formation of the μ_3 -arene cluster complexes **A** from alkenylbenzenes and sources of (C₅H₅)Co fragments becomes more difficult when the number of substituents on the arene ring and/or side chain is increased ([4]b, [3]a). This general behaviour is observed again in the present study. For example, product yields with the ring substituted propenylbenzene derivatives *o*-, *m*- and *p*-methyl- β -methylstyrene and *o*-, *m*- and *p*-fluoro- β -methylstyrene range from nothing at all to a maximum of only about 60%, compared to more than 85% for β -methylstyrene itself. Likewise, a marked decrease of the product yield is observed for α,β -disubstituted ligands compared to either the α - or β -monosubstituted arene

[e.g. C₆H₅-C(R)=CHMe: about 40% **A** versus C₆H₅-C(R)=CH₂: more than 85% **A** (R = Me, Ph)].

In addition to the fluoro-vinylbenzenes (fluorostyrenes) described previously ([4]c) two more series of the three regioisomers of monosubstituted alkenylbenzene derivatives were investigated, namely *o*-, *m*-, *p*-methyl- β -methylstyrene and *o*-, *m*-, *p*-fluoro- β -methylstyrene. In contrast to our results with the fluorostyrenes and the methyl- β -methylstyrenes, products of type **A** containing a fluoro- β -methylstyrene derivative were only obtained with the (C₅H₅)Co reagent **2**, not with the somewhat less reactive **1**. Regardless of the (C₅H₅)Co reagent, yields of **A** were consistently lower with both types of fluoroarene derivatives than those obtained with the methyl substituted propenylbenzenes. No clear correlation of the product yield with the substitution pattern is apparent across the three series, except perhaps that the *ortho* disubstituted ligand is always worst. Despite numerous attempts, a product of type **A** with such a ligand has only been obtained in one case, the μ_3 -*o*-methyl- β -methylstyrene complex **5a**, which was formed in less than 5% yield.

In earlier work, we suggested a mechanism for the formation of the μ_3 -arene cluster complexes **A** from mononuclear (C₅H₅)Co reagents and 1-alkenylarenes [8]. As one of the first steps, formation of a mononuclear intermediate **C** with $\alpha,\beta,1,2-\eta$ coordinated alkenylarene ligand was postulated. Substitution of the arene in the *ortho* position would greatly destabilise **D**, one of the two possible isomers of monosubstituted **C** (the one which has the second substituent in the 2- rather than in the 6-position). In effect, this results in a statistical kinetic disadvantage (roughly by a factor of two) for the *ortho* derivative compared to the *meta* and *para* isomers.

A number of observations support the suggestion that formation of **A** is governed by kinetic factors ([4]d). The reaction has to compete with the decomposition of the (C₅H₅)Co reagents. This, together with the above reasoning, is in line with the absence (or near absence) of derivatives with *ortho* disubstituted arene ligands. It also satisfactorily explains the formation of

Table 4

¹³C-NMR spectroscopic data^a (δ , in C₆D₆) for the complexes [$\{(C_5H_5)Co\}_3\{\mu_3-C_6H_5(R)=CHCH_3\}$] **9a** (R=CH₃) and **10a** (R=Ph)

	R	C ₅ H ₅	μ_3 -arene		C- α	C- β	R	CH ₃
			CH	C _{ipso}				
9a	CH ₃	82.6	39.8 ^b , 40.9	63.2	140.9	113.3	16.0 ^c	13.7 ^c
10a	Ph	83.1	39.5, 41.1, 42.9	58.6	148.4	118.3	126.9 ^d , 127.9 ^d , 130.6 ^e	16.0

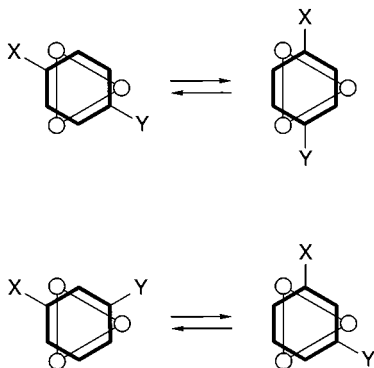
^a Assignment was supported by determination of signal multiplicities using the DEPT and *J*-modulated spin-echo techniques.

^b Broad resonance.

^c Assignment to either of the two methyl groups tentative.

^d Arene CH.

^e Arene C_{ipso}.



Scheme 1. The two 'staggered' conformers of $[\{(C_5H_5)Co\}_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_4XY)]$ (top, with a *para* disubstituted arene ligand; bottom, with a *meta* disubstituted arene ligand).

only one (complex **7**) of the two possible isomers of $[\{(C_5H_5)Co\}_3(\mu_3\text{-}ortho\text{-methylstilbene})]$, while with *para*-methoxystilbene as a ligand either of the two arene rings was found in the facial coordination mode (formation of $[\{(C_5H_5)Co\}_3(\mu_3\text{-}C_6H_5\text{-CH=CH-C}_6H_4\text{OMe-4})]$ and $[\{(C_5H_5)Co\}_3(\mu_3\text{-4-MeOC}_6H_4\text{-CH=CH-C}_6H_5)]$) ([4]b). An equivalent argument—destabilisation of **E**—explains the failure of the reaction with 1-phenylisobutene (*β,β*-dimethylstyrene) and, even more significantly, the observed complete selectivity with respect to the *E*-configuration of the alkenyl side chain. Even when starting from purely or largely *Z*-configured substrates, *E*-configuration is invariably found in the μ_3 -alkenylbenzene cluster complexes [4].

However, the much higher yield of the *meta* isomer **5b** of $[\{(C_5H_5)Co\}_3(\mu_3\text{-methyl-}\beta\text{-methylstyrene})]$ compared to that of the *ortho* and *para* derivatives cannot be explained by arguments centered on intermediates of type **C**. This is also obvious from our observations with the fluoro-*methylstyrenes*, where the μ_3 -arene cluster complexes with the *meta* (**8b**) and *para* substituted ligands (**8c**) are formed in roughly the same yield. We are also at a loss to explain the apparent differences between the three α,β -disubstituted styrene derivatives 4-phenylbut-1-ene, 1,1-diphenylpropene (both about 40% yield of **A**, complexes **9a** and **10a** ([4]b) and 1,2-diphenylpropene (no reaction). More remote groups elsewhere in the arene ligand (e.g. on a second phenyl group) also seem to play a role (compare stilbene and 1,1-diphenylethylene, more than 85% yield of **A**; ([4]b) *o*-methylstilbene, about 50%; and *p*-fluoro-1,1-diphenylethylene, no reaction).

The molecular structures of the complexes **8c** and **9a** show the features typical for the $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$ coordination mode of an arene to a molecular cluster [3,6]. These are characterised mainly by an expansion and slight Kekulé-type (threefold) distortion of the facial arene ligand, and by an out-of-plane bending of the substituents. The reasons for these distortions and their

Table 5

Selected bond lengths [Å] and angles [°] for the complexes $[\{(C_5H_5)Co\}_3(\mu_3\text{-}p\text{-fluoro-}\beta\text{-methylstyrene})]$ **8c** and $[\{(C_5H_5)Co\}_3(\mu_3\text{-}2\text{-phenylbut-2-ene})]$ **9a**

	8c	9a
Co(1)–Co(2)	2.5109(13)	2.5165(16)
Co(1)–Co(3)	2.4921(12)	2.4927(15)
Co(2)–Co(3)	2.4921(13)	2.4948(19)
Co(1)–C(1)	2.057(3)	2.054(7)
Co(1)–C(2)	2.024(3)	2.014(7)
Co(1)–C(11)...C(15)	2.094(3)...2.139(4)	2.081(7)...2.136(8)
Co(2)–C(3)	2.021(3)	2.026(7)
Co(2)–C(4)	1.990(3)	2.024(7)
Co(2)–C(21)...C(23)	2.093(4)...2.123(4)	2.066(8)...2.124(8)
Co(3)–C(5)	2.012(3)	2.019(7)
Co(3)–C(6)	2.018(3)	2.015(7)
Co(3)–C(31)...C(13)	2.084(4)...2.130(4)	2.073(8)...2.120(7)
C(1)–C(2)	1.420(5)	1.435(8)
C(1)–C(6)	1.458(4)	1.470(9)
C(1)–C(7)	1.477(4)	1.483(9)
C(2)–C(3)	1.454(4)	1.431(10)
C(3)–C(4)	1.412(5)	1.388(10)
C(4)–F(1)	1.396(4)	
C(4)–C(5)	1.434(5)	1.432(10)
C(5)–C(6)	1.431(5)	1.410(10)
C(7)–C(8)	1.319(5)	1.329(10)
C(7)–C(9)		1.517(10)
C(8)–C(9)	1.504(5)	
C(8)–C(10)		1.500(11)
C(2)–C(1)–C(6)	118.7(3)	116.4(6)
C(2)–C(1)–C(7)	118.6(3)	122.9(6)
C(6)–C(1)–C(7)	120.6(3)	117.9(5)
C(3)–C(2)–C(1)	121.1(3)	121.3(6)
C(4)–C(3)–C(2)	118.5(3)	121.1(6)
C(3)–C(4)–C(5)	122.2(3)	119.4(7)
C(3)–C(4)–F(1)	117.7(3)	
C(5)–C(4)–F(1)	114.8(3)	
C(6)–C(5)–C(4)	118.6(3)	120.7(7)
C(5)–C(6)–C(1)	120.7(3)	120.8(6)
C(8)–C(7)–C(1)	128.1(3)	121.1(7)
C(8)–C(7)–C(9)		122.3(7)
C(1)–C(7)–C(9)		116.6(6)
C(7)–C(8)–C(9)	124.0(3)	
C(7)–C(8)–C(10)		126.9(8)

consequences have been discussed in detail [6,9] and need not be reiterated here. Within the μ_3 -arene rings of the complexes **8c** and **9a**, not all of the adjacent carbon–carbon bonds differ significantly in length (the parameter $\Delta d(CC)$ ranges from less than once to nine (**8c**) and seven (**9a**) times, respectively, the standard deviation of the individual bond lengths). However, as has been shown in detail with other examples [1,6] a slight tendency of the $\mu_3\text{-}C_6$ rings to distort towards a geometry with threefold rather than sixfold symmetry is yet apparent. The substituents on the arene nucleus, even the electronically more active fluorine, do not seem to dominate the variations of the carbon–carbon bond lengths within the μ_3 ligand. This is in line with observations on a large number of free benzene deriva-

Table 6

Details of the crystal structure determinations of the complexes [$\{(C_5H_5)Co\}_3(\mu_3\text{-}p\text{-fluoro-}\beta\text{-methylstyrene})$] **8c** and [$\{(C_5H_5)Co\}_3(\mu_3\text{-}2\text{-phenylbut-2-ene})$] **9a**

	8c	9a
Formula	C ₂₄ H ₂₄ Co ₃ F	C ₂₅ H ₂₇ Co ₃
Crystal size (mm)	0.07 × 0.4 × 0.8	0.13 × 0.20 × 0.36
Crystal system	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	7.461(4)	7.479(3)
<i>b</i> (Å)	29.056(14)	9.674(5)
<i>c</i> (Å)	8.908(5)	27.770(18)
β (°)	95.24(3)	
<i>V</i> (Å ³)	1923(2)	2009(2)
<i>Z</i>	4	4
<i>M_r</i>	508.22	504.26
<i>D_{calc.}</i> (g cm ⁻³)	1.755	1.667
<i>F</i> (000)	1032	1032
μ (Mo–K α) (mm ⁻¹)	2.57	2.46
X-Radiation, λ (Å)	Mo–K α , graphite monochromated, 0.71069	Mo–K α , graphite monochromated, 0.71069
Data collected, temperature (K)]	203	Ambient
2 θ _{max} (°)	50	60
<i>h,k,l</i> -range	–8/8, 0/34, 0/10	0/10, 0/13, 0/39
Reflections measured		
Unique	3386	3345
Observed [<i>I</i> ≥ 2 σ (<i>I</i>)]	2911	2186
Absorption correction	Empirical, ψ -scans	Empirical, ψ -scans
Parameters refined	350	285
Goodness-of-fit	1.044	1.026
<i>R</i> (observation reflections only)	0.031	0.060
<i>wR</i> ₂ (all reflections)	0.083	0.096
(<i>w</i> = 1/[$\sigma^2(F_o^2) + (A \times P)^2 + B \times P$])		
A, B	0.0498, 0.81	0.0309, 0.44
P		[max(<i>F</i> _o ² , 0) + 2 × <i>F</i> _c ²]/3

tives [10]. In contrast, in the two forms of a Ru₆ cluster complex with phthalic acid dimethyl ester as the facially coordinated arene, the absence of an apparent threefold distortion was attributed to a combination of symmetry and electronic effects, caused by the *para* disubstitution of the arene [11].

In free monosubstituted benzene derivatives, the internal ring angles have been found to be more sensitive of the type of substituent than the carbon–carbon bond lengths [10]. In particular, a correlation with the σ -inductive effect of the substituent was noted [12]. In polysubstituted derivatives, the angular distortions may be interpreted as arising from the superposition of separate, independent contributions from each substituent [13]. Our structures show that this pattern is quite closely retained upon facial coordination of the arene to the tricobalt cluster. Additivity of the effects is nicely demonstrated by the geometry of the *p*-fluoro- β -methylstyrene ligand in **8c**, where the observed internal bond angles (119° at C1, 121° at C2, 119° at C3 and 122° at C4) closely match those computed using published increments [13] for each substituent. A similar pattern is also observed in the facial C₆ ring of [$\{(C_5H_5)Co\}_3(\mu_3\text{-}p\text{-fluoro-}\alpha\text{-methylstyrene})$], an isomer of **8c** ([4]e).

In the last mentioned complex, the sterically demanding *iso*-propenyl side-chain results in a large twist angle (35°) of the olefinic plane relative to the arene ring. An even larger twist (40°) is observed for the 2-buten-2-yl substituent in **9a**. As expected, the plane of the *n*-propenyl substituent is at a much smaller angle to the μ_3 -arene plane (17° both in **8c** and in [$\{(C_5H_5)Co\}_3(\mu_3\text{-}\beta\text{-methylstyrene})$] **3** ([4]a)).

The NMR spectra of the new [$\{(C_5H_5)Co\}_3(\mu_3\text{-arene})$] cluster complexes compare well with those of other derivatives. The presence of only one singlet for all the protons (and carbons, respectively) of the three cyclopentadienyl cobalt groups in the ¹H- and ¹³C-NMR spectra at and above room temperature can be explained by a rapid rotation of the μ_3 -arene in the plane parallel to the tricobalt triangle [6]. This dynamic process is found in all μ_3 -arene cluster derivatives [3]. At low temperature, it becomes slow on the NMR timescale and leads to a splitting of the cyclopentadienyl resonances.

The observed differences between the ¹H-NMR spectra of **5b** and **8c** at low temperature are consistent with the arene rotation mechanism. For **8c**, with C_{2v} symmetry of the free *para* disubstituted ligand (assuming free

rotation of the side-chain around $C_{ipso}-C-\alpha$, the elementary step of the dynamic process [6], a 60° rotation of the arene, results in the mutual conversion of a pair of enantiomers (Scheme 1). The three $(C_5H_5)Co$ groups in either enantiomer become equivalent only when arene rotation is fast on the NMR timescale. Three resonances are observed for these groups in the slow exchange regime, corresponding to a fixed staggered orientation of the C_6 and Co_3 rings, as found in the solid state. In an achiral medium identical spectra are obtained from both enantiomers.

The symmetry of a *meta* disubstituted ligand C_6H_4XY is lower (C_s). Therefore, the complexes **5b** and **8b** exist as sets of two chiral diastereomers, which are related by a 60° turn of the arene (Scheme 1). Under slow exchange conditions, two sets of three cyclopentadienyl resonances are expected, one for each of the two different staggered configurations. In contrast to the complex $[(C_5H_5)Co]_3(\mu_3-1,1\text{-diphenylethane})$, where a similar stereochemical situation is due to the asymmetric $C-\alpha$ atom [1], both diastereomers of **5b** and **8b** are present in solution even at 170 K. For both complexes, the observed intensity ratios of the two sets of cyclopentadienyl resonances indicate a slight excess of one diastereomer, consistent with an only small free energy difference (compare Fig. 2).

4. Experimental Section

4.1. 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% of deoxygenated water and stored under nitrogen. The Jonas reagent **1** and complex **2** were synthesised as described in the literature [14]. *o*-Methylstilbene (mixture of *E/Z* isomers) was prepared from *o*-methylbenzyl magnesium chloride and benzaldehyde [15]. The product was obtained as an unseparable mixture with 20% of the Wurtz coupling product 1,2-bis(*o*-methylphenyl)ethane. Literature procedures were employed for the syntheses of fluoroarenes; [15–17] during some of the procedures involving Grignard compounds these intermediates had to be isolated in order to obtain products free of bromobenzene derivatives. NMR spectra were obtained on Bruker AC 200 (200.1 MHz for 1H , 50.3 MHz for ^{13}C) and JEOL FX90Q (84.25 MHz for ^{19}F) instruments. 1H and ^{13}C chemical shifts are reported versus $SiMe_4$ and were determined by reference to internal $SiMe_4$ or residual solvent peaks. To assign the carbon resonances, their multiplicities were deter-

mined using the DEPT or *J*-modulated spin-echo techniques. The ^{19}F chemical shifts are referenced to external $CFCl_3$. 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 by Mikroanalytisches Labor Beller, Gottingen.

4.2. $[(C_5H_5)Co]_3(\mu_3-\beta\text{-methylstyrene})$ derivatives from allylbenzenes and **1**

4.2.1. General procedure

The allylbenzene derivative is slowly added to a petroleum ether solution (ca. 100–150 ml) of **1** at room temperature. The mixture is slowly heated to 40–45°C and stirred at this temperature for several hours. At regular intervals, samples are taken and analysed by 1H -NMR spectroscopy. If complex **4** is still absent after 3–4 h, the mixture is heated to 60°C for about 1 h. Otherwise, the temperature is immediately reduced by 5–10°C, and the reaction allowed to proceed at this temperature (ca. 3–4 h). Completion of the reaction is indicated by complete consumption of **1**. The crude product is purified by chromatography on a 30×2.5 cm column of deactivated (5% H_2O) alumina, and recrystallised.

4.3. $[(C_5H_5)Co]_3\{\mu_3-(o\text{-methyl})-\beta\text{-methylstyrene}\}$ (**5a**)

A 1.80 g (10.0 mmol) sample of **1** was reacted with 0.48 g of *o*-allyltoluene. After chromatography with petroleum ether/toluene (1:1) the crude product was found to still contain about 30% of **4**. Recrystallisation from toluene at $-20^\circ C$ gave 100 mg of a brown solid, which was about 80% pure. Repeated crystallisation gave 80 mg pure **5a** (5%).

4.4. $[(C_5H_5)Co]_3\{\mu_3-(m\text{-methyl})-\beta\text{-methylstyrene}\}$ (**5b**)

From 1.34 g (7.44 mmol) of **1** and 0.36 g (2.73 mmol) of *m*-allyltoluene 0.72 g (58%) of **5b** was obtained as dark brown crystals after chromatography (petroleum ether/toluene, 1:1) and recrystallisation (toluene). M.p. $187^\circ C$, 1H -NMR ($[D_8]$ -toluene, 170 K) 1.71 (br, 6H, CH_3); 4.1–4.4 (m, br, 8H, arene-H); 4.46, 4.50, 4.51, 4.54, 4.58, 4.62 (each s, 5H, C_5H_5); 5.50 (br, 2H, $H-\beta$); 5.72 (“d”, br, 2H, $H-\alpha$). MS (EI) *m/z* (relative intensity) 504 (13, M^+), 370 (37, $[(C_5H_5)Co]_3-2H]^+$), 190 (10, $[(C_5H_5)(C_5H_6)Co]^+$), 132 (22, L^+), 124 (26, $[(C_5H_5)Co]^+$), 117 (27, $[L-CH_3]^+$), 105 (13, $[C_8H_9]^+$), 59 (17, Co^+); (L = propenyltoluene). Anal. Calc. (found): C, 59.54 (59.17); H, 5.40 (5.53).

4.5. $[(C_5H_5)Co]_3\{\mu_3-p\text{-methyl})-\beta\text{-methylstyrene}\}$ (**5c**)

A 0.65 g (3.61 mmol) sample of **1** and 0.18 g (1.32

mmol) of *p*-allyltoluene gave a black tar-like residue after chromatography (toluene) and removal of the solvent. The oily impurity (*p*-methyl- β -methylstyrene) was removed from the product by repeated washing with petroleum ether at -20°C to give **5c** (30 mg, 5%) as a dark brown solid.

4.6. $[\{(C_5H_5)Co\}_3\{\mu_3-(3,5\text{-dimethyl})-\beta\text{-methylstyrene}\}]$ (**6**)

A mixture of 1.33 g (7.39 mmol) **1** and 0.40 g (2.74 mmol) 5-allyl-*m*-xylene in 120 ml of petroleum ether was stirred at room temperature for 4 days and then at $30\text{--}35^{\circ}\text{C}$ for 20 h. Removal of solvent under vacuum gave an oily black residue which was redissolved in toluene and chromatographed. With petroleum ether, a reddish fraction was eluted first. A brownish band was then washed from the column with petroleum ether/toluene. This fraction consisted of mainly **4** with some (about 10%) **6**. By repeated chromatography, **6** could be enriched but not completely separated from **4**.

4.7. $[\{(C_5H_5)Co\}_3\{\mu_3-\{1-(o\text{-methylphenyl})-2\text{-phenyl-ethene}\}\}]$ (**7**)

A 1.08 g (6.0 mmol) sample of **1** was reacted with 1.46 g of a mixture of *o*-methylstilbene and 1,2-bis(*o*-methylphenyl)ethane (about 6.0 mmol of (*E*)/(*Z*)-*o*-methylstilbene). A first crop of product (530 mg) was crystallised from the reaction mixture at -78°C . Chromatography of the mother liquor (*n*-hexane/toluene, 2:1) gave a 50 mg yield of crude **7**. Both product fractions were combined and chromatographed again (toluene) to give 180 mg (16%) of pure **7** after removal of solvent. M.p. dec. 180°C , MS (EI) m/z (relative intensity) 566 (58, M^+), 377 (35), 370 (80, $[\{(C_5H_5)Co\}_3-2H]^+$), 355 (10), 293 (11), 247 (12, $[\{(C_5H_5)Co\}_2-H]^+$), 194 (39), 189 (100, $[(C_5H_5)_2Co]^+$), 179 (46), 178 (31), 149 (15), 124 (18, $[(C_5H_5)Co]^+$). Anal. Calc. (found): C, 63.62 (61.49); H, 5.12 (4.72).

4.8. $[\{(C_5H_5)Co\}_3\{\mu_3-(m\text{-fluoro})-\beta\text{-methylstyrene}\}]$ (**8b**)

A 320 mg (2.3 mmol) sample of *m*-fluoro-allylbenzene was slowly added to a thf solution of **2** (980 mg, 3.4 mmol) at room temperature. After 3 h, the dark red solution became brown. The mixture was stirred for 24 h. All volatiles were then removed under reduced pressure. The residue was washed with petroleum ether and then redissolved in toluene. The product **8b** crystallised from the dark solution as brown microcrystals (200 mg, 37%). $^1\text{H-NMR}$ ($[\text{D}_8]$ -toluene, 225 K) 1.71 ("d", 6H, CH_3); 3.55–4.4 (m, br, 8H, arene-H); 4.44, 4.47, 4.48, 4.59, 4.67, 4.79 (each s, 5H, C_5H_5); 5.42 (m, 2H, H- β); 5.7 (m, 2H, H- α); MS (EI) m/z (relative intensity) 508 (3, M^+), 370 (5, $[\{(C_5H_5)Co\}_3-2H]^+$), 247 (6,

$[\{(C_5H_5)Co\}_2-H]^+$), 189 (100, $[(C_5H_5)_2Co]^+$), 124 (35, $[(C_5H_5)Co]^+$).

4.9. $[\{(C_5H_5)Co\}_3\{\mu_3-p\text{-fluoro})-\beta\text{-methylstyrene}\}]$ (**8c**)

A 1.10 g (4.0 mmol) sample **2** was treated with 360 mg (2.6 mmol) of *p*-fluoro-allylbenzene as described above. After stirring over night the solvent was removed under reduced pressure and the residue triturated with *n*-hexane. The insoluble residue was collected on a glass frit, washed several times with cold *n*-hexane and recrystallised from toluene at -20°C . Yield 190 mg (30%) **8c** as black microcrystals. $^1\text{H-NMR}$ ($[\text{D}_8]$ -toluene, 223 K) 1.63 (dd, 3H, CH_3); 4.06 (m, br, 2H, arene-H); 4.32 (m, 2H, arene-H); 4.40, 4.55, 4.65 (each s, 5H, C_5H_5); 5.38 (m, 1H, H- β); 5.63 (m, br, 1H, H- α); MS (EI) m/z (relative intensity) 508 (11, M^+), 371 (10, $[\{(C_5H_5)Co\}_3-H]^+$), 370 (50, $[\{(C_5H_5)Co\}_3-2H]^+$), 247 (13, $[\{(C_5H_5)Co\}_2-H]^+$), 189 (100, $[(C_5H_5)_2Co]^+$), 124 (29, $[(C_5H_5)Co]^+$).

4.10. $[\{(C_5H_5)Co\}_3(\mu_3-2\text{-phenylbut-2-ene})]$ (**9a**)

A 800 mg (2.8 mmol) sample of **2** was treated with 200 μl (180 mg, 1.36 mmol) of 2-phenylbut-2-ene as described above (reaction time 4 h). The solvent was then removed under reduced pressure and the residue extracted with toluene (10 ml). The mixture was filtered through a fine glass frit. Solvent was removed from the filtrate under vacuum. Most of the hexamethylbenzene was then removed from the residue by sublimation at $55\text{--}65^{\circ}\text{C}/0.01\text{--}0.001$ mbar. The product was redissolved in the minimum amount of toluene and chromatographed on deactivated alumina (2.5×10 cm column; toluene/petroleum ether, 1:1). The product was recrystallised from toluene/petroleum ether at -20°C . Yield 200 mg (43%) **9a** as black shiny crystals—MS (EI) m/z (relative intensity) 504 (25, M^+), 372 (13, $[\{(C_5H_5)Co\}_3]^+$), 371 (17, $[\{(C_5H_5)Co\}_3-H]^+$), 370 (100, $[\{(C_5H_5)Co\}_3-2H]^+$) 311 (17), 310 (13), 247 (16, $[\{(C_5H_5)Co\}_2-H]^+$), 189 (34, $[(C_5H_5)_2Co]^+$), 124 (8, $[(C_5H_5)Co]^+$), 59 (4, Co^+).

4.11. Crystal structure determinations

Single crystals of **8c** were grown by slow evaporation of solvent from a benzene solution. Complex **9a** crystallised from a toluene/petroleum ether solution at 5°C . Intensity data were collected on Siemens Stoe AED2 (**8c**) and Nicolet R3 (**9a**) four circle diffractometers and corrected for Lorentz, polarisation and absorption effects (Table 6). 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-hydrogen atoms were given anisotropic displacement

parameters. All hydrogen atoms of complex **8c** and those of the 2-phenylbut-2-ene ligand (except the methyl groups) of complex **9a** were located in difference Fourier syntheses and refined with isotropic displacement parameters. All other hydrogen atoms were inserted in calculated positions [18]. The absolute structure of **9a** was determined by means of the Flack *x*-parameter [19], which, when the crystal was treated as a racemic twin, refined to 0.00(5). The calculations were performed using the programs SHELXS-86 and SHELXL-97 [20]. Graphical representations were drawn with ORTEP-II [21] (Table 4).

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