

NEW η -ALLYL η -CYCLOPENTADIENYLCOBALT CATIONS

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Summary

$[\text{Co}(\eta\text{-C}_3\text{H}_4)(\eta\text{-C}_5\text{H}_5)\text{I}]$ is a good precursor for the preparation of some new cationic complexes as the iodide can easily be replaced; thus addition of PEt_3 to the iodo-complex ($\text{R} = \text{H}$) gives $[\text{Co}(\eta\text{-C}_3\text{H}_5)(\eta\text{-C}_5\text{H}_5)(\text{PEt}_3)]^+$. The reactions of $[\text{Co}(\text{R-}\eta\text{-C}_3\text{H}_4)(\eta\text{-C}_5\text{H}_5)\text{I}]$ ($\text{R} = \text{H}$ or 2-Me) with AgBF_4 give solutions containing the coordinatively unsaturated species $[\text{Co}(\text{R-}\eta\text{-C}_3\text{H}_4)(\eta\text{-C}_5\text{H}_5)]^+$. The presence of traces of water leads to the formation of $[\text{Co}(\text{R-}\eta\text{-C}_3\text{H}_4)(\eta\text{-C}_5\text{H}_5)(\text{H}_2\text{O})]^+$. The addition of monodentate ligands $\text{L} = \text{PEt}_3$, PPh_3 , AsPh_3 , SbPh_3 , CNCH_3 and bidentate ligands $\text{L-L} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (dppe) and $o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2$ (diars), gives, respectively mononuclear $[\text{Co}(2\text{-Me-}\eta\text{-C}_3\text{H}_4)(\eta\text{-C}_5\text{H}_5)\text{L}]^+$ and binuclear ligand-bridged $[(2\text{-Me-}\eta\text{-C}_3\text{H}_4)(\eta\text{-C}_5\text{H}_5)\text{Co-L-L-Co}(2\text{-Me-}\eta\text{-C}_3\text{H}_4)(\eta\text{-C}_5\text{H}_5)]^{2+}$ complexes. Crystals of $[\text{Co}(2\text{-Me-}\eta\text{-C}_3\text{H}_4)(\eta\text{-C}_5\text{H}_5)(\text{H}_2\text{O})]^+[\text{BF}_4]^-$ are monoclinic, space group $P2_1/c$, with a 7.858(3), b 10.262(4), c 15.078(4) Å, β 98.36(1)°. The molecular structure contains the cobalt atom bonded to planar 2-Me-allyl and cyclopentadienyl substituents, which are almost parallel with the H_2O molecule in a staggered conformation with respect to the 2-Me group.

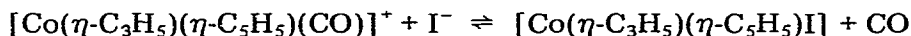
Introduction

Studies of nucleophilic additions to organotransition metal cations have led to an increasing interest in the preparation of these complexes. The oxidation of η -cyclopentadienylcobalt(I) complexes with R-allyl halides [1] and the substitution of iodide in the neutral complexes [2] have provided the usual methods for isolation of such cations. We describe below an additional effective method based on the formation of a coordinatively unsaturated complex by removal of iodide with a silver salt.

Results and discussion

Preparative results

Addition of PEt_3 to a solution of $[\text{Co}(\eta\text{-C}_3\text{H}_5)(\eta\text{-C}_5\text{H}_5)\text{I}]$ gave the cationic species, which was isolated as the salt $[\text{Co}(\eta\text{-C}_3\text{H}_5)(\eta\text{-C}_5\text{H}_5)(\text{PEt}_3)]^+ [\text{BPh}_4]^-$ (I). The main disadvantage of this method was that $[\text{Co}(\eta\text{-C}_3\text{H}_5)(\eta\text{-C}_5\text{H}_5)\text{I}]$ can be isolated only in a very low yield (10%) by the previously described route [1] involving direct oxidation of $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]$ with allyl iodide, the main product being the salt $[\text{Co}(\eta\text{-C}_3\text{H}_5)(\eta\text{-C}_5\text{H}_5)(\text{CO})]^+ \text{I}^-$ (30%). The yield can be increased by adding an excess of NaI which displaces the following equilibrium to the right.



Nevertheless the yield is always too low.

We decided to carry out our study with the 2-Me- $\eta\text{-C}_3\text{H}_4$ complex because the formation of neutral iodide is favoured in this case and may be obtained in a high yield (70%) by the method previously described [2].

The reaction of $[\text{Co}(2\text{-Me-}\eta\text{-C}_3\text{H}_4)(\eta\text{-C}_5\text{H}_5)\text{I}]$ with $\text{Mg}(\text{C}_6\text{F}_5)\text{Br}$ in diethyl ether gives $[\text{Co}(2\text{-Me-}\eta\text{-C}_3\text{H}_4)(\eta\text{-C}_5\text{H}_5)(\text{C}_6\text{F}_5)]$, as orange-red crystals.

When $[\text{Co}(2\text{-Me-}\eta\text{-C}_3\text{H}_4)(\eta\text{-C}_5\text{H}_5)\text{I}]$ is treated with AgBF_4 in CH_2Cl_2 and AgI removed by filtration, black crystals of the aquo complex (III) are obtained upon evaporating the solution. The coordinatively unsaturated complex $[\text{Co}(2\text{-Me-}\eta\text{-C}_3\text{H}_4)(\eta\text{-C}_5\text{H}_5)]^+ [\text{BF}_4]^-$ might be formed in the absence of water, but traces of water present under the experimental conditions used gave rise to the aquo complex III.

The analytical composition given in Table 1 for complex III agrees with its formulation. The presence of water is proved by the infrared spectrum, which shows absorption bands at 3400 and 1640 cm^{-1} . The ^1H NMR spectrum in chloroform-*d* shows single resonances for H(syn) (τ 4.36), $\eta\text{-C}_5\text{H}_5$ (τ 4.78) and CH_3 (τ 8.22) as well as two other single resonances at τ 8.17 and 7.57 which may be due to either H_2O or H(a). In order to assign these two resonances unambiguously we prepared the complex $[\text{Co}(\eta\text{-C}_3\text{H}_5)(\eta\text{-C}_5\text{H}_5)(\text{H}_2\text{O})]^+ [\text{BF}_4]^-$ (IV) by a similar reaction. This complex shows a ^1H NMR spectrum containing a single resonance for $\eta\text{-C}_5\text{H}_5$ (τ 4.71) and a doublet for H(syn) (τ 4.15) with coupling constant $J(\text{H}(\text{syn})\text{—H(c)})$ 9.3 Hz, as well as two additional doublets at τ 7.57 (J 7.87 Hz) and τ 7.80 (J 12.6 Hz). Comparison of the two spectra suggests assignment of the resonance at τ 7.57 to H_2O in both and the other peak to H(a). A definitive structural identification was made by X-ray diffraction as described below.

The coordinatively unsaturated or, more probably, the aquocomplex present in solution reacts readily with various ligands to give orange to red solutions of the cationic complexes V–XI, as confirmed by the analytical data in Table 1. Complexes V–IX contain mononuclear cations $[\text{Co}(2\text{-Me-}\eta\text{-C}_3\text{H}_4)(\eta\text{-C}_5\text{H}_5)\text{L}]^+$ with $\text{L} = \text{PEt}_3$, PPh_3 , AsPh_3 , SbPh_3 and CH_3CN , whereas complexes X–XI contain dinuclear cations $[(2\text{-Me-}\eta\text{-C}_3\text{H}_4)(\eta\text{-C}_5\text{H}_5)\text{Co—L—L—Co}(2\text{-Me-}\eta\text{-C}_3\text{H}_4)(\eta\text{-C}_5\text{H}_5)]^{2+}$ in which the ligand acts as a bridge between the two metal atoms. In accord with this formulation, complexes X–XI behave as 2/1 electrolytes in acetone, showing conductivities of 153.2 $\text{ohm}^{-1} \text{mol}^{-1} \text{cm}^2$.

SCHEME 1

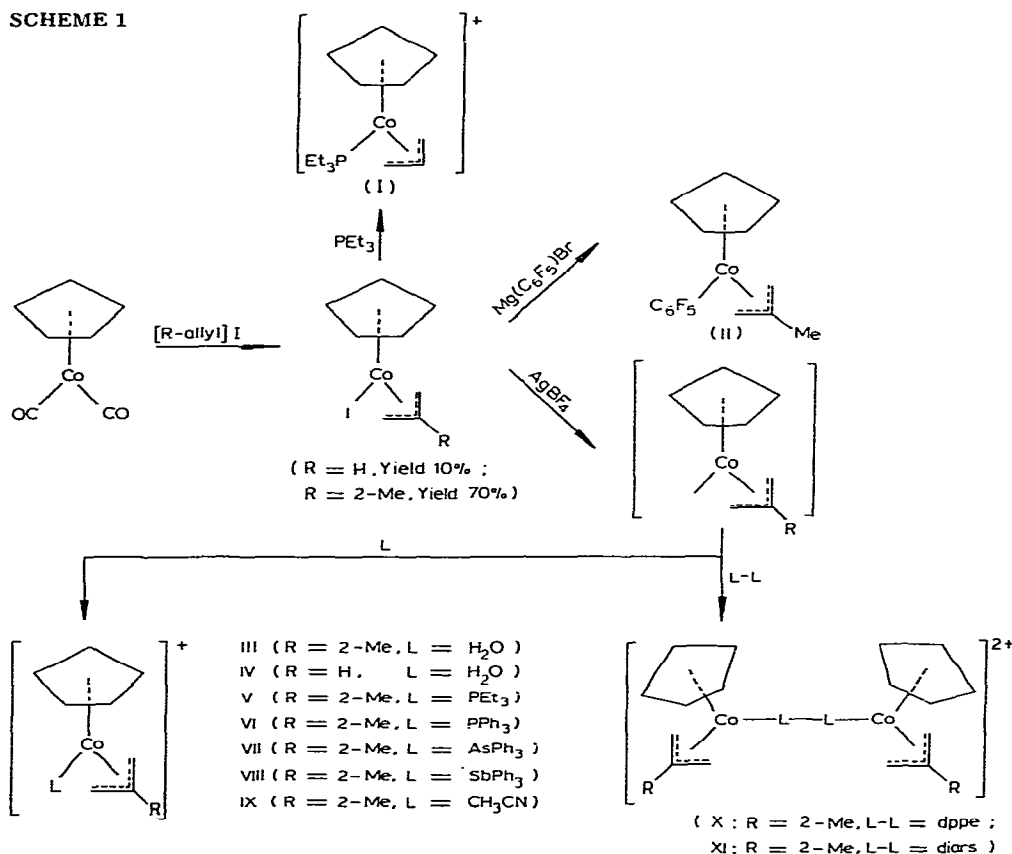


TABLE 1

ANALYTICAL DATA FOR η -ALLYL η -CYCLOPENTADIENYLCOBALT COMPLEXES

Complex	Colour	Analysis (Found (calc.) (%))		
		C	H	N
$[\text{Co}(\text{Al})(\text{Cp})(\text{PET}_3)] [\text{BPh}_4]^a$ (I)	orange	76.08 (75.74)	7.48 (7.47)	
$[\text{Co}(\text{R-Al})(\text{Cp})(\text{C}_6\text{F}_5)]$ (II)	orange-red	52.43 (52.02)	3.83 (3.47)	
$[\text{Co}(\text{R-Al})(\text{Cp})(\text{H}_2\text{O})] [\text{BF}_4]$ (III)	black	38.04 (38.07)	5.07 (4.93)	
$[\text{Co}(\text{Al})(\text{Cp})(\text{H}_2\text{O})] [\text{BF}_4]$ (IV)	black	35.60 (35.69)	4.46 (4.46)	
$[\text{Co}(\text{R-Al})(\text{Cp})(\text{PET}_3)] [\text{PF}_6]$ (V)	orange	40.49 (40.73)	6.71 (6.11)	
$[\text{Co}(\text{R-Al})(\text{Cp})(\text{PPh}_3)] [\text{BF}_4]$ (VI)	orange	61.35 (61.34)	5.67 (5.11)	
$[\text{Co}(\text{R-Al})(\text{Cp})(\text{AsPh}_3)] [\text{BF}_4]$ 1/2S (VII)	red	53.76 (53.30)	4.75 (4.52)	
$[\text{Co}(\text{R-Al})(\text{Cp})(\text{SbPh}_3)] [\text{BF}_4]$ 1/2S (VIII)	orange-red	49.94 (49.93)	4.74 (4.24)	
$[\text{Co}(\text{R-Al})(\text{Cp})(\text{CH}_3\text{CN})] [\text{BF}_4]$ (IX)	red	43.31 (43.02)	5.10 (4.88)	3.80 (4.56)
$\{[\text{Co}(\text{R-Al})(\text{Cp})]_2(\text{dppe})\} [\text{BF}_4]_2$ (X)	red	56.54 (56.77)	5.24 (5.16)	
$\{[\text{Co}(\text{R-Al})(\text{Cp})]_2(\text{diars})\} [\text{BF}_4]_2$ (XI)	red	41.08 (41.10)	4.67 (4.89)	

^a Al = η -C₃H₅; R-Al = 2-Me- η -C₃H₄; Cp = η -C₅H₅; S = CH₂Cl₂; dppe = Ph₂PCH₂CH₂PPh₂; diars = o-C₆H₄(AsMe₂)₂.

IR spectra

The IR spectra of all the complexes show the characteristic absorptions for the η -C₅H₅ ring [3] and the other relevant ligands. Characteristic absorptions for C₆F₅ are observed in complex II at 1500, 1055 and 955 cm⁻¹ [4]. An intense, broad absorption is observed at 1070 cm⁻¹ for BF₄⁻ in all the cationic complexes. The PF₆⁻ anion in complex V gives a broad band between 800 and 875 cm⁻¹.

¹H NMR spectra

Assignments of the ¹H NMR data are given in Table 2. Each spectrum corresponds to only one isomer or a mixture of the various possible rapidly interconverting isomers. The η -C₅H₅ appears as a single resonance in all the complexes except V and VI, each of which shows a doublet, with coupling constants $J(^{31}\text{P}-\text{H})$ 1.10 and 0.88 Hz respectively. This coupling is not observed in complex X with Ph₂PCH₂CH₂PPh₂. The ¹H H(syn) resonances appear as single lines,

TABLE 2
NMR DATA

Complex	¹ H NMR ^a
[Co(η -C ₃ H ₅)(η -C ₅ H ₅)(PEt ₃)] [BPh ₄] (I) ^d	8.20–8.80(17), c, H(a) + Et ₃ P; 5.85(2), d(J (H(c) – H(s)) 7.47) H(s); 4.49(6), s, Cp + H(c)
[Co(2-Me- η -C ₃ H ₄)(η -C ₅ H ₅)(C ₆ F ₅)] (II) ^c	8.89(2), s, H(a); 8.61(3), s, CH ₃ ; 6.21(2), s, H(s); 5.78(5), s, Cp
[Co(2-Me- η -C ₃ H ₄)(η -C ₅ H ₅)(H ₂ O)] [BF ₄] (III) ^b	8.22(3), s, CH ₃ ; 8.17(2), s, H(a); 7.57(2), s, H ₂ O; 4.78(5), s, Cp; 4.36(2), s, H(s)
[Co(η -C ₃ H ₅)(η -C ₅ H ₅)(H ₂ O)] [BF ₄] (IV) ^b	7.80(2), d(J (H(a) – H(c)) 12.57), H(a); 7.57(2), d(J , 7.87), H ₂ O; 4.71(5), s, Cp; 4.15(2), d(J (H(s) – H(c)) 9.38), H(s)
[Co(2-Me- η -C ₃ H ₄)(η -C ₅ H ₅)(PEt ₃)] [PF ₆] (V) ^d	8.53(17), c, H(a) + Et ₃ P; 7.69(3), s, CH ₃ ; 5.98(2), s, H(s); 4.56(5), d(J (Cp – ³¹ P) 1.10), Cp
[Co(2-Me- η -C ₃ H ₄)(η -C ₅ H ₅)(PPh ₃)] [BF ₄] (VI) ^d	8.60(2), d(J (H(a) – ³¹ P) 13.19), H(a); 7.70(3), s, CH ₃ ; 5.57(2), s, H(s); 4.69(5), d(J (Cp – ³¹ P) 0.88), Cp; 2.20(15), c, Ph ₃ P
[Co(2-Me- η -C ₃ H ₄)(η -C ₅ H ₅)(AsPh ₃)] [BF ₄] (VII) ^d	8.50(2), s, H(a); 7.70(3), s, CH ₃ ; 5.45(2), s, H(s); 4.15(5), s, Cp; 2.30(15), c, Ph ₃ As
[Co(2-Me- η -C ₃ H ₄)(η -C ₅ H ₅)(SbPh ₃)] [BF ₄] (VIII) ^d	8.43(2), s, H(a); 7.61(3), s, CH ₃ ; 5.76(2), s, H(s); 4.33(5), s, Cp; 2.32(15), c, Ph ₃ Sb
[Co(2-Me- η -C ₃ H ₄)(η -C ₅ H ₅)(CH ₃ CN)] [BF ₄] (IX) ^d	7.99(3), s, CH ₃ CN; 7.76(2), s, H(a); 7.65(3), s, CH ₃ ; 4.76(2), s, H(s); 4.44(5), s, Cp
{[Co(2-Me- η -C ₃ H ₄)(η -C ₅ H ₅)] ₂ (dppe)} [BF ₄] ₂ (X) ^d	8.80(4), d(J (H(a) – ³¹ P) 14.02), H(a); 7.77(4), s, P(CH ₂) ₂ P; 7.36(6), s, CH ₃ ; 5.84(4), s, H(s); 4.68(10), s, Cp; 2.33(20), c, Ph ₂ P
{[Co(2-Me- η -C ₃ H ₄)(η -C ₅ H ₅)] ₂ (diars)} [BF ₄] ₂ ^d	8.22(4), s, H(a); 8.13(6), s, CH ₃ ; 8.07(12), s, CH ₃ – As; 5.60(4), d(J , 23.5), H(s); 4.64(10), s, Cp; 2.10(2) and 2.20(2), c, C ₆ H ₄

^a Given as chemical shift τ , (relative intensity), multiplicity (J (Hz)), assignment. ^b In chloroform-*d*. ^c In benzene-*d*₆. ^d In acetone-*d*₆.

no coupling $J(^{31}\text{P}-\text{H}(\text{syn}))$ being observed, whereas complex XI with $o\text{-(C}_6\text{H}_4\text{)}\text{-(AsMe}_2\text{)}_2$ gives a doublet with J 23.5 Hz. A doublet is observed for H(a) for all the phosphine complexes, with $J(^{31}\text{P}-\text{H}(\text{a}))$ between 13.19 and 14.02 Hz, although this is difficult to assign in complexes V and XI as other CH_3 ligand resonances are also present. The resonance due to the CH_3 group appears as a singlet in all the complexes. Other assignments are shown in Table 2.

Crystal and molecular structure of $[\text{Co}(2\text{-Me-}\eta\text{-C}_3\text{H}_4)(\eta\text{-C}_5\text{H}_5)(\text{H}_2\text{O})]^+ [\text{BF}_4]^-$

Crystals are monoclinic, a 7.858(3), b 10.262(4), c 15.078(4) Å, β 98.36(1)°. Space group $P2_1/c$, $Z = 4$, V 1203 Å³, $d(\text{calc})$ 1.468 gcm⁻³, $\mu(\text{Mo-K}\alpha)$ 15.01 cm⁻¹.

The coordination of Co is shown in the stereoplot in minimum overlap view (Fig. 1). The atomic numbering is given in Fig. 2. The cobalt atom is situated between the cyclopentadienyl ring and the 2-Me-allyl group at equal distances from both. The oxygen atom is attached to the cobalt in a staggered conformation with respect to C(10); (torsion angle $\text{O}-\text{Co}(1)-\text{C}(3)-\text{C}(10) = 175^\circ$).

Neither the 2-Me-allyl nor the cyclopentadienyl ring shows significant deviation from planarity. The distance of the cobalt atom from the plane of the cyclopentadienyl ring is 1.66 Å.

The planes of the 2-Me-allyl and the cyclopentadienyl ring are nearly parallel (angle between normals 14°). The $\text{Co}(1)-\text{O}(2)$ vector makes an angle of 70° with the normal to the 2-Me-allyl plane and an angle of 55° with the normal to the cyclopentadienyl plane.

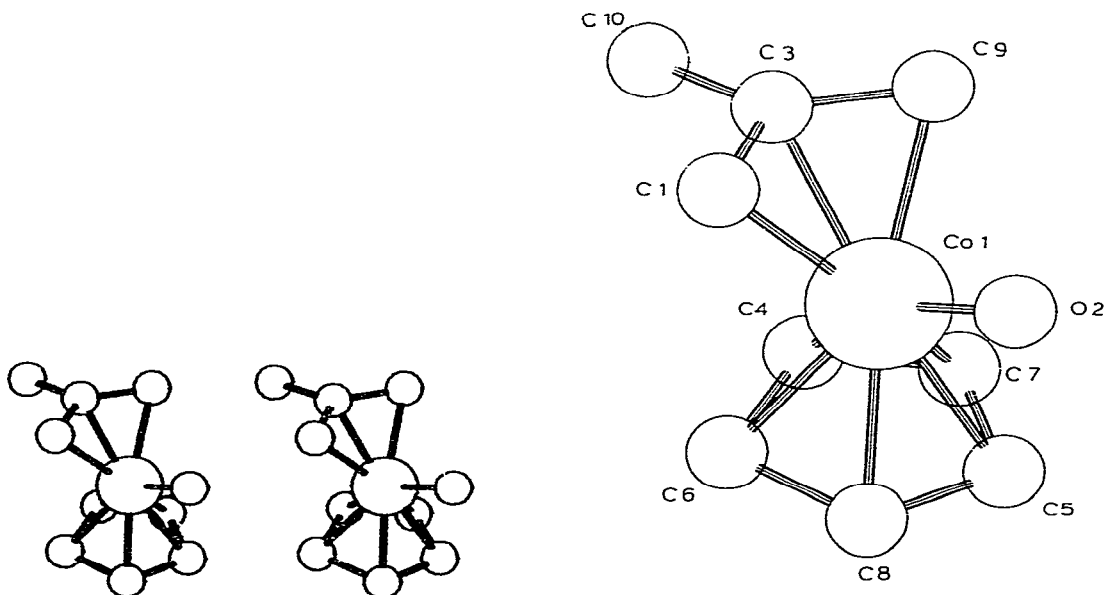


Fig. 1. Stereoplot of coordination of the $\text{Co}(2\text{-Me-}\eta\text{-C}_3\text{H}_4)(\eta\text{-C}_5\text{H}_5)(\text{H}_2\text{O})^+$ grouping.

Fig. 2. Atomic numbering scheme of the $\text{Co}(2\text{-Me-}\eta\text{-C}_3\text{H}_4)(\eta\text{-C}_5\text{H}_5)(\text{H}_2\text{O})^+$ grouping.

Experimental

All experiments were performed under vacuum in an inert atmosphere using Schlenk type glassware, with solvents previously distilled and dried before use. IR spectra were recorded on a Perkin–Elmer 599 spectrophotometer (over the range 4000–200 cm^{-1}) using Nujol between CsI plates. NMR spectra were recorded using a Varian FT 80A or eventually a Bruker 90 spectrophotometers. Conductivity measurements were made in a LF-42 conductimeter. Microanalyses were performed with a Perkin–Elmer 240B microanalyser.

Collection and reduction of diffraction data

Intensity data were measured with a CAD4 diffractometer (Mo- K_α radiation; λ 0.70926 Å), using θ - 2θ scans. For data collection the crystal was mounted in a glass capillary because the crystals decompose upon exposure to the atmosphere. All possible reflections in the sphere up to $\theta = 20^\circ$ were measured (4428). No significant crystal decay was observed during data collection. Multiple measured reflections were averaged, resulting in 1118 unique reflections, of which 908 were treated as observed ($I > 3\sigma(I)$ counting statistics). Averaging agreement index $R(\text{av}) = \Sigma(I - \bar{I})/\Sigma I = 0.021$. Absorption correction was not applied and the intensity data were corrected for Lorentz and polarisation effects. The Co atom was determined from a Patterson synthesis and the remaining atoms were solved by direct methods [5]. Anisotropic least-squares refinement of the Co atom and isotropic refinement of the other atoms converged to and R value of 0.135 with unrealistic thermal parameters for the BF_4^- ion, an indication of

TABLE 3

FRACTIONAL ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS WITH e.s.d.'s IN PARENTHESES

Atom	x	y	z	U_{eq} (X100)
Co(1)	0.2329(3)	0.1740(2)	0.1293(2)	6.1(1)
C(1)	0.236(3)	0.231(3)	0.261(2)	11.1(9)
O(2)	0.066(2)	0.320(1)	0.101(1)	5.8(5)
C(3)	0.180(3)	0.096(3)	0.246(2)	9.1(9)
C(4)	0.398(4)	0.033(2)	0.108(2)	10.9(9)
C(5)	0.284(4)	0.165(4)	−0.002(2)	11.8(9)
C(6)	0.492(3)	0.157(4)	0.123(2)	12.9(9)
C(7)	0.286(4)	0.039(3)	0.036(2)	11.4(9)
C(8)	0.404(5)	0.237(3)	0.051(3)	12.9(9)
C(9)	0.041(3)	0.080(3)	0.184(2)	9.8(8)
C(10)	0.284(3)	−0.008(2)	0.297(2)	10.9(9)
B(11)	0.763	0.149	0.395	16.9(4)
F(11)	0.773	0.058	0.327	16.9(4)
F(21)	0.621	0.227	0.372	16.9(4)
F(31)	0.751	0.082	0.474	16.9(4)
F(41)	0.914	0.223	0.406	16.9(4)
B(12)	0.788	0.153	0.405	17.6(4)
F(12)	0.750	0.220	0.324	17.6(4)
F(22)	0.660	0.062	0.412	17.6(4)
F(32)	0.797	0.243	0.475	17.6(4)
F(42)	0.946	0.092	0.407	17.6(4)

TABLE 4

BOND DISTANCES (e.s.d.'s) IN Å AND BOND ANGLES (e.s.d.'s) IN °

Atoms	Distance	Atoms	Angle
Co(1)—C(4)	2.00(3)	C(4)—C(3)—C(9)	115(2)
C(1)—C(5)	2.07(3)	C(9)—C(3)—C(10)	127(2)
Co(1)—C(6)	2.06(3)	C(1)—C(3)—C(10)	118(2)
Co(1)—C(7)	2.07(3)	C(4)—C(7)—C(5)	110(3)
Co(1)—C(8)	2.02(3)	C(7)—C(5)—C(8)	107(3)
Co(1)—C(1)	2.07(2)	C(5)—C(8)—C(6)	110(3)
Co(1)—C(3)	2.03(2)	C(8)—C(6)—C(4)	101(2)
Co(1)—C(9)	2.06(2)	C(6)—C(4)—C(7)	111(3)
Co(1)—O(2)	2.00(2)		
C(4)—C(7)	1.30(3)		
C(7)—C(5)	1.41(5)		
C(5)—C(8)	1.36(4)		
C(6)—C(8)	1.45(4)		
C(4)—C(6)	1.48(4)		
C(1)—C(3)	1.46(4)		
C(3)—C(9)	1.35(3)		
C(3)—C(10)	1.48(3)		

disorder in this ion. A difference Fourier calculated without the BF_4^- ion clearly showed to superposed tetrahedra. Therefore a disordered model consisting of two ideal tetrahedra, fitted to the observed electron density was introduced. In the subsequent least-squares refinement cycles, these two tetrahedra were only allowed to shift as a group with isotropic thermal parameters, one with an occupancy factor of 2/3 and one with an occupancy factor of 1/3. Refinement of the other atoms was with anisotropic thermal parameters. In the final stages of the refinement weights were used according to $\sigma^2 = \sigma_c^2 + 0.0002F_o^2$. Shifts in the final refinement cycle were less than 1 e.s.d. and the final R factor is 0.109. Hydrogen atoms were not included in the model as there was no evidence for them in a final difference Fourier. Final atomic coordinates and thermal parameters are given in Table 3. Interatomic distances and angles are given in Table 4. The atomic scattering factor data were taken from [6]. Scattering factor data for H were taken from [7]. XRAY76 programs were used [8]. Tables of calculated and observed structure factors may be obtained from the authors.

Preparation of (η -allyl)(η -cyclopentadienyl)triethylphosphinecobalt tetraphenylborate (I)

PET_3 (0.1 ml, 0.68 mmol) was added to a solution of $[\text{Co}(\eta\text{-C}_3\text{H}_5)(\eta\text{-C}_5\text{H}_5)\text{I}]$ (0.20 g, 0.68 mmol) in acetone and the mixture was stirred for 30 min at room temperature. Addition of NH_4BPh_4 gave an immediate yellow orange precipitate, which was filtered off and washed with toluene and petroleum ether. Extraction with acetone and evaporation of the extract gave orange crystals (ca. 50%).

Preparation of (2-methyl- η -allyl)(η -cyclopentadienyl)(pentafluorophenyl)-cobalt (II)

Mg(C₆F₅)Br prepared as in [9] in diethyl ether was added to a solution of [Co(2-Me- η -C₃H₄)(η -C₅H₅)I] [2] (0.50 g, 1.64 mmol) in the same solvent. The mixture was stirred under reflux for 12 h and then evaporated to dryness under vacuum. The solid was extracted with toluene and evaporated. Addition of petroleum ether gave red orange crystals of II (ca. 44%).

Preparation of the aquocomplexes III and IV

AgBF₄ (0.13 g, 0.67 mmol) was added to a solution of [Co(R- η -C₃H₄)(η -C₅H₅)I] (R = H, or 2-Me) (0.67 mmol) in CH₂Cl₂ and the mixture was stirred at room temperature in the dark for 0.5 h. After removal of the AgI by filtration, the solution was evaporated to give black crystals of the aquo complexes [Co(R- η -C₃H₄)(η -C₅H₅)(H₂O)]⁺ [BF₄]⁻, R = 2-Me (III) and H (IV). (Yields between 35–40%).

Preparation of cationic complexes V–XI

The solution obtained as above was filtered (to remove the AgI) into an anhydrous CH₂Cl₂ solution containing an equimolar amount of the ligand. The reaction took place rapidly and the solution was subsequently evaporated under vacuum. The residue was washed several times with warm toluene and then extracted with acetone. Crystallization from acetone/diethyl ether gave orange-red crystals, which were filtered off, washed, and dried under vacuum. (Yields between 35–50%). Complex IX was prepared adding the filtered solution to acetonitrile and adding diethyl ether after concentration, to give red crystals. (Yield 45%.)

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