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Amino-substituted cyclopentadienyl cobalt complexes

Sigrid Holle, Peter W. Jolly *

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr, Germany

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Abstract

Reduction of the (η^1,η^5-$R_2NC_2H_4C_5Me_4$)CoCl complexes (R = Me, R_2 = cyclo-C_4H_8), prepared by treating $CoCl_2$ with 2-dimethylaminoethyl- or 2-pyrrolidinylethyl-tetramethylcyclopentadienyl-lithium, with active-Mg in the presence of ethylene or dienes leads to the formation of (η^5-$R_2NC_2H_4C_5Me_4$)(CH_2:CH_2)$_2$Co(I) or (η^5-$R_2NC_2H_4C_5Me_4$)(diene)Co(I) complexes. These react with ethereal HBF_4 with protonation of the amine followed, in the case of the diene complexes, by transfer of the proton to the diene to give (η^1,η^5-$R_2NC_2H_4C_5Me_4$)(η^3-allyl)Co(III)-salts. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Cobalt; Cyclopentadienyl; Ethylene; Butadiene; Diene; Allyl

1. Introduction

Recently we reported that methylalumoxane-activation of the amino-substituted cyclopentadienyl complexes of chromium leads to the formation of highly active catalysts for the polymerisation of ethylene [1,2]. The analogous compounds of cobalt have received only limited attention [3] and since it has been shown that diimine-complexes of this metal are excellent catalyst-precursors [4,5], we decided to investigate the reaction of the amine-substituted system with cobalt chloride in more detail.

2. Results and discussion

Reaction of $CoCl_2$ with 2-dimethylaminoethyl- or 2-pyrrolidinylethyl-tetramethylcyclo pentadienyl-lithium in THF leads to the formation of **1** and **2** as navy-blue, crystalline solids in good yield (Scheme 1). The product of the reaction leading to **1** has been previously reported [6] to be the dinuclear species [($Me_2NC_2H_4C_5Me_4$)CrCl]$_2$, however, an X-ray diffraction study of the sample we have isolated confirms the mononuclear structure: the unit cell contains two independent molecules and although the data could not be refined satisfactorily (R = 10.2%), the compound is without doubt monomeric with the N-donor atom bonded to the metal atom (Co–N 2.003(7), Co–Cl 2.215(7) Å).

Reduction of **1** or **2** with active-Mg [7] in the presence of ethylene or of a diene leads to the formation of the bis(ethylene)- or (diene)Co(I)-complexes **3**–**9** (Scheme 1) in which the N-donor atom has been displaced from the metal.

Bis(ethylene)Co(I) complexes analogous to **3** and **6** are among the standard reagents in organocobalt chemistry [8] and whereas **6** is apparently new, the orange, crystalline compound **3** has been suggested to be the green or the green–brown oil(!) formed in the reaction between (η^1,η^5-$Me_2NC_2H_4C_5Me_4$)CoI_2 and Na/Hg-amalgam in the presence of ethylene [6]. (η^4-Butadiene)Co(I) complexes related to **4** and **7** are well known (see for example [9–11]) whereas compounds containing unconjugated dienes seem to be limited to a few unstable examples prepared by alkene exchange from Cp(CH_2:CH_2)$_2$Co [12].

The NMR spectra of the product of the reaction with 1,6-heptadiene indicates that in addition to **9** (60%), two isomers are formed in equal amounts and one of these has been identified as the *trans*-1,5-heptadiene derivative **10** (see Section 3). The reaction with 1,4-pentadiene is also accompanied by isomerization of the diene and the product is the *trans*-piperylene species **11**.

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* Corresponding author. Tel.: +49-208-3061; fax: +49-208-306 2980.

E-mail address: jolly@mpi-muelheim.mpg.de (P.W. Jolly).

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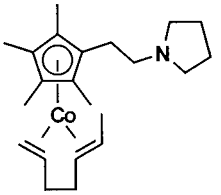
Related diene-isomerization reactions involving CpCo-species have been reported [12–14].



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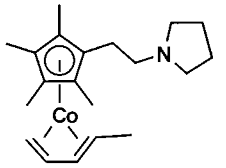
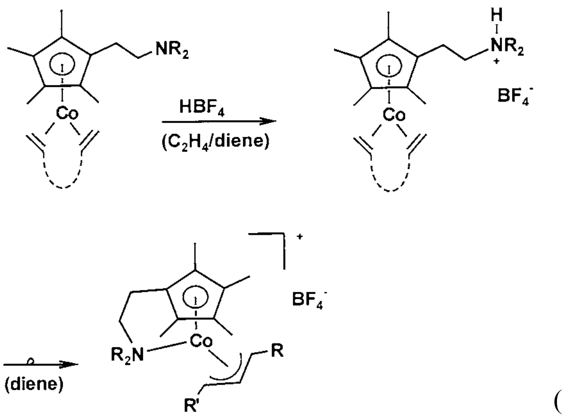


11

The crystal structure of the 1,5-hexadiene complex **5** has been established by X-ray diffraction (Fig. 1). The diene adopts an *R*,*S*-arrangement with parallel double bonds and with the amine-substitutent directed away from the metal atom.

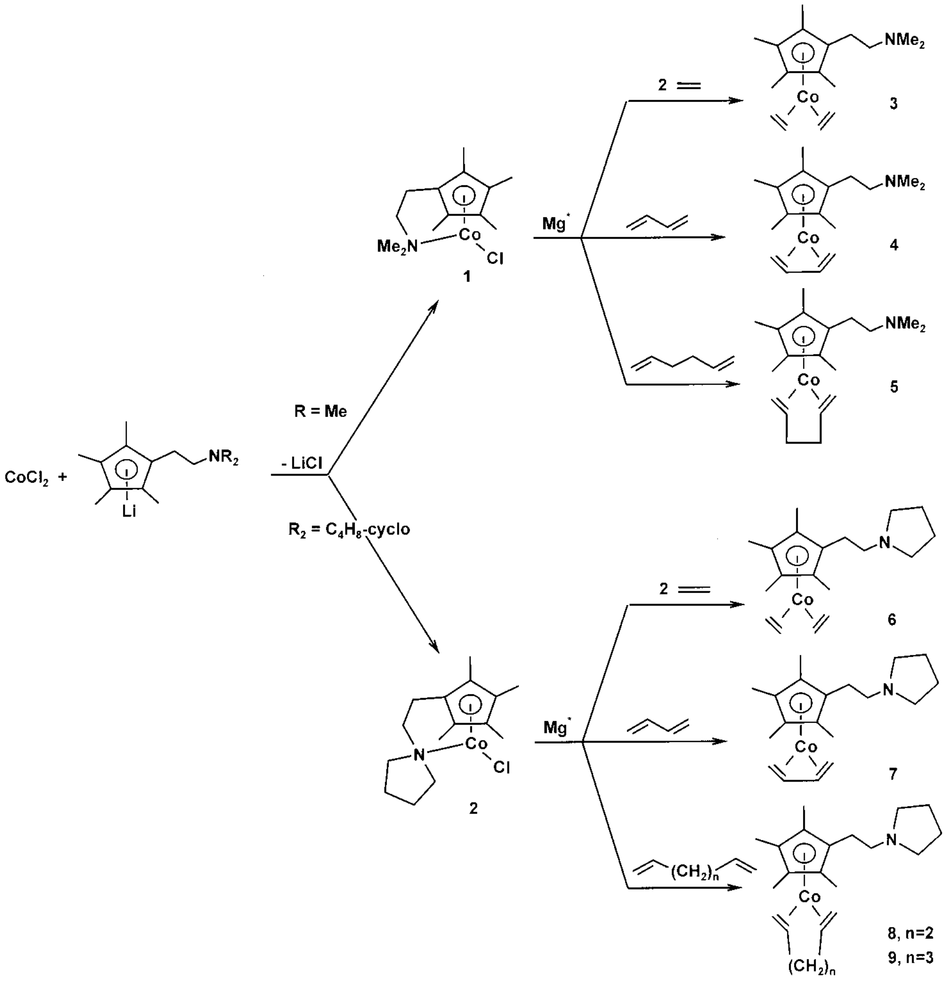
Transition metal-η^2,η^2-hexadiene complexes with both parallel and twisted arrangements of the double bonds have been reported previously for Co [12], Fe [15], Ni [16] and Cu [17].

Reaction of these bis(ethylene)- and (diene)Co(I)-complexes with ethereal HBF_4 occurs initially with protonation of the amine and this is followed, in the case of the diene complexes, by rearrangement to an (η^3-allyl)Co(III)-species (Eq. (1)).



(1)

Thus, the product of the reaction of the bis-(ethylene)Co(I)-complexes **3** and **6** with HBF_4 is the ammonium salt **12** and **13** while the (η^4-1,3-butadiene)Co(I)-species **4** and **7** react initially to give the ammonium salt [(η^5-$HNR_2C_2H_4C_5Me_4$)(η^4-1,3-C_4H_6)-



Scheme 1.

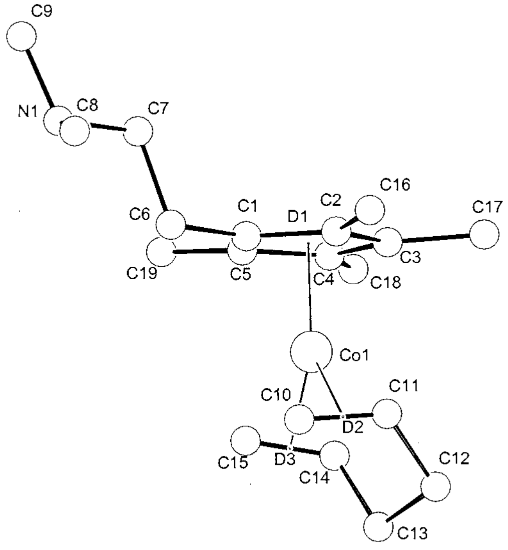
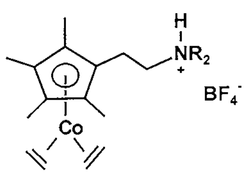
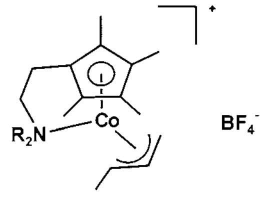


Fig. 1. The molecular structure of (η^5-$Me_2NC_2H_4C_5Me_4$)(η^2,η^2-1,5-C_6H_{10})Co (**5**). Co–D1 1.714, Co–D2 1.886, Co–D3 1.907, Co–C10 2.013(1), Co–C11 2.019(1), Co–C14 2.037(1), Co–C15 2.028(1), C10–C11 1.416(2), C14–C15 1.406(2), C11–C12 1.512(2), C13–C14 1.521(2), C12–C13 1.526(2), C1–C6 1.503(2), C6–C7 1.534(2), C7–N1 1.468(2), C8–N1 1.454(2), C9–N1 1.459(2), C1–C2 1.438(2), C2–C3 1.439(2), C3–C4 1.422(2), C2–C16 1.503(2), C3–C17 1.501(2) Å; D2–Co–D3 95.4, C10–C11–C12 123.2(1), C13–C14–C15 121.0(1), C11–C12–C13 108.9(1), C12–C13–C14 108.8(1), C1–C6–C7 112.1(1), C6–C7–N 112.7(1)°.

Co]$^+$$BF_4^-$ (**14**, R = Me; **15**, $R_2 = C_4H_8$-cyclo) which rearranges to the (η^3-crotyl)Co(III) complexes **16** and **17**.



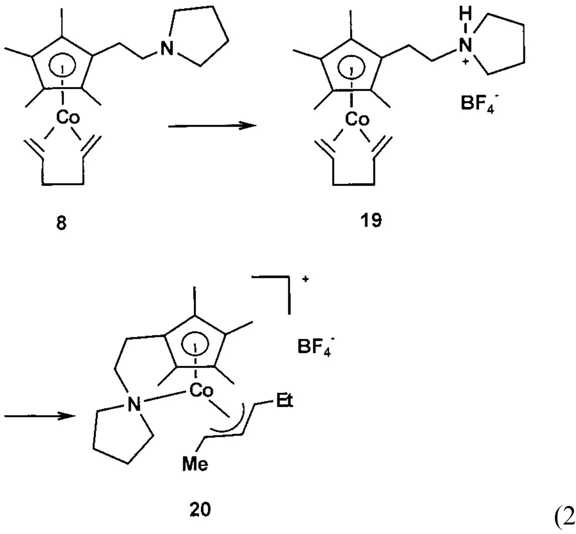
12 (R=Me), 13 (R$_2$=C$_4$H$_8$-cyclo)



16 (R=Me), 17 (R$_2$=C$_4$H$_8$-cyclo)

The (η^2,η^2-1,5-hexadiene)Co-complexes react similarly with the difference that whereas the ammonium salt derived from **5**, [(η^5-$HNMe_2C_2H_4C_5Me_4$)(η^2,η^2-1,5-C_6H_{10})Co]$^+$$BF_4^-$ (**18**), shows no tendency to react further, that derived being **8** (**19**) rearranges to give the (η^3-1-Me,3-EtC_3H_3)Co species **20** (Eq. (2)).

In other cases a mixture of ammonium salt and η^3-allyl complex is formed: **11** reacts to give both [(η^5 - HN(C_4H_8 - cyclo)$C_2H_4C_5Me_4$)(η^4 - 1 - MeC_4H_5)-Co]$^+$$BF_4^-$ (**21**) and [(cyclo-$C_4H_8NC_2H_4C_5Me_4$)(η^3-1,3-$Me_2C_3H_3$)Co]$^+$$BF_4^-$ (**22**) while the 1,6-heptadiene complex **9** reacts to give [(η^5-HN(C_4H_8-cyclo)-$C_2H_4C_5Me_4$)(η^2,η^2-1,6-C_7H_{12})Co]$^+$$BF_4^-$ (**23**) and a mixture of compounds containing isomeric η^3-1,3-$R_2C_3H_3$ groups (see Section 3).



(2)

The structural characterization of these compounds is based largely on their NMR spectra (Tables 1 and 2) while the configuration of the crotyl-group in **17**, with the Me-group and pyrrolidine ring on the same side of the molecule, has been confirmed by a crystal structure determination (Fig. 2).

A second isomer of **17** is formed if **7** is reacted with HBF_4 in a diethyl ether–acetone mixture at 0°C (instead of at room temperature (r.t.)) and although the NMR spectroscopic data clearly indicate the presence of an η^3-crotyl-group, they do no allow a distinction to be made between the various possibilities (*syn*/*anti*-Me group, pron/supin arrangement of the organic ligands, conformation of the cyclo-C_4H_8N fragment) and we have not been able to obtain suitable crystals for an X-ray diffraction study.

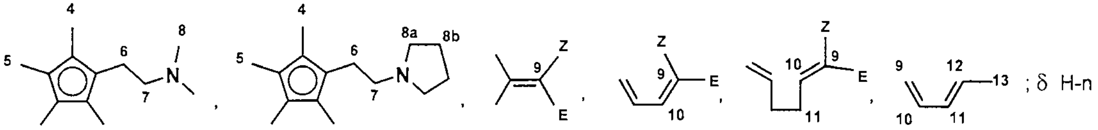
It should be mentioned that the preparation of the d_6-acetone solutions of these ionic compounds for NMR spectroscopic study must be carried out at low (−70°C) temperatures since above −10°C the solutions change colour from orange or red to dark green and at the same time become paramagnetic. Similar effects are observed if the ionic compounds are stirred for several days in CH_2Cl_2 or MeOH and although the exact nature of these species has not been elucidated, elemental analyses and the MS/ESI spectra of the green product formed by reaction of ($R_2NC_2H_4C_5Me_4$)-(CH_2:CH_2)$_2$Co (**3**, **6**) with HBF_4 in CH_2Cl_2 as solvent suggest that they may well be cationic cobaltocene derivatives, e.g. [($R_2NC_2H_4C_5Me_4$)$_2$Co]$^{2+}$2BF_4^-.

Protonation of the N-atom has been reported for related amino-substituted cyclopentadienyl transition metal derivatives [3] while the driving force for the transfer of the proton from the N-atom to the diene, to give an (η^3-allyl)Co complex may well be the complexation of the amine to the metal. Whether this transfer proceeds directly or involves the intermediacy of a cobalt-hydride species has still to be decided.

Table 1
^{1}H-NMR spectroscopic data for the (η^5-$R_2NC_2H_4C_5Me_4$)(CH_2:CH_2)$_2$Co and (η^5-$R_2NC_2H_4C_5Me_4$)(diene)Co complexes and their ammonium salts [a]

Compound	H-4	H-5	H-6	H-7	H-8a	H-8b	H-9E	H-9Z	H-10	H-11a	H-11b/Misc
($Me_2NC_2H_4C_5Me_4$)(CH_2:CH_2)$_2$Co (**3**) [b]	1.48	1.41	2.21	2.32		2.12	1.69	0.93			
($Me_2NC_2H_4C_5Me_4$)(1,3-C_4H_6)Co (**4**) [b]	1.75	1.70	2.26	2.51		2.15	1.20	−0.26	4.34		
($Me_2NC_2H_4C_5Me_4$)(1,5-C_6H_{10})Co (**5**) [c]	1.46	1.41	2.4/2.1			2.11	1.53	1.33	2.88	1.33/2.4-2.1	
(cyclo-$C_4H_8NC_2H_4C_5Me_4$)(CH_2:CH_2)$_2$Co (**6**) [b]	1.48	1.44	2.39	2.39	2.39	1.60	1.71	0.94			
(cyclo-$C_4H_8NC_2H_4C_5Me_4$)(1,3-C_4H_6)Co (**7**) [b]	1.78	1.71	2.46	2.56	2.43	1.64	1.21	−0.26	4.35		
(cyclo-$C_4H_8NC_2H_4C_5Me_4$)(1,5-C_6H_{10})Co (**8**) [b]	1.48	1.46	2.38	2.38	2.38	1.64	1.51	1.28	2.88	1.28	2.21
(cyclo-$C_4H_8NC_2H_4C_5Me_4$)(1-MeC_4H_5)Co (**11**) [b]	1.78/1.76/1.72/1.70		2.45	2.57	2.43	1.64	1.10	−0.51	4.28/4.25		0.11(H-12), 1.02(H-13)
[($HNMe_2C_2H_4C_5Me_4$)(CH_2:CH_2)$_2$Co]$^+BF_4^-$ (**12**) [d]	1.66	1.31	2.97	3.44	3.22		1.51	0.64			8.38(NH)
[($HNMe_2C_2H_4C_5Me_4$)(1,3-C_4H_6)Co]$^+BF_4^-$ (**14**) [d]	1.77	1.72	3.00	3.41	3.19/3.17		1.09	−0.62	4.43		8.90(NH)
[(HN(C_4H_8-cyclo)$C_2H_4C_5Me_4$)(CH_2:CH_2)$_2$Co]$^+BF_4^-$ (**13**) [d]	1.66	1.30	2.93	3.52	4.01/3.37/2.18		1.49	0.63			8.50(NH)
[(HN(C_4H_8-cyclo)$C_2H_4C_5Me_4$)(1,3-C_4H_6)Co]$^+BF_4^-$ (**15**) [d]	1.78	1.72	2.98	3.53	3.98/3.35/2.18	1.10		−0.63	4.42		8.52(NH)
[(HN(C_4H_8-cyclo)$C_2H_4C_5Me_4$)(1,5-C_6H_{10})Co]$^+BF_4^-$ (**19**) [d]											8.98(NH)

[a] Numbering scheme:

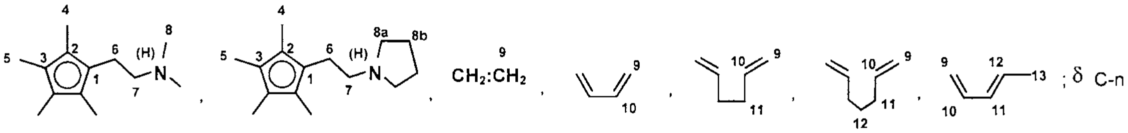


[b] 300K, d_8-toluene.
[c] 243K, d_8-toluene.
[d] 193K, d_6-acetone.

Table 2
^{13}C-NMR spectroscopic data for the (η^5-$R_2NC_2H_4C_5Me_4$)(CH_2:CH_2)$_2$Co and (η^5-$R_2NC_2H_4C_5Me_4$)(diene)Co complexes and their ammonium salts [a]

Compound	C-1	C-2/3	C-4/5	C-6	C-7	C-8	C-9	C-10	C-11	C-12/13
($Me_2NC_2H_4C_5Me_4$)(CH_2:CH_2)$_2$Co (**3**) [b]	95.1	93.0/92.1	9.2/8.9	24.1	60.3	45.6	45.0			
($Me_2NC_2H_4C_5Me_4$)(1,3-C_4H_6)Co (**4**) [b]	92.6	89.7/89.4	10.4/10.3	24.8	61.3	45.6	35.8	80.6		
($Me_2NC_2H_4C_5Me_4$)(1,5-C_6H_{10})Co (**5**) [c]	94.2	92.2/91.2	9.1/8.8	23.8	60.2	45.6	46.3	70.3	34.1	
(cyclo-$C_4H_8NC_2H_4C_5Me_4$)(CH_2:CH_2)$_2$Co (**6**) [d]	96.5	92.8/91.8	9.2/8.7	25.2	56.8	54.3(a)/23.4(b)	44.5			
(cyclo-$C_4H_8NC_2H_4C_5Me_4$)(1,3-C_4H_6)Co (**7**) [b]	92.7	89.6/89.3	10.4/10.3	26.2	57.8	54.4(a)/24.0(b)	35.7	80.6		
(cyclo-$C_4H_8NC_2H_4C_5Me_4$)(1,5-C_6H_{10})Co (**8**) [b]	94.7	92.4/91.5	9.1/9.0	25.3	56.9	54.4(a)/24.0(b)	46.5	70.6	34.2	
(cyclo-$C_4H_8NC_2H_4C_5Me_4$)(1-MeC_4H_5)Co (**11**) [b]	92.4	89.5/89.2/88.9	10.3/10.2	26.1	57.8	54.5(a)/24.0(b)	37.0		78.2/83.3	44.9/17.6
(cyclo-$C_4H_8NC_2H_4C_5Me_4$)(1,6-C_7H_{12})Co (**9**) [b]	95.2	92.9/91.9	8.9/8.6	25.1	56.9	54.4(a)/23.9	42.1	51.4	29.3	19.3
[($HNMe_2C_2H_4C_5Me_4$)(CH_2:CH_2)$_2$Co]$^+BF_4^-$ (**12**) [e]	90.8	94.4/92.4	9.4/7.9	20.8	57.7	43.3	44.5			
[($HNMe_2C_2H_4C_5Me_4$)(1,3-C_4H_6)Co]$^+BF_4^-$ (**14**) [e]	88.3	90.6/90.1	10.1/9.9	21.0	58.2	43.1	35.6	80.6		
[($HNMe_2C_2H_4C_5Me_4$)(1,5-C_6H_{10})Co]$^+BF_4^-$ (**18**) [f]	91.0	93.8/92.4	9.7/9.4	26.4	68.2	44.0	46.6	71.1	34.3	
[(HN(C_4H_8-cyclo)$C_2H_4C_5Me_4$)(CH_2:CH_2)$_2$Co]$^+BF_4^-$ (**13**) [e]	90.8	94.4/92.3	9.4/7.9	22.2	55.2	54.9(a)/23.3(b)	44.4			
[(HN(C_4H_8-cyclo)$C_2H_4C_5Me_4$)(1,3-C_4H_6)Co]$^+BF_4^-$ (**15**) [e]	88.5	90.6/90.1	10.2/9.9	22.5	56.0	54.8(a)/23.4(b)	35.6	80.6		
[(HN(C_4H_8-cyclo)$C_2H_4C_5Me_4$)(1-MeC_4H_5)Co]$^+BF_4^-$ (**21**) [e]		100-90	10.3–8.5	22.5	55.1	55.1(a)/23.4(b)	36.7	83.3?	78.3	45.3/17.5
[(HN(C_4H_8-cyclo)$C_2H_4C_5Me_4$)(1,5-C_6H_{10})Co]$^+BF_4^-$ (**19**) [e]	90.4	93.6/91.8	9.2/8.1	21.9	66.0	54.7(a)/23.3(b)	45.7	70.4	33.6	
[(HN(C_4H_8-cyclo)$C_2H_4C_5Me_4$)(1,6-C_7H_{12})Co]$^+BF_4^-$ (**23**) [e]	90.8	94.3/92.0	9.2/7.4	21.7	55.1	54.6(a)/23.3(b)	50.6	71.8	40.7	37.8

[a] Numbering scheme:



[b] 300K, d_8-toluene.
[c] 243K, d_8-toluene.
[d] 188K, d_8-toluene.
[e] 193K, d_6-acetone.
[f] 243K, d_8-THF.

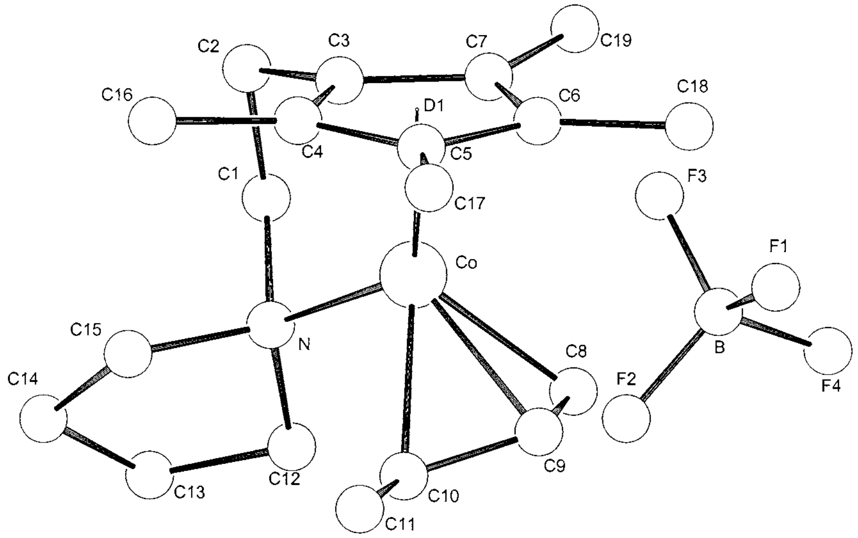


Fig. 2. The molecular structure of [(η^1,η^5-cyclo-$C_4H_8NC_2H_4C_5Me_4$)(η^3-1-MeC_3H_4)Co]$^+BF_4^-$ (**17**). Co–D1 1.692, Co–N 2.102(3), Co–C8 2.066(4), Co–C9 2.019(4), Co–C10 2.124(4), C8–C9 1.399(6), C9–C10 1.402(5), C10–C11 1.488(6), C2–C3 1.507(5), C1–C2 1.522(5), C1–N 1.508(4), C12–N 1.505(4), C15–N 1.508(4), C12–C13 1.536(5), C13–C14 1.534(5), C14–C15 1.527(5), C3–C4 1.435(5), C4–C5 1.419(5), C5–C6 1.442(5), C4–C16 1.511(5), C5–C17 1.496(5) Å; D1–Co–N 118.0, Co–N–C1 104.4(2), N–C1–C2 110.5(3), C1–C2–C3 108.1(3), C12–N–C15 101.6(2), N–C12–C13 105.9(3), C12–C13–C14 104.9(3), C13–C14–C15 105.4(3), C14–C15–N 106.8(3), C8–C9–C10 120.4(3), C9–C10–C11 122.2(3)°.

3. Experimental

The organocobalt complexes described below are air sensitive and all reactions were carried out in an atmosphere or argon. $R_2NC_2H_4C_5Me_4Li$ (R = Me, R_2 = C_4H_8-cyclo) were prepared as mentioned in [1] and active-Mg as described in [7].

In spite of repeated attempts, we have not been able to obtain satisfactory elemental analyses for all of the compounds reported (Table 3) and the compounds have been characterised by a combination of MS and NMR spectra as well as X-ray diffraction.

3.1. *(η^1,η^5-$Me_2NC_2H_4C_5Me_4$)CoCl (**1**)*

A suspension of $CoCl_2$ (1.49 g, 11.1 mmol) in THF (200 ml) was cooled to − 78°C and treated with $Me_2NC_2H_4C_5Me_4Li$ (2.27 g, 11.1 mmol). A dark blue solution was slowly formed which was stirred and allowed to reach r.t. during 16 h. The reaction mixture was evaporated to dryness under oil-pump vacuum and the black residue extracted with toluene (200 ml). The dark blue extract was concentrated to 60 ml and cooled to − 78°C to give the compound as blue–black microcrystalline needles which were isolated and dried under

Table 3
Elemental analyses

Compound	Yield (%)	Elemental analysis: Found (calc.)			
		C	H	Co	N
($Me_2NC_2H_4C_5Me_4$)CoCl (**1**) [a]	67	54.2 (54.5)	8.0 (7.7)	20.4 (20.6)	4.8 (4.9)
(cyclo-$C_4H_8NC_2H_4C_5Me_4$)CoCl (**2**) [b]	73	58.0 (57.6)	7.9 (7.9)	18.3 (18.9)	4.4 (4.5)
($Me_2NC_2H_4C_5Me_4$)(1,3-C_4H_6)Co (**4**)	91	66.6 (66.9)	9.6 (9.2)	19.2 (19.3)	4.6 (4.6)
(cyclo-$C_4H_8NC_2H_4C_5Me_4$)(CH_2:CH_2)$_2$Co (**6**)	91	67.3 (68.5)	10.1 (9.6)	18.3 (17.7)	4.3 (4.2)
(cyclo-$C_4H_8NC_2H_4C_5Me_4$)(1,5-C_6H_{10})Co (**8**)	87	69.9 (70.2)	9.9 (9.5)	16.4 (16.4)	3.9 (3.9)
(cyclo-$C_4H_8NC_2H_4C_5Me_4$)(1-MeC_4H_5)Co (**11**)	77	70.7 (69.6)	8.9 (9.3)	17.1 (17.1)	3.5 (4.1)
[($HNMe_2C_2H_4C_5Me_4$)(CH_2:CH_2)$_2$Co]$^+BF_4^-$ (**12**)	80	–	–	14.2 (14.9)	3.4 (3.5)
[(HN(C_4H_8-cyclo)$C_2H_4C_5Me_4$)(CH_2:CH_2)$_2$Co]$^+$ BF_4^- (**13**)	91	–	–	13.6 (14.0)	3.3 (3.4)
[$HNMe_2C_2H_4C_5Me_4$)(1,5-C_6H_{10})Co]$^+BF_4^-$ (**18**)	95	–	–	13.7 (14.0)	3.5 (3.3)
[(HN(C_4H_8-cyclo)$C_2H_4C_5Me_4$)(C_7H_{12})Co]$^+BF_4^-$ (**23**)	96	–	–	13.2 (12.8)	3.1 (3.0)

[a] Cl 12.5 (12.4).

[b] Cl 11.2 (11.4).

Table 4
Atomic coordinates and equivalent isotropic thermal parameters (Å^2) for **5** with S.D. values in parentheses [a]

Atom	x	y	z	U_{eq}
C(1)	0.2954(1)	0.4257(1)	1.0820(1)	0.016(1)
C(2)	0.2459(1)	0.4900(1)	11631(1)	0.015(1)
C(3)	0.1648(1)	0.4504(1)	1.1248(1)	0.014(1)
C(4)	0.1638(1)	0.637(1)	1.0166(1)	0.014(1)
C(5)	0.2450(1)	0.3478(1)	0.9927(1)	0.015(1)
C(6)	0.3846(1)	0.4368(1)	1.0940(2)	0.021(1)
C(7)	0.4336(1)	0.3670(1)	1.2299(2)	0.019(1)
C(8)	0.5561(1)	0.4694(1)	1.2898(2)	0.026(1)
C(9)	0.5609(1)	0.2864(1)	1.3403(2)	0.035(1)
C(10)	0.2523(1)	0.6342(1)	0.8625(2)	0.021(1)
C(11)	0.1785(1)	0.6528(1)	0.9116(2)	0.019(1)
C(12)	0.1011(1)	0.6802(1)	0.7908(2)	0.023(1)
C(13)	0.0924(1)	0.6099(1)	0.6387(2)	0.022(1)
C(14)	0.1153(1)	0.4990(1)	0.6960(2)	0.019(1)
C(15)	0.1866(1)	0.4528(1)	0.6688(2)	0.022(1)
C(16)	0.2764(1)	0.5771(1)	1.2821(2)	0.022(1)
C(17)	0.0959(1)	0.4896(1)	1.1956(2)	0.019(1)
C(18)	0.0926(1)	0.2965(1)	0.9447(2)	0.020(1)
C(19)	0.2726(1)	0.2585(1)	0.9015(2)	0.023(1)
H(1)	0.529(1)	0.527(1)	1.223(2)	0.028(4)
H(2)	0.613(1)	0.474(2)	1.289(2)	0.028(5)
H(3)	0.552(1)	0.484(2)	1.402(3)	0.041(6)
H(4)	0.552(1)	0.291(2)	1.453(3)	0.039(5)
H(5)	0.540(1)	0.219(2)	1.294(3)	0.044(6)
H(5)	0.617(1)	0.284(2)	1.340(2)	0.039(5)
H(7)	0.424(1)	0.388(1)	1.343(2)	0.024(4)
H(8)	0.416(1)	0.292(1)	1.205(2)	0.025(4)
H(9)	0.401(1)	0.510(1)	1.116(2)	0.026(5)
H(10)	0.398(1)	0.418(1)	0.990(2)	0.030(5)
H(11)	0.132(1)	0.622(2)	1.241(2)	0.039(5)
H(12)	0.305(1)	0.551(2)	1.391(3)	0.037(5)
H(13)	0.233(1)	0.618(2)	1.310(3)	0.045(6)
H(14)	0.094(1)	0.563(2)	1.200(2)	0.035(5)
H(15)	0.096(1)	0.461(2)	1.302(3)	0.041(5)
H(16)	0.047(1)	0.470(2)	1.128(2)	0.035(5)
H(17)	0.042(1)	0.332(2)	0.940(2)	0.036(5)
H(18)	0.090(1)	0.236(2)	1.012(3)	0.042(5)
H(19)	0.096(1)	0.271(2)	0.834(3)	0.043(6)
H(20)	0.228(1)	0.229(2)	0.820(3)	0.042(5)
H(21)	0.315(1)	0.282(2)	0.849(2)	0.036(5)
H(21)	0.294(1)	0.202(2)	0.981(2)	0.037(5)
H(23)	0.256(1)	0.643(1)	0.746(2)	0.021(4)
H(23)	0.302(1)	0.646(1)	0.938(2)	0.018(4)
H(25)	0.179(1)	0.679(1)	1.021(2)	0.022(4)
H(26)	0.100(1)	0.754(1)	0.763(2)	0.025(4)
H(27)	0.056(1)	0.668(1)	0.846(2)	0.031(5)
H(28)	0.129(1)	0.634(1)	0.565(2)	0.026(4)
H(29)	0.037(1)	0.611(1)	0.571(2)	0.025(4)
H(30)	0.072(1)	0.457(1)	0.711(2)	0.025(4)
H(31)	0.220(1)	0.489(1)	0.609(2)	0.026(5)
H(32)	0.193(1)	0.377(2)	0.633(2)	0.033(5)

[a] $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a*_i a*_j \bar{a}_i \bar{a}_j$ or U_{iso}.

high vacuum. Yield: 2.2 g (67%). Elemental analyses: see Table 3. IR (KBr) : v 2945, 2908, 2858, 1467, 1444. MS (105°C): m/e 286 (M$^+$, 100%).

3.1.1. Crystal structure

Dark blue needles from toluene. The unit cell contained two independent molecules and the data could not be refined satisfactorily; $C_{13}H_{22}ClCoN$, monoclinic, space group $P2_1/c$ (no. 14), $a = 9.1645(2)$ Å, $b = 20.1431(4)$ Å, $c = 14.9304(3)$ Å, $\beta = 90.1370$ (10)°, $v = 2756.17(10)$ Å^3, $Z = 8$, D_{calc} 1.382 Mg m^{-3}, 21 510 measured reflections, 4833 unique, $R = 0.1018$ [$I > 2\sigma(I)$].

3.2. (η^1,η^5-cyclo-$C_4H_8NC_2H_4C_5Me_4$)CoCl (**2**)

Prepared as described above as blue–black needles by reacting $CoCl_2$ with cyclo-$C_4H_8NC_2H_4C_5Me_4Li$ in THF. Yield: 73%. Elemental analyses: see Table 3. IR (KBr) : v 2969, 2916, 2883, 1495, 1456. FIR (KBr): v 320 (CoCl). MS (95°C): m/e 312 (M$^+$, 100%).

3.3. (η^5-$Me_2NC_2H_4C_5Me_4$)(CH_2:CH_2)$_2$Co (**3**)

A solution of ($Me_2NC_2H_4C_5Me_4$)CoCl (**1**, 0.34 g, 1.18 mmol) in THF (30 ml) was saturated with ethylene at r.t. and stirred with active-Mg (0.04 g, 1.67 mmol). The resulting orange–brown solution was stirred at r.t. for 2 h and evaporated to dryness. The brown residue was extracted with pentane (20 ml) and the extract cooled to − 78°C to give the compound as orange crystals. Yield: 0.29 g (81% theory). IR (KBr) : v 3014, 2954, 2909, 2858, 2788, 1501, 1456, 1144. MS (50°C): m/e 307 (M$^+$, 100%), 279, 251. ^{1}H- and ^{13}C-NMR spectra: see Tables 1 and 2.

3.4. (η^5-$Me_2NC_2H_4C_5Me_4$)(η^4-1,3-C_4H_6)Co (**4**)

Prepared as orange crystals, low melting (ca. 20°C) crystals as described above for **3** by reacting ($Me_2NC_2H_4C_5Me_4$)CoCl (**1**) with active-Mg and 1,3-butadiene in THF. Yield: 91%. Elemental analyses: see Table 3. IR (KBr): v 3031, 2937, 2856, 2816, 2778, 1460. MS (40°C): m/e 305 (M$^+$), 249 (100%). ^{1}H- and ^{13}C-NMR spectra: see Tables 1 and 2.

3.5. (η^5-$Me_2NC_2H_4C_5Me_4$)(η^2,η^2-1,5-C_6H_{10})Co (**5**)

Prepared as orange–red, low melting (ca. 0°C) crystals as described above for **3** by reacting ($Me_2NC_2H_4C_5Me_4$)CoCl (**1**) with active-Mg and 1,5-hexadiene in THF. Yield: 72%. IR (KBr): v 3036, 2975, 2920, 2858, 2817, 2763, 1464, 1377. MS (28°C): m/e 333 (M$^+$), 249 (100%). ^{1}H- and ^{13}C-NMR spectra: see Tables 1 and 2.

3.5.1. Crystal structure analyses

$C_{19}H_{32}CoN$, molecular weight 333.39 g mol^{-1}, crystal colour red, crystal size 0.91 × 0.51 × 0.50 mm, $a = 16.9698(4)$ Å, $b = 12.8005(3)$ Å, $c = 8.2481(2)$ Å, $\beta = 102.2580$ (10)°, $v = 1750.82(7)$ Å^3, $T = 100$ K, D_{calc} 1.265 Mg m^{-3}, $\mu = 9.75$ cm^{-1}, Z = 4, monoclinic, space group $P2_1/c$ (no. 14). Siemens SMART CCD diffractometer , $\lambda = 0.71069$ Å, scan mode CCD/ω-scan, 18 781 measured reflections ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta/\lambda]_{\max}$ 0.64 Å^{-1}, 6287 independent reflections, 5160 observed reflections $[I > 2\sigma(I)]$ for 318 refined parameters, structure solved by SHELXS-97, H atom positions and isotropic thermal parameters refined, $R = 0.0331$, $R_w^2 = 0.0795$, residual electron density 0.615 e Å^{-3}, Atomic positional parameters and equivalent isotropic thermal parameters are given in Table 4. The molecular structure with selected bond distances and angles is shown in Fig. 1.

3.6. *(η^5-cyclo-$C_4H_8NC_2H_4C_5Me_4$)(CH_2:CH_2)$_2$Co (**6**)*

Prepared as described above for **3** as orange crystals by reacting (cyclo-$C_4H_8NC_2H_4C_5Me_4$)CoCl (**2**) with active-Mg and ethylene in THF. Yield: 91%. Elemental analyses: see Table 3. IR (KBr) : ν 3047, 2968, 2948, 2913, 2788, 1484, 1457, 1444, 1427. MS (40°C): *m/e* 333 (M^+), 305 (1%), 277 (3%). ^{1}H- and ^{13}C-NMR spectra: see Tables 1 and 2.

The compound can also be prepared (yield: 42%) by reacting (cyclo-$C_4H_8NC_2H_4C_5Me_4$)CoCl (**2**) with EtMgBr in THF at −78°C to r.t.

3.7. *(η^5-cyclo-$C_4H_8NC_2H_4C_5Me_4$)(η^4-1,3-C_4H_6)Co (7)*

Prepared as orange–red crystals as described above for **3** by reacting (cyclo-$C_4H_8NC_2H_4C_5Me_4$)CoCl (**2**) with active-Mg and 1,3-butadiene in THF at −78°C to r.t. Yield: 72%. IR (KBr) : ν 3032, 2965, 2909, 2783, 1458. MS (30°C): *m/e* 331 (M^+), 275 (73%), 273 (100%). ^{1}H- and ^{13}C-NMR spectra: see Tables 1 and 2.

3.8. *(η^5-cyclo-$C_4H_8NC_2H_4C_5Me_4$)(η^2,η^2-1,5-C_6H_{10})Co (**8**)*

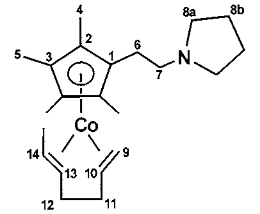
Prepared as orange–red crystals as described above for **3** by reacting (cyclo-$C_4H_8NC_2H_4C_5Me_4$)CoCl (**2**) with active-Mg and 1,5-hexadiene in THF at r.t. Yield: 87%. Elemental analyses: see Table 3. IR (KBr) : ν 3033, 2966, 2922, 2872, 2823, 2786, 1458, 1378. MS (70°C): *m/e* 359 (M^+, 8%), 277 (44%), 275 (88%), 273 (100%). ^{1}H- and ^{13}C-NMR spectra: see Tables 1 and 2.

3.9. *(η^5-cyclo-$C_4H_8NC_2H_4C_5Me_4$)(η^2,η^2-1,6-C_7H_{12})Co (9)*

Prepared as a red oil as described above for **3** by reacting (cyclo-$C_4H_8NC_2H_4C_5Me_4$)CoCl (**2**) with active-Mg and 1,6-heptadiene in THF at r.t. Yield: 89%. IR (KBr) : ν 3041, 2964, 2920, 2872, 2783, 1500, 1458, 1441. MS (55°C): *m/e* 373 (M^+, 10%), 277 (51%), 275 (100%), 273 (99%). ^{13}C-NMR spectra: see Table 2. The ^{13}C-NMR spectra indicates that isomers are present and among these one (20%) is provisionally assigned to (η^5-cyclo-$C_4H_8NC_2H_4C_5Me_4$)(η^2,η^2-1,5-C_7H_{12})Co (**10**).

3.10. *(η^5-cyclo-$C_4H_8NC_2H_4C_5Me_4$)(η^2,η^2-1,5-C_7H_{12})Co (**10**)*

^{13}C-NMR (d_8-toluene, 300 K): δ 94.8 or 94.6 (C-1), 92.7 or 91.9 or 91.7 (C-2/3), 25.9 or 25.0 (C-6), 56.8 or 56.7 (C-7), 10.3–8.5 (Me)–$C_4H_8NC_2H_4C_5Me_4$; 72.1 or 71.2 or 69.4 (C-10/13), 50.4 (C-14), 37.9 (C-9), 37.1 (C-11), 29.2 (C-12), 15.0 (Me); numbering scheme shown below.



10

3.11. *(η^5-cyclo-$C_4H_8NC_2H_4C_5Me_4$)(η^4-1-MeC_4H_5)Co (**11**)*

Prepared as orange–red, low melting (ca. 20°C) crystals as described above for **3** by reacting (cyclo-$C_4H_8NC_2H_4C_5Me_4$)CoCl (**2**) with active-Mg and 1,4-pentadiene in THF at r.t. Yield: 77%. Elemental analysis: see Table 3. IR (KBr) : ν 3033, 2965, 2908, 2779, 1459. MS (55°C): *m/e* 345 (M^+, 11%), 277, 275, 273. ^{1}H- and ^{13}C-NMR spectra: see Tables 1 and 2.

3.12. *[(η^5-HN$Me_2C_2H_4C_5Me_4$)(CH_2:CH_2)$_2$Co]$^+$ BF_4^- (**12**)*

To a solution of ($Me_2NC_2H_4C_5Me_4$)(CH_2:CH_2)$_2$Co (**3**, 0.29 g, 0.95 mmol) in diethyl ether (20 ml) was added at 0°C an ethereal solution of HBF_4 (0.13 ml of a 54% solution, 0.96 mmol). An orange–brown precipitate was formed. The reaction mixture was evaporated to dryness and the residue washed with pentane and then extracted with acetone. Addition of diethyl ether to the extract gave the compound as an orange precipitate. Yield: 0.30 g (80% theory). Elemental analysis: see Table 3. IR (KBr): ν 3175, 3061, 2993, 2967, 2913, 1473, 1199, 1181, 1083. MS: dec. ^{1}H- and ^{13}C-NMR spectra: see Tables 1 and 2.

3.13. *[(η^5-HN(C_4H_8-cyclo)$C_2H_4C_5Me_4$)-(CH_2:CH_2)$_2$Co]$^+$ BF_4^- (**13**)*

Prepared as an orange compound as described above for **12** by reacting (cyclo-$C_4H_8NC_2H_4C_5Me_4$)-(CH_2:CH_2)$_2$Co (**6**) with an ethereal solution of HBF_4 in diethyl ether. Yield: 91%. Elemental analysis: see Table 3. IR (KBr): ν 3180, 3058, 2989, 2950, 2911, 1487, 1458, 1197, 1179, 1087. MS (FAB): *m/e* 334 (M^+-BF_4), 306, 274. ^{1}H- and ^{13}C-NMR spectra: see Tables 1 and 2.

3.14. $[(\eta^5\text{-}HNMe_2C_2H_4C_5Me_4)(\eta^4\text{-}1,3\text{-}C_4H_6)Co]^+BF_4^-$ (14)

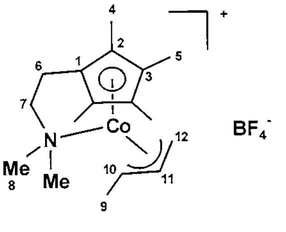
A solution of $(Me_2NC_2H_4C_5Me_4)(\eta^4\text{-}1,3\text{-}C_4H_6)Co$ (**4**, 1.12 g, 3.67 mmol) in diethyl ether (40 ml) was treated at −78°C with an ethereal solution of HBF_4 (0.50 ml of a 54% solution, 3.67 mmol). The resulting orange precipitate was isolated washed with pentane at −78°C and dried under high vacuum. Yield: 1.38 g (95% theory). IR (KBr): ν 3169, 3027, 2972, 2916, 1475. ^1H- and ^{13}C-NMR spectra: see Tables 1 and 2.

3.15. $[(\eta^5\text{-}HN(C_4H_8\text{-}cyclo)C_2H_4C_5Me_4)\text{-}(\eta^4\text{-}1,3\text{-}C_4H_6)Co]^+BF_4^-$ (15)

Prepared as an orange solid as described above for **14** by reacting $(cyclo\text{-}C_4H_8NC_2H_4C_5Me_4)(\eta^4\text{-}1,3\text{-}C_4H_6)Co$ (**7**) with ethereal HBF_4 at 0°C. Yield: 91% theory. IR (KBr): ν 3175, 3032, 2972, 2911, 1461, 1056. MS (ESI, MeOH): *m/e* 332 (M^+). ^1H- and ^{13}C-NMR spectra: see Tables 1 and 2.

3.16. $[(\eta^1,\eta^5\text{-}Me_2NC_2H_4C_5Me_4)\text{-}(\eta^3\text{-}1\text{-}syn\text{-}MeC_3H_4)Co]^+BF_4^-$ (16)

Prepared as a red–orange solid by stirring a solution of $[(\eta^5\text{-}HNMe_2C_2H_4C_5Me_4)(\eta^4\text{-}1,3\text{-}C_4H_6)Co]^+BF_4^-$ (**14**) in acetone at r.t. for 5 days. ^{13}C-NMR (d_6-acetone, 193 K): δ 97.8 (C-11), 79.4 (C-10), 75.6 (C-12), 16.9 (C-9); 95/92/91 (C-1/2/3), 55.8 (C-7), 52.5/51.2 (C-8), 21.8 (C-6), 10.1/8.5/8.3/7.6 (Me); numbering scheme, see below.

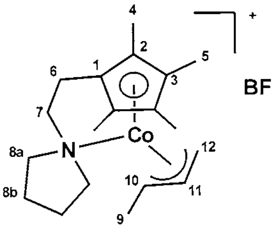


16

A second isomer of **16** is formed upon treating a solution of $(\eta^5\text{-}Me_2NC_2H_4C_5Me_4)(\eta^4\text{-}1,3\text{-}C_4H_6)Co$ (**4**) (0.32 g, 1.05 mmol) in diethyl ether (30 ml) with an ethereal solution of HBF_4 (0.14 ml of a 54% solution, 1.05 mmol) at 0°C. The compound precipitated immediately as a red solid which was washed with pentane and extracted with acetone. Evaporation gave the compound as a red–orange solid. Yield: 0.29 g (70% theory). MS (ESI, MeOH): *m/e* 306 (M^+, 100%), 192 (15%). ^1H-NMR (d_6-acetone, 193 K): δ 4.88 (H-12E), 4.53 (H-11), 2.2/1.9 (H-12Z/10); 3.38/3.01 (H-6/7), 3.16 (H-8), 1.85/1.59/1.49/1.46/1.44 (Me). ^{13}C-NMR (d_6-acetone, 193 K): δ 101.1 (C-11), 80.0 (C-10), 62.0 (C-12), 18.1 (C-9); 97.2/97.0/95.9/95.2/91.9 (C-1/2/3), 55.1 (C-7), 43.4/43.1 (C-8), 20.1 (C-6), 8.8/8.6/8.4 (Me); numbering scheme, see above.

3.17. $[(\eta^1,\eta^5\text{-}cyclo\text{-}C_4H_8NC_2H_4C_5Me_4)\text{-}(\eta^3\text{-}1\text{-}syn\text{-}MeC_3H_4)Co]^+BF_4^-$ (17)

Prepared as a red–brown solid by stirring $[(\eta^5\text{-}HN(C_4H_8\text{-}cyclo)C_2H_4C_5Me_4)(\eta^4\text{-}1,3\text{-}C_4H_6)\text{-}Co]^+BF_4^-$ (**15**) in acetone for 1 week at r.t. The NMR spectra (−70°C) indicate that 75% conversion has occurred. ^1H-NMR (d_6-acetone, 193 K): δ 4.4 (H-12 E), 4.3 (H-11), 1.9 (H-10), 1.6 (H-12 Z); 4-3 (H-6/7/8), 2.4/2.5/1.1/1.0/0.85 (5 Me). ^{13}C-NMR (d_6-acetone, 193K): δ 97.7 (C-11), 79.0 (C-10), 68.9 (C-12), 17.4 (C-9); 94.2/93.8/92.2/88.8 (C-1/2/3), 58.2/57.4 (C-8a), 54.9 (C-7), 21.5/21.1 (C-8b), 19.4 (C-6), 10.1/8.9/8.5/7.3 (Me); numbering scheme, see below; the assignment was hindered by contamination of the sample with the starting material (25%).



17

A second isomer of **17** is formed upon treating $(\eta^5\text{-}cyclo\text{-}C_4H_8NC_2H_4C_5Me_4)(\eta^4\text{-}1,3\text{-}C_4H_6)Co$ (**7**) (2.35 g , 7.1 mmol) with ethereal HBF_4 (0.97 ml of a 54% solution, 7.1 mmol) in diethyl ether (50 ml) at 0°C. The compound precipitated immediately as an orange solid which was isolated and washed with ether. The product was taken up in acetone and precipitated by the addition of ether. Yield: 1.50 g (50% theory). The ^{13}C-NMR spectra indicates that the compound is contaminated by **15** (13%). MS (ESI, MeOH): *m/e* 332 (100%), 218 (8%). ^{13}C-NMR (d_6-acetone, 193 K): δ 96.9 (C-11), 79.0 (C-10), 59.3 (C-12), 14.7 (C-9); 100.7/98.4/95.8/93.4/92.4 (C-1/2/3), 55.0/54.8 (C-8a), 53.1 (C-7), 23.2 (C-8b), 21.4 (C-6), 9.1/8.7/8.5/8.4 (Me); numbering scheme, see above; arrangement of η^3-crotyl group unknown; the assignment was hindered by contamination of the sample with **15** (13%).

3.17.1. Crystal structure analysis for 17

$C_{19}H_{31}BCoF_4N$, molecular weight 419.19 g mol^{-1}, crystal colour black, crystal size 0.35 × 0.28 × 0.17 mm, $a = 8.6975(4)$ Å, $b = 8.5901(4)$ Å, $c = 25.3377(11)$ Å, $\beta = 95.725\ (2)°$, $v = 1883.60(15)$ Å^3, $T = 100$ K, D_{calc} 1.478 Mg m^{-3}, $\mu = 9.51$ cm^{-1}, $Z = 4$, monoclinic, space group $P2_1/n$ (no. 14). Siemens SMART CCD diffractometer , $\lambda = 0.71073$ Å, scan mode CCD/ω-scan, 13 917 measured reflections ($\pm h$, $\pm k$, $\pm l$),

[$(\sin\theta/\lambda)_{\max}$ 0.64 Å^{-1}, 3287 independent reflections, 2829 observed reflections [$I > 2\sigma(I)$] for 235 refined parameters, structure solved by SHELXS-97, H atom positions calculated, $R = 0.0466$, $R_w^2 = 0.1458$, residual electron density 1.043 e Å^{-3}. Atomic positional parameters and equivalent isotropic thermal parameters are given in Table 5. The molecular structure with selected bond distances and angles is shown in Fig. 2.

*3.18. [(η^5-HNMe$_2$C$_2$H$_4$C$_5$Me$_4$)(η^2,η^2-1,5-C$_6$H$_{10}$)Co]$^+$BF$_4^-$ (**18**)*

A solution of (Me$_2$NC$_2$H$_4$C$_5$Me$_4$)(1,5-C$_6$H$_{10}$)Co (**5**, 0.42 g, 1.26 mmol) in THF (20 ml) was treated at 0°C with an ethereal solution of HBF$_4$ (0.17 ml of a 54% solution, 1.26 mmol). The resulting brown solution was stirred at r.t. for 16 h, cooled to −78°C and the compound isolated as a yellow–brown precipitate which was dried under high vacuum. Yield: 0.50 g (95% theory). Elemental analysis: see Table 3. IR (KBr) : *v* 3182, 3039, 2976, 2921, 2872, 1474, 1080. MS (FAB): *m*/*e* 334 (M$^+$, 100%), 250 (50%). ^{13}C-NMR spectra: see Table 2.

Table 5
Atomic coordinates and equivalent isotropic thermal parameters (Å^2) for **17** with S.D. values in parentheses [a]

Atom	*x*	*y*	*z*	U_{eq}
Co	0.3633(1)	0.7984(1)	0.1229(1)	0.020(1)
F(1)	0.9261(3)	0.1259(3)	0.1101(1)	0.047(1)
F(2)	1.0420(4)	0.2355(4)	0.1849(1)	0.071(2)
F(3)	1.0493(5)	0.3521(5)	0.1061(1)	0.102(3)
F(4)	0.8277(4)	0.3379(4)	0.1438(2)	0.090(3)
N	0.4863(3)	0.9658(3)	0.1706(1)	0.020(1)
B	0.9657(5)	0.2642(5)	0.1361(2)	0.030(2)
C(1)	0.5077(4)	1.0994(4)	0.1335(1)	0.024(2)
C(2)	0.5689(4)	1.0409(4)	0.0829(1)	0.024(2)
C(3)	0.4821(4)	0.8947(4)	0.0658(1)	0.022(2)
C(4)	0.5358(4)	0.7378(4)	0.0741(1)	0.023(2)
C(5)	0.4058(4)	0.6394(4)	0.0627(1)	0.025(2)
C(6)	0.2742(4)	0.7.61(4)	0.0463(1)	0.024(2)
C(7)	0.3203(4)	0.8932(4)	0.0470(1)	0.022(2)
C(8)	0.1534(4)	0.8418(5)	0.1515(1)	0.031(2)
C(9)	0.1990(4)	0.6866(4)	0.1592(1)	0.031(2)
C(10)	0.3395(5)	0.6502(5)	0.1886(1)	0.031(2)
C(11)	0.3985(2)	0.4878(5)	0.1940(2)	0.036(2)
C(12)	0.4241(4)	1.0329(4)	0.2191(1)	0.025(2)
C(13)	0.5625(4)	1.1090(4)	0.2516(1)	0.030(2)
C(14)	0.7040(4)	1.0196(5)	0.2362(1)	0.031(2)
C(15)	0.6413(4)	0.9046(4)	0.1935(1)	0.027(2)
C(16)	0.7004(5)	0.6831(5)	0.0869(2)	0.034(2)
C(17)	0.4078(5)	0.4653(4)	0.0638(2)	0.038(2)
C(18)	0.1144(5)	0.6777(5)	0.0265(2)	0.037(2)
C(19)	0.2224(4)	1.0303(4)	0.0292(1)	0.029(2)

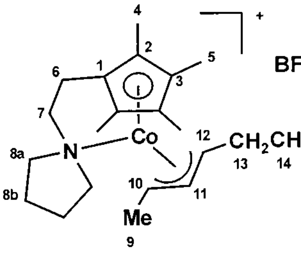
[a] $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a*_i a*_j \bar{a}_i \bar{a}_j$ or U_{iso}.

*3.19. [(η^5-HN(C$_4$H$_8$-cyclo)C$_2$H$_4$C$_5$Me$_4$)(η^2,η^2-1,5-C$_6$H$_{10}$)Co]$^+$BF$_4^-$ (**19**)*

Prepared as an orange solid as described above for **18** by reacting (cyclo-C$_4$H$_8$NC$_2$H$_4$C$_5$Me$_4$)(1,5-C$_6$H$_{10}$)Co (**8**) with ethereal HBF$_4$ at −78°C in diethyl ether. Yield: 68% theory. IR (KBr) : *v* 3171, 3038, 2977, 2919, 2871, 2820, 1470, 1383, 1089. MS (ESI, MeOH): *m*/*e* 360 (M$^+$, 100%). ^{13}C-NMR spectrum: see Table 2.

*3.20. [(η^1,η^5-cyclo-C$_4$H$_8$NC$_2$H$_4$C$_5$Me$_4$)(η^3-1,3-Me,EtC$_3$H$_3$)Co]$^+$BF$_4^-$ (**20**)*

A solution of (cyclo-C$_4$H$_8$NC$_2$H$_4$C$_5$Me$_4$)(1,5-C$_6$H$_{10}$)Co (**8**, 0.67 g, 1.87 mmol) in THF (40 ml) was treated with ethereal HBF$_4$ (0.25 ml of a 54% solution, 1.87 mmol) at 0°C. The resulting brown solution was stirred at r.t. for 16 h. The reaction mixture was evaporated to dryness and the residue extracted with acetone. Evaporation of the extract gave the compound as a brown powder. Yield: 0.40 g (48% theory). IR (KBr): *v* 3182, 2968, 2930, 1662 (Me$_2$CO), 1461, 1073 (BF$_4$). MS (ESI, MeOH): *m*/*e* 360 (M$^+$, 100%). ^{13}C-NMR (d_6-acetone, 193 K): δ 100.2 (C-11), 81.8/76.6 (C-10/12), 26.9 (C-13), 18.4/15.8(C-9/14); 95.8/95.6 (C-2/3), 91.7 (C-1), 54.8 (C-8a), 52.0 (C-7), 23.1 (C-8b), 21.2 (C-6), 8.8/8.7 (C-4/5); numbering scheme shown below.

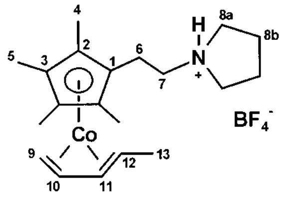


20

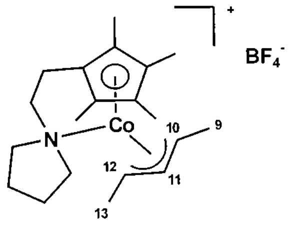
*3.21. [(η^5-HN(C$_4$H$_8$-cyclo)C$_2$H$_4$C$_5$Me$_4$)(η^4-1-MeC$_4$H$_5$)Co]$^+$BF$_4^-$ (**21**), (η^1,η^5-cyclo-C$_4$H$_8$NC$_2$H$_4$C$_5$Me$_4$)(η^3-1,3-Me$_2$C$_3$H$_3$)Co]$^+$BF$_4^-$ (**22**)*

Prepared as an orange coloured mixture as described above for **18** by reacting (cyclo-C$_4$H$_8$NC$_2$H$_4$C$_5$Me$_4$)(η^4-1-MeC$_4$H$_5$)Co (**11**) with ethereal HBF$_4$ at 0°C in diethyl ether. Yield: 80% theory. IR (KBr): *v* 3175 (NH), 3031, 2968, 2911, 1456, 1051 (BF$_4$). MS (ESI): *m*/*e* 346 (M$^+$, 100%). ^{13}C-NMR (d_6-acetone, 193 K): δ 83.3/78.3 or 70.0 (C-10/11), 45.3 (C-12), 36.7 (C-9), 17.5 (C-13); 100-90 (C-1/2/3), 55.1 (C-7/8a), 23.4 (C-8b), 10.3-8.5 (C-4/5), 22.5 (C-6)—**21** (65%); 97.5 (C-11), 78.3 or 70.0 (C-10), 67.7 (C-12 ?), 17.4 (C-9/13); 100-90 (C-1/2/3), 57.0 (C-8a), 55.1 (C-7), 21.5 (C-8b), 19.3 (C-6), 10.3–

8.5 (C-4/5)—**22** (35%); numbering scheme shown below.



21



22

3.22. $[(\eta^5\text{-HN}(C_4H_8\text{-cyclo})C_2H_4C_5Me_4)(\eta^2,\eta^2\text{-}1,6\text{-}C_7H_{12})Co]^+BF_4^-$ (**23**)

A solution of (cyclo-$C_4H_8NC_2H_4C_5Me_4$)(1,6-C_7H_{12})Co (**9**, 0.27 g, 0.72 mmol) in diethyl ether (20 ml) was treated at 0°C with ethereal solution of HBF_4 (0.10 ml of a 54% solution, 0.72 mmol). An orange precipitate formed which was stirred for 16 h at r.t. The reaction mixture was evaporated to dryness and the residue washed with pentane and extracted with acetone. The compound was precipitated as an orange solid out of the acetone solution by the addition of diethyl ether (2–3 ml). Yield: 0.32 g (96% theory). Elemental analysis: see Table 3. IR (KBr): ν 3176, 3039, 2969, 2920, 1458, 1080. MS (ESI): *m*/*e* 374 (M^+, 80%), 218. ^{13}C-NMR spectrum: see Table 2; the compound is contaminated by small amounts of a second compound whose NMR spectrum suggests the presence of η^3-1,3-$R_2C_3H_3$ groups.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 141200 (**5**) and no. 141199 (**17**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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