# Reaction Chemistry of the Carbenoid Butadienyl Complex Ion $[CpCo(\sigma,\eta^4\text{-}C_4HMe_4)]^+$ Formed by Protonation of the Cyclobutadiene Complex $[CpCo(C_4Me_4)]$

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The protonation of $[CpCo(C_4Me_4)]$ (**1**) with excess acid, which produces the carbenoid ion $\mathbf{3}^+$, is shown to be reversible under conditions of low proton activity. Treatment of $\mathbf{3}^+$ with *one equivalent* of $NEt_3$ mainly produces **1** (60 %, isolated yield), and in DMSO the solvent acts as base transforming $[\mathbf{3}]BF_4$ into **1** (67 %, isolated yield). Deprotonation of $[\mathbf{3}]BF_4$ with *excess* $NEt_3$ affords (cyclopentadienyl)[(2–5-η)-(3Z,4Z)-3,4-dimethylhexa-1,2,4-triene]cobalt (**5**) in high yield (83 %). The structure of **5** has been determined by X-ray work. In the reaction of $\mathbf{3}^+$ with pyridine four reaction channels could be unveiled by low-temperature NMR spectroscopy: i) Reversible deprotonation to form **5** in a kinetic shunt; ii) reversible nucleophilic addition at the carbenoid center to form a pyridinium ion complex $\mathbf{6}^+$ as a low-temperature species with a terminal *anti*-Me group; iii) irreversible isomerization of $\mathbf{6}^+$ to the more stable stereoisomer $\mathbf{7}^+$ with a terminal *syn*-Me group; iv) very slow formation of **1**. Using very high concentrations of pyridine (mixing at –60 °C, slowly warming to 20 °C) allowed the preparation of $[\mathbf{7}]BF_4$ in near quantitative yield (97 %). The pyridine rings in $\mathbf{6}^+$ and $\mathbf{7}^+$ display hindered rotation (NMR), and the structure of $[\mathbf{7}]CF_3SO_3$ shows considerable steric crowding. On treatment with a large excess of $CF_3CO_2H$ ( ≥ 7 equiv.) the hexatriene complex **5** quantitatively reverts to the carbenoid $\mathbf{3}^+$. Reaction of **5** with $(C_5H_5NH)CF_3SO_3$ (–80 °C, 3 weeks) produced $[\mathbf{6}]CF_3SO_3$ with retention of the stereochemistry at C-4 (NMR), while the same reaction at ambient temperature and in presence of a large excess of pyridine is accompanied by stereoisomerization and afforded $[\mathbf{7}]CF_3SO_3$ (94 %). Nucleophilic addition of excess $PPh_3$ to $\mathbf{3}^+$ gave a phosphonium salt $[\mathbf{8}]BF_4$, again with stereoisomerization, in near quantitative yield (98 %). Addition of CN*t*Bu with concomitant rearrangement produced a (*tert*-butylamino)cobaltocenium salt $[\mathbf{9}]CF_3SO_3$ (90 %). Nucleophilic substitution of the pyridine moiety of $\mathbf{7}^+$ with 4-picoline gave the 4-picoline addition product $[\mathbf{10}]CF_3SO_3$ (96 %). With $CN^-$ a hexa-2,4-dienenitrile complex $[CpCo(\eta^4\text{-}C_4HMe_4CN)]$ (**11**) was obtained (85 %), which on protonation gave an aminocobaltocenium ion $[CpCo\{C_5Me_4(NH_2)\}]^+$ ($\mathbf{12}^+$), isolated as $[\mathbf{12}]BF_4$ (94 %). Acid removes the pyridine moiety from $\mathbf{7}^+$ to produce a carbenoid ion $\mathbf{13}^+$ with a 4-Me group in *syn*-position (a stereoisomer of $\mathbf{3}^+$) which was characterized by NMR spectroscopy. Deprotonation of $\mathbf{13}^+$ affords a hexatriene complex **14** (a stereoisomer of **5**) in good yield (57 %). Thermolyses of **5** and **14** show that **14** is the lower-energy isomer and produce a dinuclear complex $[(\mu\text{-}C_5H_3Me_3)(CoCp)_2\textit{(Co–Co)}]$ (**15**) (91 %) with a bridging penta-2,4-dienylidene ligand.



## Introduction

In an earlier communication[1] we described the protonation of (cyclopentadienyl)(tetramethylcyclobutadiene)cobalt [CpCoCb*] (Cb* = $C_4Me_4$) (**1**).[1,2] According to a DFT study this protonation takes place from the *endo*-side to give a primary agostic intermediate $\mathbf{2}^+$. This intermediate rearranges by way of a stereospecific ring-opening reaction to give a carbenoid cation $\mathbf{3}^+$ with a $\sigma,\eta^4$-butadienyl substructure and an *anti*-Me group. While $\mathbf{2}^+$ has not been observed experimentally, the rearranged cation $\mathbf{3}^+$ was isolated as tetrafluoroborate in quantitative yield (97%) and has fully been characterized.[1]

If this protonation reaction is performed with a large excess of acid (for instance with 9 equivalents of $HBF_4$ in $Et_2O$ at –50 °C or in neat $CF_3CO_2H$), product formation is fast and clean. At lower proton activity some solid material is formed, possibly by some decomposition processes. These observations suggest that the protonation reaction of **1** might be reversible, but only in this paper can we present straightforward experimental evidence for the reversibility of the sequence $\mathbf{1} \rightarrow \mathbf{2}^+ \rightarrow \mathbf{3}^+$.

The carbenoid cation $\mathbf{3}^+$ is a highly reactive species. At temperatures above –10 °C it undergoes thermal rearrangement with formation of [(cyclopentadienyl){$\eta^5$-(2*Z*,3*Z*,4*E*)-

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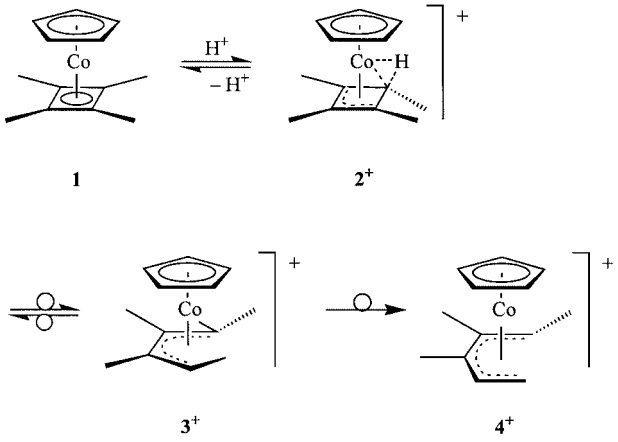



Scheme 1. Primary protonation equilibrium/rearrangement.

3,4-dimethylhexa-2,4-dienyl}cobalt] cation (**4**$^+$), a half-open cobaltocenium ion. This chemistry is summarized in Scheme 1.[1]

Early papers on (cyclobutadiene)(cyclopentadienyl)cobalt derivatives describe electrophilic H/D-exchange as well as some other electrophilic aromatic substitution reactions as characteristic reactions in this family of complexes,[3] the most notable examples being the parent complex [CpCo($C_4H_4$)][4] and the tetraphenyl derivative CpCo($C_4Ph_4$).[5] The boratabenzene analogue of **1**, [Cb*Co($C_5H_5BMe$)],[6] which is less electron-rich than **1**, displays similar reactivity with very fast H/D exchange, but ring opening of the Cb* ring has never been observed. We conclude that only the most electron-rich complexes of the [CpCoCb]-type can undergo the protonation/rearrangement sequence of Scheme 1.

Complexes with σ,η$^4$-butadienyl-type ligands are known in some variety, for instance of the fragments CpRu,[7] Cp*Ru,[8] CpRe,[9] and CpMo[10] as well as of other complexes of Nb,[11] Mo,[12] and W.[12] To the best of our knowledge, cation **3**$^+$ is the first such complex of a 3d metal. Since the ion **3**$^+$ originates from a protonation reaction, it seemed particularly interesting to study its reactions with bases and/or nucleophiles. During our work, it quickly turned out that the reactions of **3**$^+$ depend in a subtle manner on the nature of the attacking reagents and on the reaction conditions. In this paper we describe the deprotonation of **3**$^+$, conditions which result in a reversal of the ring opening of complex **1** (in Scheme 1), furthermore nucleophilic addition to **3**$^+$, and some closely related chemistry of the products obtained.

## Results and Discussion

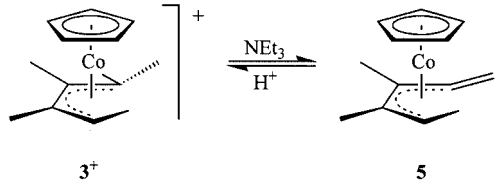
### Deprotonation of the Carbenoid Complex 3$^+$

Reaction of [**3**]$BF_4$ in dichloromethane with a large excess of triethylamine effects deprotonation and produces (cyclopentadienyl)[(2–5-η)-(3*Z*,4*Z*)-3,4-dimethylhexa-1,2,4-triene]cobalt (**5**). For instance, an NMR experiment with a 1:5 ratio of the reactants showed the formation of the hexatriene complex **5** as the sole complex product and of $NHEt_3^+$; no further change was seen at ambient temperature after 16 h. Preparative runs yielded **5** as air-sensitive, low-melting, orange-red crystals. Other strongly basic reagents, as for instance allylmagnesium chloride in ether, gave the same product **5**. Note that **5** is an isomer of **1**, but does not spontaneously convert to **1** under the conditions given here.

$^1$H NMR spectra of **5** show that the terminal MeCH= moiety of **3**$^+$ with an *anti*-Me group is retained in **5** and that one methyl group is now replaced with a noncoordinated methylene function. This result was later confirmed by a single-crystal structure determination (see below). Marked C–H acidity at a carbon atom ß to a carbene center is well known for Fischer carbene complexes,[13] and has previously been observed for some of the known σ,η$^4$-butadienyl complexes.[10,14]

When **3**$^+$ was deprotonated with $NEt_3$ in a 1:1 ratio, i.e. under conditions where a low proton activity is retained, some unidentified solid material was deposited. The $^1$H NMR of the solution, recorded without delay, indicated the presence of two complex products, the hexatriene complex **5** and the cyclobutadiene complex **1** in roughly a 1:1 ratio. Upon standing at ambient temperature, the concentration of **1** grew at the expense of **5**, and after 16 h, complex **1** had become the sole complex product. Conventional workup of the NMR tube contents including chromatography on alumina with hexane as eluent afforded a 60% yield of spectroscopically pure **1**. In a related experiment [**3**]$BF_4$ was dissolved in $CH_2Cl_2$/DMSO (2:1, v/v) and kept at 30 °C for 30 min; in this case the basicity of the medium is sufficient to allow the transformation of **3**$^+$ into complex **1** which was isolated in 67% yield.

These observations imply reversibility of the deprotonation of **3**$^+$ (Scheme 2) and of the ring-opening reaction of **1** (Scheme 1). Protonation of **5** by protic reagents other than the relatively weak acid $NHEt_3^+$ will be described below.




Scheme 2. Protonation/deprotonation equilibrium.

We summarize and conclude: i) In strongly acidic medium the stable complex species is the carbenoid ion **3**$^+$ which is formed either from the cyclobutadiene complex **1** (Scheme 1)[1] or from the hexatriene complex **5** (Scheme 2). ii) In strongly basic medium, i.e. with a large excess of base or with strong bases, a kinetically controlled deprotonation of **3**$^+$ affords the hexatriene complex **5**. iii) Under conditions of low, but noticeable proton activity reversibility comes into play. The product now is the cyclobutadiene complex **1**, both in the reaction of **3**$^+$ with bases and in the

protonation of **5**; thus the cyclobutadiene complex **1** is seen to be thermodynamically more stable than its isomer **5**.

### Structure of 5

The structure of **5** was determined by single-crystal X-ray diffraction (Figure 1) and confirms the presence of an $\eta^4$-bonded vinylallene-type ligand and the *anti*-position of the terminal Me group. Related structures are known for $[Fe(CO)_3]$[16] and CpRu compounds[14c] and a $[RhCl(PPh_3)]$ complex.[17] We note the short bond length C3–C4 [1.408(11) Å] of the central diene bond, which is now shorter than the former diene double bonds C2–C3 [1.449(9) Å] and C4–C5 [1.438(11) Å], furthermore the remarkably short bond length Co–C2 [1.883(5) Å], and the bond angle C1–C2–C3 [137.2(6)°]; the methyl group at C5 is bent away from the metal. These details are all indicative of pronounced metal-to-ligand back-bonding, as expected for a complex which belongs to the CpCo(diene) family in a broad sense.

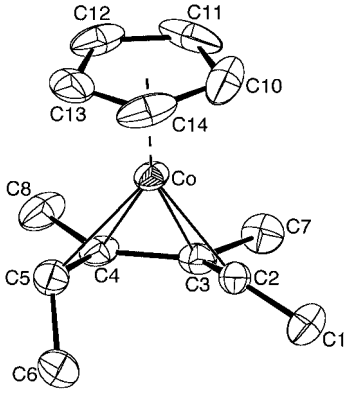


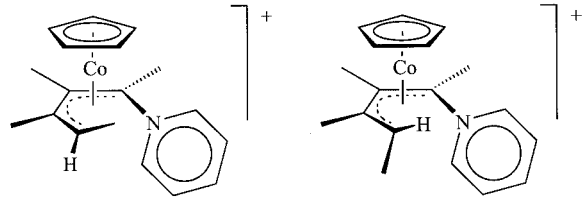

Figure 1. Molecular structure of **5** in the crystal (PLATON plot[15] at the 30% probability level); selected bond lengths (Å) and angles (°): Co–C2 1.883(5), Co–C3 1.988(5), Co–C4 1.979(5), Co–C5 2.050(6), Co–C(Cp) 2.053 (av.), C1–C2 1.316(8), C2–C3 1.449(9), C3–C4 1.408(11), C4–C5 1.438(11); C1–C2–C3 137.2(6), C4–C5–C6 126.3(6), C2–C3–C4–C5 9.5, C3–C4–C5–C6 56.3, C1–C2–C3–C4 147.1.

### Nucleophilic Addition to the Carbenoid Complex $3^+$

In this chapter we describe nucleophilic addition reactions which are the preferred reactions for weak bases such as pyridine, $PPh_3$, and CN*t*Bu. The case of pyridine addition, which revealed an unexpected complexity of the reaction system, was investigated by means of low-temperature NMR experiments and by varying the substrate/base ratio.

#### *Addition of Pyridine*

In one NMR tube experiment pyridine (1 equiv.) was added to a solution of $[\mathbf{3}]BF_4$ in $CD_2Cl_2$ at –80 °C and the reaction mixture was kept at this temperature for several days. Four different cobalt complexes were observed as products: i) The hexatriene complex **5**, ii) a primary addition product $[\mathbf{6}]BF_4$, iii) an isomeric addition product $[\mathbf{7}]BF_4$, and iv) the cyclobutadiene complex **1**. In the early stages of the reaction (up to 30 h) the major product was the hexatriene complex **5**; after 30 h at –80 °C the product ratios (normalized to 100%) were $\mathbf{5}:\mathbf{6}^+:\mathbf{7}^+:\mathbf{1}$ = 53:37:8:2. Later the primary addition product $\mathbf{6}^+$ grew at the expense of **5** and amounted to 80% of the product mixture after 7 days; the product ratios now were $\mathbf{5}:\mathbf{6}^+:\mathbf{7}^+:\mathbf{1}$ = 5:80:10:6. It is remarkable that **1** already appears at –80 °C with its concentration very slowly increasing with time at this temperature.




$\mathbf{6}^+$ $\mathbf{7}^+$

In a second NMR tube experiment the temperature of the reaction mixture ($\mathbf{3}^+/C_5H_5N$, 1:1) was increased in steps of 10 K. Under these conditions the hexatriene complex **5** was the major product up to –60 °C, but had disappeared completely below –30 °C. The primary addition product $\mathbf{6}^+$ reached its maximum concentration at –30 °C. At higher temperatures the concentration of **1** grew quickly at the expense of $\mathbf{6}^+$; at 10 °C ratios of $\mathbf{5}:\mathbf{6}^+:\mathbf{7}^+:\mathbf{1}$ = 0:0:14:86 were observed. A similar experiment with a higher pyridine concentration ($\mathbf{3}^+/C_5H_5N$, 1:7) differed in two respects. Above –50 °C the isomerization $\mathbf{6}^+ \rightarrow \mathbf{7}^+$ was clearly seen and was the main process above –25 °C, while the formation of **1** was markedly slowed down; at 10 °C ratios of $\mathbf{5}:\mathbf{6}^+:\mathbf{7}^+:\mathbf{1}$ = 0:1.5:76:23 were reached. In all these experiments the primary addition product $\mathbf{6}^+$ seemed to be the sole source for the formation of **1**. We may conclude i) that the pyridine addition to $\mathbf{3}^+$ is reversible allowing the formation of **1**, and ii) that the isomerization $\mathbf{6}^+ \rightarrow \mathbf{7}^+$ is an irreversible reaction (Scheme 3).


Scheme 3. Pyridine addition equilibrium and stereoisomerization.

The primary addition product $[\mathbf{6}]BF_4$ could, of course, only be characterized by its $^1H$ NMR and $^{13}C$ NMR spectra. For the preparation of the more stable isomeric addition product $[\mathbf{7}]BF_4$ a very high concentration of pyridine $[CH_2Cl_2/C_5H_5N$ , 1:1 (v/v)] has to be used. Mixing the reagents at –60 °C effected an immediate color change from dark red to orange-red; while the temperature was slowly increased the color began to deepen and was burgundy at ambient temperature. From this solution the product was isolated in near quantitative yield.

The $^1H$ NMR spectra of the isomeric ions $\mathbf{6}^+$ and $\mathbf{7}^+$ are rather similar, but differ conspicuously in the doublet/quartet pattern of the terminal MeCH= moiety [for $\mathbf{6}^+$: $\delta$ = –0.49 ppm (d, $J$ = 7.6 Hz, 4-Me) and 3.76 ppm (q, $J$ = 7.6 Hz, 4-H); for $\mathbf{7}^+$: $\delta$ = 1.18 (d, $J$ = 6.1 Hz, 4-Me) and –0.37 ppm (q, $J$ = 6.1 Hz, 4-H)]. These data show that $\mathbf{6}^+$

still possesses an *anti*-Me group (with a negative chemical shift) which has become a *syn*-Me group in **7**$^+$. This result is in agreement with the structure determination of [**7**]$CF_3SO_3$ (see below). In contrast to **6**$^+$ the cation **7**$^+$ displays an additional long-range coupling ($^4J$ = 0.7 Hz) between the proton 4-$H_{anti}$ and the methyl group 3-Me which are in a zigzag arrangement in this isomer. Both ions **6**$^+$ and **7**$^+$ display separate signals for the proton pairs 2-H/6-H and 3-H/5-H of the pyridine ring. This indicates hindered rotation of the pyridine ring. When the solution of [**7**]$BF_4$ in $MeNO_2$ was warmed, five sharp lines were observed up to 50 °C; at higher temperatures the spectra deteriorated due to decomposition, but even at 80 °C five signals were seen. Hindered rotation of pyridine ligands has occasionally been observed, albeit only at low temperatures.[18] We comment on the origin of this barrier in the context of the structure description of the structure of [**7**]$CF_3SO_3$.

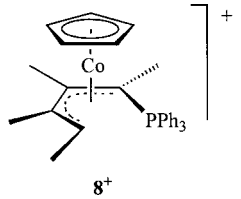
We noted above that low concentration of pyridine and higher temperatures favor the formation of the cyclobutadiene complex **1** while very high concentrations of pyridine favor the stereoisomerization **6**$^+$ → **7**$^+$. Excess pyridine and low temperature will suppress the dissociation of the primary addition product **6**$^+$ → **3**$^+$ and hence the formation of **1** (cf. Scheme 1 and Scheme 3). As a consequence, the slow stereoisomerization can come into play. Note also, that in the preparation of [**7**]$BF_4$ mixing at low temperature and slow warm up are features which are essential for the excellent yields obtained. We consider this interpretation as the most likely one. However, in the absence of kinetic data we cannot exclude that pyridine does actively participate in the stereoisomerization; in such a case high pyridine concentrations would directly accelerate the formation of **7**$^+$.

### *Addition of Triphenylphosphane*

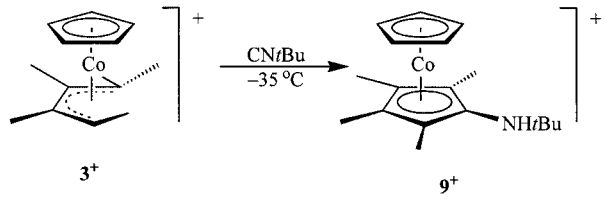
Under the same reaction conditions used for the preparation of [**7**]$BF_4$, the carbenoid complex [**3**]$BF_4$ reacts with excess $PPh_3$ (7 equiv.) to undergo nucleophilic addition, again with stereoisomerization of the diene chain. The resulting complex phosphonium ion **8**$^+$ was isolated as tetrafluoroborate [**8**]$BF_4$ in quantitative yield. The ion **8**$^+$ has a remarkably small direct coupling constant $^1J_{PC}$ = 46.0 Hz as has the related ion [CpCo{$\eta^4$-$C_4HPh_4(PPh_3)$}]$^+$ ($^1J_{PC}$ = 36.6 Hz).[19] If only 1 equivalent of $PPh_3$ was used the familiar complications appeared again: Formation of **1** and of insoluble material. Trimethylphosphane reacted unselectively to produce several unidentified [CpCo($PMe_3$)] species (NMR).

### *Addition of tert-Butyl Isocyanide*

The reaction of [**3**]$CF_3SO_3$ with CN*t*Bu is fast at –35 °C, showing a fast color change from dark red to yellow, and produced the (*tert*-butylamino)cobaltocenium derivative [**9**]$CF_3SO_3$ (Scheme 4). The new cobaltocenium ion was readily identified and characterized by its simple NMR spectra which show effective lateral symmetry for the cation. This fascinating ring formation has precedence in M. Green's chemistry,[19] and will be discussed below.




**8**$^+$




**3**$^+$ **9**$^+$

Scheme 4. Reaction with CN*t*Bu.

### Protonation of the Hexatriene Complex 5

The protonation of **5** (Scheme 2) had first been deduced from the evolution of the system **3**$^+$/$C_5H_5N$ with time, but can be confirmed by independent experiments. Indeed, when **5** was treated with a large excess $CF_3CO_2H$ (≥ 7 equiv., NMR tube experiment), the reverse protonation reaction took place and produced **3**$^+$ in a very clean reaction; no species other than **3**$^+$ and $CF_3CO_2H$ were seen. With only stoichiometric quantities (**5**/$CF_3CO_2H$, 1:1) we found again formation of **1** and of insoluble material.

The protonation of **5** by the pyridinium salt ($C_5H_5NH$) $CF_3SO_3$ in $CD_2Cl_2$ was monitored by low-temperature NMR spectroscopy. When the reaction mixture was kept at –80 °C, the main process was the slow formation of [**6**]$CF_3SO_3$, and both [**7**]$CF_3SO_3$ and **1** remained trace products. After 3 weeks at –80 °C the product ratios were **5**:**6**$^+$:**7**$^+$:**1** = 0:93:5:2. In contrast to this low-temperature situation, the synthetic version of this experiment required high concentrations of pyridine in $CH_2Cl_2$ (4:6 v/v) to ensure high chemoselectivity, and at ambient temperature afforded the complex triflate [**7**]$CF_3SO_3$ in excellent yield (94%).

### Structure of [7]$CF_3SO_3$

The structure determination of [**7**]$CF_3SO_3$ confirms the constitution of **7**$^+$ and specifically the *syn*-position of the Me group at C4 (in chemical notation C-4′) and the *anti*-stereochemistry of the pyridinio substituent at C1 (Figure 2). Thus, the cation **7**$^+$ is a CpCo(diene) derivative with the unusual feature of a positively charged substituent in the terminal *anti*-position of the diene ligand. The short central bond of the diene substructure [C2–C3 1.384(4) Å] and the long former double bonds [C1–C2 1.441(3) and C3–C4 1.443(4) Å] show again that metal-to-diene back bonding is rather pronounced as in **5**. We also note that the bond N–C1 [1.498(3) Å] is longer than expected. A search in the CSD database[20] for structures with comparable ge ometry[21] resulted in 692 hits with an average C–N distance

of 1.392(1) Å; only six of the 692 matches showed a C–N distance longer than the one observed in **7**$^+$. We explain the unusual length of the N–C1 bond by a steric labilization caused by two short interactions between the pentadienyl chain and the pyridinium N atom, namely N···H5–C5 of 2.61 and N···H4–C4 of 2.19 Å. Of course, we cannot exclude an additional electronic effect due to the neighboring metal center.

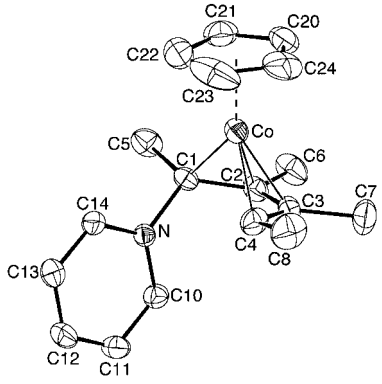



Figure 2. Structure of the ion **7**$^+$ in the crystal of [**7**]$CF_3SO_3$ (PLATON plot[15] at the 30% probability level); selected bond lengths (Å) and angles (°): Co–C1 1.975(2), Co–C2 1.971(2), Co–C3 1.966(3), Co–C4 2.053(3), Co–C(Cp) 2.057 (av.), N–C1 1.498(3), C1–C2 1.441(3), C2–C3 1.384(4), C3–C4 1.443(4); C2–C1–N 118.5(2), C2–C1–C5 120.8(2), N–C1–C5 106.31(19); C1–C2–C3–C4 2.1, N–C1–C2–C3 59.0, C5–C1–N–C10 100.6, C5–C1–N–C14 76.6.

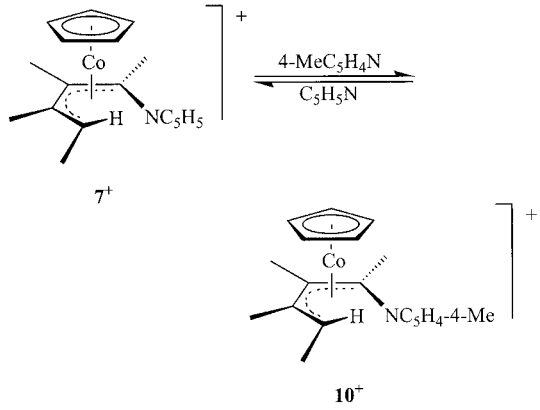
If the (trimethylpentadienyl)pyridinium ligand of **7**$^+$ were planar we would have a prohibitively strong repulsive 1,6-interaction between a C atom in the *ortho*-position of the pyridinium ring and C4 of the pentadienyl chain. In the structure this 1,6-interaction is reduced by a bending of the ring out of the pentadienyl plane and away from the metal [dihedral angle N–C1–C2–C3 59.0°] and by a near orthogonal rotational position of the ring. This situation explains the unusually high barrier to internal rotation of the pyridine ring which is seen in the NMR spectra.

## Nucleophilic Substitution of the Pyridine Moiety of 7$^+$

In the system **3**$^+$/pyridine we had observed the slow formation of the cyclobutadiene complex **1** from the pyridine addition product **6**$^+$, most likely via the carbenoid ion **3**$^+$ (cf. Scheme 1 and Scheme 3). Given the low thermal stability of **6**$^+$, it would be difficult to verify the reversibility of the pyridine addition to **3**$^+$ directly. However, the more stable isomer **7**$^+$ is prone to reactions which suggest that pyridine can dissociate from the complex.

### *A Pyridine/4-Picoline Exchange Reaction*

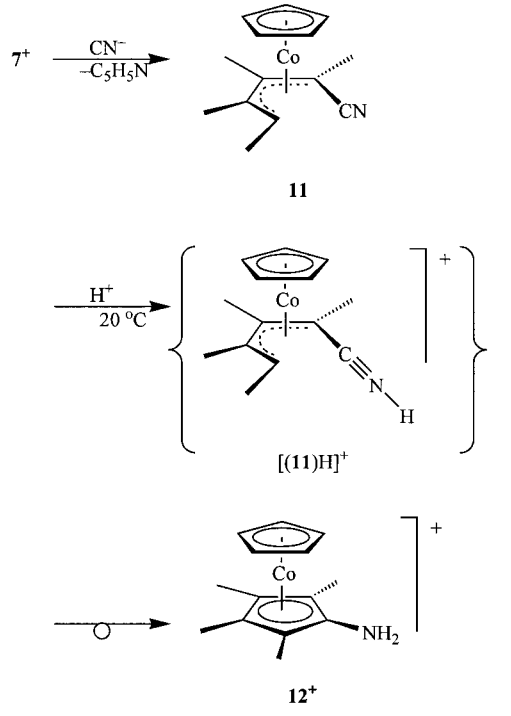
When 4-picoline (4-methylpyridine) was added to a solution of [**7**]$CF_3SO_3$ in $CD_2Cl_2$ a new species **10**$^+$ was seen in a slow exchange reaction at ambient temperature (NMR, two Cp signals) with a slight preference of **3**$^+$ for 4-picoline over pyridine (Scheme 5). The pure 4-picoline addition product [**10**]$BF_4$ could be prepared in $CH_2Cl_2$ by repeated removal of the volatiles and addition of fresh $CH_2Cl_2$ and 4-picoline.




Scheme 5. Pyridine/4-picoline exchange.

### *Substitution Reaction of 7$^+$ with Cyanide*

Attempted nucleophilic addition of cyanide to **3**$^+$ produced the hexatriene complex **5** because of the high basicity of $CN^-$ in an aprotic medium. However, the reaction of **7**$^+$ with $(NBu_4)CN$ resulted in a smooth substitution of pyridine with cyanide and afforded the neutral complex **11** as a robust crystalline compound (Scheme 6). This nitrile **11** could readily be protonated in an NMR tube experiment. The reaction with $CF_3CO_2H$ (3 equiv.) in $CD_2Cl_2$ effected a fast color change from red to yellow. The cation so formed was precipitated from aqueous solution as hexafluorophosphate [**12**]$PF_6$ (Scheme 6). A synthetically more




Scheme 6. Cyanide reaction, protonation, rearrangement.

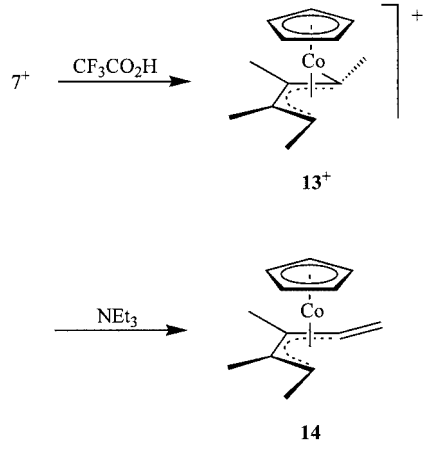
convenient reaction with $HBF_4$ in ether afforded [**12**]$BF_4$ in near quantitative yield. Mechanistically, this transformation is thought to involve protonation at the nitrilic nitrogen of **11** forming a nitrilium intermediate [(**11**)H]$^+$, which by way of an electrocyclic ring closure and subsequent proton migration rearranges into the aminocobaltocenium cation **12**$^+$. Details of the metal-participation involved and potential further intermediates must at present remain undefined.

### *Substitution Reaction of 7$^+$ with tert-Butyl Isocyanide*

Isocyanides are much less basic than cyanide ion. Therefore, the direct nucleophilic addition of CN*t*Bu to **3**$^+$ described above was feasible. We then found that [**7**]$CF_3SO_3$ also reacts with CN*t*Bu, though much slower than **3**$^+$, and also gave the (*tert*-butylamino)cobaltocenium derivative [**9**]$CF_3SO_3$. Both reactions, that of CN*t*Bu with **3**$^+$ (Scheme 4) and that with **7**$^+$ follow the same mechanistic pattern exemplified Scheme 6.

### Abstraction of Pyridine from the Pyridinium Ion 7$^+$

The demonstrated lability of the pyridine moiety in **7**$^+$ suggested that acid should be able to remove pyridine from **7**$^+$, thereby producing the carbenoid ion **13**$^+$, the alternative stereoisomer of **3**$^+$. Indeed, treatment of the triflate [**7**]$CF_3SO_3$ with a large excess of $CF_3CO_2H$ (1:7) at ambient temperature resulted in the formation of **13**$^+$ and pyridinium ion $C_5H_5NH^+$ (Scheme 7). The new complex ion is labile and decomposes above –20 °C. It could be characterized by its NMR spectra by recording the spectra a few minutes after mixing the reagents. The $^1$H NMR spectra of **13**$^+$ and **3**$^+$ are remarkably similar, except for the doublet/quartet patterns of the terminal MeCH= moiety [for **13**$^+$: $\delta$ = 2.37 (d, $J$ = 6.6 Hz, 4-Me) and 3.13 ppm (q, $J$ = 6.6 Hz, 4-H); for **3**$^+$: $\delta$ = 0.55 (d, $J$ = 6.7 Hz, 4-Me) and 6.49 ppm (q, $J$ = 6.7 Hz, 4-H)] which readily distinguish the two stereoisomers. In the $^{13}$C NMR spectrum of **13**$^+$ a signal at very high chemical shift [for **13**$^+$$\delta$ = 288.4 and for **3**$^+$$\delta$ = 292.1 ppm] indicates the presence of a carbenoid center at C-1 as in **3**$^+$, and small shifts to lower chemical shifts for 3-Me, C-4, and C-5 reflect the presence of steric strain in **3**$^+$, but not in **13**$^+$.




Scheme 7. Reaction with acid / deprotonation.

One would expect that the new isomer **13**$^+$ should be amenable to deprotonation in the same way that was successful in the case of **3**$^+$. To verify this expectation [**7**]$BF_4$ was treated with excess of $CF_3CO_2H$ (1:8) and subsequently with a very large excess of $NEt_3$. Workup afforded the hexatriene complex **14** (57%), the alternative stereoisomer of **5**, as a low-melting red solid (Scheme 7). As may be verified by inspection, the NMR spectra of **14** and **5** are largely similar and, as discussed above in detail for the pair **13**$^+$/**3**$^+$, allow a straightforward distinction of the respective stereochemistries.

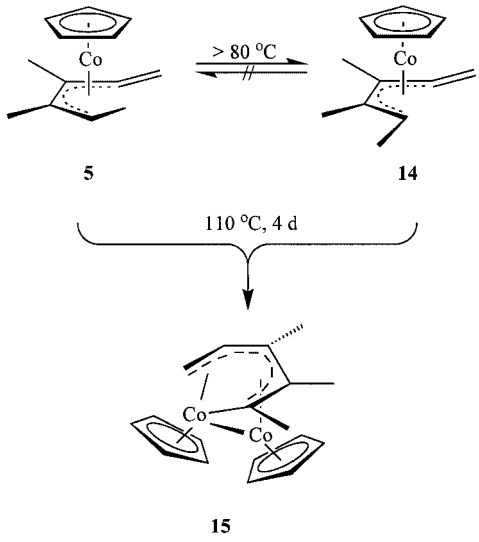
### Thermolysis Reactions of the Hexatriene Complexes 5 and 14

It is intuitively clear that complex **14** with its terminal methyl group in *syn* position should be more stable than its stereochemical counterpart **5** with a terminal *anti*-Me group. Experimental support for this notion comes from the thermal behavior of **5**. Monitoring a solution of **5** in [$D_8$]-toluene showed the onset of a slow thermolysis reaction around 80 °C. Complex **5** partially isomerized to produce its stereoisomer **14**, and partially decomposed with formation of a new dinuclear complex **15** and free olefins. After three days at 80 °C the molar product ratio amounted to **5**:**14**:**15** = 2.8:3.4:4.8 and after seven days it was 0.3:4.2:6.1. This result demonstrates that **14** is indeed more stable than **5**. Unfortunately it was not possible to selectively produce the isomer **14** by a meticulous choice and control of the reaction temperature. A stereoisomerization related to the transformation **5** → **14** has been described for vinylallene complexes of the [RhCl($PPh_3$)] fragment.[17] M. Murakami et al. argue that the isomerization occurs via a 14e complex with a 2,5-$\sigma^2$-coordinated vinylallene (1,2,4-pentatriene) ligand and present an example where this arrangement becomes the groundstate of the molecular system. Most likely the isomerization **5** → **14** follows the same path.

Thermolysis of **14** in [$D_8$]toluene was found to be markedly slower and again produced the dinuclear complex **15** and free olefins. Complex **5** was not found in the product mixtures. For the practical synthesis of **15** the more readily accessible complex **5** was used as starting material. Heating **5** in toluene at 110 °C for 4 days gave, after workup, **15** as black crystals in high yield (91%) (Scheme 8).

The $^1$H NMR spectrum of **15** displayed two singlets of equal intensity for two CoCp moieties, three doublets of doublets for a coordinated vinyl group, and three singlets for methyl groups. These observations suggested the presence of a 1,2,3-trimethylpenta-2,4-dien-1-ylidene ligand in a dinuclear complex. The $^{13}$C NMR spectrum of **15** was in agreement with this conclusion, and the signal with the highest chemical shift ($\delta$ = 166.1 ppm) indicated that the ylidene carbon was in a bridging position between the two metal centers. It was then found that complexes of this type have previously been obtained from the thermolysis of (cyclopentadienyl)[(1–4-η)-(2Z,3*E*)-1,3,5-hexatriene]cobalt and have structurally been characterized.[22]




Scheme 8. **5** → **14** + **15** and **14** → **15** at higher temperature.

## Conclusion

In this paper we have demonstrated that the carbenoid complex ion **3**$^+$ can react to give the cyclobutadiene complex **1**. Thus we have now a kind of acid/base equilibrium between **1** and **3**$^+$ as already expressed in Scheme 1. According to our earlier theoretical analysis by means of DFT calculations the forward reaction consists of a protonation step followed by a ring-opening step.[1] The principle of microscopic reversibility suggests that the reverse transformation begins with a ring closure (**3**$^+$ → **2**$^+$), and subsequent deprotonation (**2**$^+$ → **1**) gives the cyclobutadiene complex **1**.

As we have seen the experimental situation is much more complicated. i) At temperatures above –20 °C the acid **3**$^+$ rearranges irreversibly to give the half-open cobaltocenium ion **4**$^+$ (Scheme 1). ii) Bases effect reversible deprotonation of **3**$^+$ with formation of the hexatriene complex **5** (Scheme 2) at a rate which is higher than the rate of the reverse reaction of Scheme 1; alternatively they may undergo competing nucleophilic addition reactions (Scheme 3). iii) The formation of **3**$^+$ from **1** is a clean reaction only under strongly acidic conditions. Likewise the formation of **5** from **3**$^+$ is a clean reaction only under strongly basic conditions. Whenever the acid **3**$^+$ is allowed to coexist for some time (minutes to several hours at ambient temperature) with its deprotonated forms (**1** or **5**) we observed undefined decomposition.

The irreversible isomerization of the low-temperature pyridine addition product **6**$^+$ with formation of the more robust stereoisomer **7**$^+$ (Scheme 3) opened a route to sterically less crowded complexes with the terminal methyl group in *syn*-position. Thus we have pairs of stereoisomers, the pyridine addition products **6**$^+$ and **7**$^+$, the carbenoid complex ions **3**$^+$ and **13**$^+$, and the hexatriene complexes **5** and **14**. In the cases **6**$^+$/**7**$^+$ and **5**/**14**, the species with the *syn*-Me group are the more stable isomers, in agreement with expectation.

## Experimental Section

**General:** All manipulations were carried out under nitrogen by means of standard Schlenk techniques. THF and $Et_2O$ were distilled from sodium benzophenone ketyl and $CH_2Cl_2$ was distilled from $CaH_2$. Hexane was distilled from potassium and toluene from sodium. Alumina for chromatography was deactivated with 5% water. Elemental analyses were performed by Analytische Laboratorien, 51789 Lindlar, Germany. Melting points were determined with a Büchi 510 melting point apparatus and are uncorrected. NMR spectra were recorded with a Varian 200 ($^1$H, 200.0 MHz; $^{13}$C{$^1$H}, 50.29 MHz; $^{31}$P{$^1$H}, 80.96 MHz), with a Varian Unity 500 ($^1$H, 499.6 MHz; $^{13}$C, 125.6 MHz; $^{31}$P{$^1$H}, 202.2 MHz) or with a Varian Inova 400 ($^1$H, 400.0 MHz; $^{13}$C, 100.6 MHz). Chemical shifts are given in ppm; they were measured at ambient temperature and are referenced to internal TMS for $^1$H and $^{13}$C, and relative to $H_3PO_4$ (85%) as external reference for $^{31}$P. IR spectra were measured with a Nicolet Avatar 360 FT-IR instrument.

**Deprotonation of [3]BF$_4$ and Synthesis of (Cyclopentadienyl)[(2–5-η)-(3*Z*,4*Z*)-3,4-dimethylhexa-1,2,4-triene]cobalt (5):** Triethylamine (20 mL) was added to [**3**]$BF_4$ (1.28 g, 4 mmol) in $CH_2Cl_2$ (30 mL) at –60 °C. The color of the solution changed immediately from deep wine-red to orange. After dilution with hexane (150–200 mL) the reaction mixture was filtered through a short column of alumina at –80 °C. Thorough removal of all volatiles under vacuum left **5** (0.775 g, 83%) as orange-red crystalline product. The product was recrystallized by cooling $Et_2O$ or hexane solutions to –80 °C; m.p. 37–39 °C. $C_{13}H_{17}Co$ (232.21): calcd. C 67.24, H 7.38; found C 67.07, H 7.42. $^1$H NMR (500 MHz, $CD_2Cl_2$): $\delta$ = 0.47 (d, $J$ = 7.02 Hz, 5-Me), 1.83 (s, 3-Me), 2.09 (s, 4-Me), 3.37 (q, $J$ = 7.02 Hz, 5-H), 4.68 (s, Cp), 4.72 (d, $J$ = 2.14 Hz, 1-H$_{anti}$), 4.95 (d, $J$ = 2.14 Hz, 1-H$_{syn}$) ppm. $^{13}$C{$^1$H} NMR (126 MHz, $CD_2Cl_2$): $\delta$ = 17.9 (3-Me), 18.5 (5-Me), 21.1 (4-Me), 49.4 (C-5), 77.2 (C-3), 82.6 (Cp), 97.5 (C-1), 99.0 (C-4), 175.6 (C-2) ppm.[23]

**Deprotonation of 3$^+$ by an Allyl Grignard Reagent:** Allylmagnesium chloride (0.87 mL, 1.74 mmol, 2 M solution in THF) was added with stirring to [**3**]$BF_4$ (279 mg, 0.87 mmol) in $CH_2Cl_2$ (20 mL) at –90 °C. After warming to ambient temperature overnight, evaporation to dryness, extraction of the residue with hexane, filtration of the combined extracts through a plug of alumina, and finally removal of the hexane afforded **5** (165 mg, 81%) which was identified by its $^1$H NMR spectrum.

**Deprotonation of 3$^+$ with One Equivalent of NEt$_3$ and Formation of the Cyclobutadiene Complex 1:** In an NMR tube a sample of [**3**]$BF_4$ (109 mg, 0.34 mmol) was dissolved in $CD_2Cl_2$ (0.7 mL). One equivalent of $NEt_3$ (47 μL, 0.34 mmol, $d$ = 0.73 g·mL$^{-1}$) was added at ambient temperature. After shaking the mixture vigorously some insoluble material was separated utilizing a centrifuge. The $^1$H NMR (200 MHz, $CD_2Cl_2$) spectrum, recorded without delay, displayed three species in the mixture: the cyclobutadiene complex **1** and the hexatriene complex **5** in roughly equal amounts, and $NHEt_3^+$ [$\delta$ = 1.32 (t, Me), 3.18 (q, $CH_2$), 6.75 (broad, H) ppm]. After 16 h **5** had disappeared completely. Chromatography of the reaction mixture on alumina (20 cm) with hexane, followed by removal of the eluent under vacuum gave **1** (47 mg, 60%) as deep yellow crystalline solid.

**Deprotonation of 3$^+$ in CH$_2$Cl$_2$/DMSO and Formation of the Cyclobutadiene Complex 1:** A Schlenk tube was charged with [**3**]$BF_4$ (253 mg, 0.79 mmol), $CH_2Cl_2$ (10 mL), and finally with dimethylsulfoxide (5 mL) at ca. –40 °C. Then the solution was warmed to 30 °C and stirred for 30 min. Concentrating the solution under vacuum, extraction of the yellow product with hexane, followed by

filtration of the combined extracts through short plug of alumina, and finally removal of the hexane afforded **1** (124 mg, 67%) as deep yellow crystalline solid.

**The System [3]$BF_4$/$C_5H_5N$ in the NMR Tube:** A solution of [**3**]$BF_4$ (26 mg, 0.08 mmol) in $CD_2Cl_2$ (0.7 mL) was prepared in an NMR tube at –50 °C. The $^1H$ NMR spectrum of the sample showed the spectrum of [**3**]$BF_4$ and impurity signals due to traces of $Et_2O$ and of [**4**]$BF_4$. One equivalent of pyridine (6.5 μL, 0.08 mmol, $d$ = 0.98 g·mL$^{-1}$) was then added at –80 °C. The reagents were mixed utilizing an ultrasonic bath at –80 °C. $^1H$ NMR spectra were recorded on a 200 MHz spectrometer. In one experiment the temperature was kept below –70 °C for 7 d. In a second experiment the temperature was increased in 10 K steps over the range from –80 to 10 °C, and the sample was kept at the chosen temperature for 10 minutes before the spectrum was recorded. Integral intensities of the pertinent Cp ring signals were measured using the signal of the residual solvent protons as internal standard.

**Data for $6^+$:** $^1H$ NMR (200 MHz, $CD_2Cl_2$, –30 °C): $\delta$ = –0.45 (d, $J$ = 7.6 Hz, 4-Me), 1.95 (s, Me), 2.12 (s, Me), 2.20 (s, Me), 3.78 (q, $J$ = 7.6 Hz, 4-H), 4.90 (s, Cp); pyridine: 7.61 (t, $J$ = 6.4 Hz, 1 H, β-$H_{exo}$), 7.97 (t, $J$ = 6.4 Hz, 2 H, β-$H_{endo}$ + α-$H_{exo}$), 8.23 (t, $J$ = 7.8 Hz, γ-H), 9.26 (d, $J$ = 5.6 Hz, 1 H, α-$H_{endo}$) ppm; partial assignments by analogy to $7^+$. Multiplets at $\delta$ = 8.08 (t), 8.47 (t), 8.83 (d) ppm were assigned to the pyridine/pyridinium mixture. For $^{13}C\{^1H\}$ NMR spectroscopic data see below.

**Synthesis of [(Cyclopentadienyl){*N*-[η$^4$-(1′*Z*,2′*Z*,3′*E*)-1′,2′,3′-trimethylpenta-1′,3′-dienyl]pyridinium}cobalt] Tetrafluoroborate ([7]$BF_4$):** Pyridine (10 mL) was added to a solution of [**3**]$BF_4$ (640 mg, 2.00 mmol) in $CH_2Cl_2$ (10 mL) at –60 °C. The reaction mixture was warmed to ambient temperature overnight. Addition of $Et_2O$ precipitated a raw product which was purified by re-precipitation from $CH_2Cl_2$ solutions yielding [**7**]$BF_4$ (775 mg, 97%) as deep red, crystalline solid; m.p. 112 °C (dec). $C_{18}H_{23}BCoF_4N$ (399.12): calcd. C 54.17, H 5.80, N 3.51; found C 54.09, H 5.70, N 3.71. $^1H$ NMR (500 MHz, $CD_2Cl_2$): $\delta$ = –0.37 (qq, $J$ = 6.1, 0.7 Hz, 4-H), 1.18 (d, $J$ = 6.1 Hz, 4-Me), 1.94 (s, 1-Me), 2.17 (d, $J$ = 0.7 Hz, 3-Me), 2.21 (s, 2-Me), 4.82 (s, Cp); pyridine: 7.52 (t, $J$ = 6.7 Hz, β-$H_{exo}$), 7.66 (d, $J$ = 6.1 Hz, α-$H_{exo}$), 8.00 (t, $J$ = 6.7 Hz, β-$H_{endo}$), 8.23 (t, $J$ = 7.6 Hz, γ-H), 9.34 (d, $J$ = 6.1 Hz, α-$H_{endo}$) ppm. Note the $^4J$ coupling between 4-H and 3-Me which can be observed under favorable conditions and which is absent in $6^+$; the coupling constant was measured applying digital filtering with a Lorentz Gauss function. $^{13}C\{^1H\}$ NMR (126 MHz, $CD_2Cl_2$): $\delta$ = 16.0 (3-Me), 16.3 (2-Me), 20.2 (4-Me), 32.3 (1-Me), 53.7 (C-4), 80.4 (C-2), 81.8 (C-1), 84.6 (Cp), 100.0 (C-3); pyridine: 126.8 (β-$C_{exo}$), 129.3 (β-$C_{endo}$), 143.3 (α-$C_{exo}$), 143.9 (γ-C), 147.6 (α-$C_{endo}$) ppm.[23]

**Synthesis of [(Cyclopentadienyl){*P*,*P*,*P*-triphenyl-*P*-[η$^4$-(1′*Z*,2′*Z*,3′*E*)-1′,2′,3′-trimethylpenta-1′,3′-dienyl]phosphonium}-cobalt] Tetrafluoroborate ([8]$BF_4$):** Triphenylphosphane (3.67 g, 14 mmol) in $CH_2Cl_2$ (50 mL) was added to [**3**]$BF_4$ (640 mg, 2.00 mmol) in $CH_2Cl_2$ (10 mL) at –60 °C. The reaction mixture was warmed to ambient temperature overnight. The solution was concentrated to a small volume (ca.10 mL) and THF (100 mL) was added. A raw product precipitated, which was purified by re-precipitation from $CH_2Cl_2$ solution to give [**8**]$BF_4$ (1.14 g, 98%) as a dark red powder; m.p. 145 °C, dec. 150 °C. $C_{31}H_{33}BCoF_4P$ (582.30): calcd. C 63.94, H 5.71; found C 64.00, H 5.70. $^1H$ NMR (500 MHz, $CD_2Cl_2$): $\delta$ = 0.85 (d, $J$ = 6.4 Hz, 4-Me), 1.24 (q, $J$ = 6.4 Hz, 4-H), 1.34 (d, $^3J_{PH}$ = 16.2 Hz, 1-Me), 1.83 (s, 3-Me), 2.56 (d, $^4J_{PH}$ = 2.4 Hz, 2-Me), 4.76 (s, Cp); $PPh_3$: 7.63 (m, α-H), 7.73 (m, β-H), 7.75 (m, γ-H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CD_2Cl_2$): $\delta$ = 14.9 (3-Me), 17.5 (2-Me), 18.4 (4-Me), 29.0 (C-1) 30.0 (d, $^2J_{PC}$ = 12.4 Hz, 1-Me), 52.1 (C-4), 85.2 (Cp), 92.3 (C-2), 97.3 (C-3); $PPh_3$: 122.4 (d, $^1J_{PC}$ = 80.6 Hz, $C_i$), 129.9 (d, $^2J_{PC}$ = 11.5 Hz, $C_o$), 134.0 (d, $^3J_{PC}$ = 8.6 Hz, $C_m$), 134.2 (d, $^4J_{PC}$ = 2.8 Hz, $C_p$) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, $CD_2Cl_2$): $\delta$ = 14.8 (3-Me), 17.4 (d, $^3J_{PC}$ = 2.75 Hz, 2-Me), 18.3 (4-Me), 29.4 (d, $^1J_{PC}$ = 46.0 Hz, C-1), 29.9 (d, $^2J_{PC}$ = 13.05 Hz, 1-Me), 52.0 (d, $J_{PC}$ = 3.43 Hz, C-4), 84.9 (Cp), 92.0 (d, $^2J_{PC}$ = 1.48 Hz, C-2), 97.0 (d, $^3J_{PC}$ = 1.96 Hz, C-3); $PPh_3$: 122.1 (d, $^1J_{PC}$ = 80.23 Hz, $C_i$), 129.7 (d, $^2J_{PC}$ = 11.9 Hz, $C_o$), 133.8 (d, $^3J_{PC}$ = 8.45 Hz, $C_m$), 134.0 (d, $^4J_{PC}$ = 2.98 Hz, $C_p$) ppm. $P\{^1H\}$ NMR (202 MHz, $CD_2Cl_2$): $\delta$ = 25.91 ($PPh_3$) ppm.

**Synthesis of [{1-(*tert*-Butylamino)-2,3,4,5-tetramethylcyclopentadienyl}(cyclopentadienyl)cobalt] Trifluoromethanesulfonate ([9]$CF_3SO_3$):** A solution of [CpCoCb*] (**1**) (237 mg, 1.02 mmol) in $CH_2Cl_2$ (10 mL) was treated with $CF_3SO_3H$ (90 μL, 1.02 mmol, $d$ = 1.708 g·mL$^{-1}$) at –35 °C. After 5 min *tert*-butyl isocyanide (0.12 mL, 1.06 mmol, $d$ = 0.736 g·mL$^{-1}$) was added to the solution of [**3**]$CF_3SO_3$ so obtained, resulting in an immediate color change from dark red to yellow. Addition of $Et_2O$ (35 mL) and cooling to –80 °C overnight gave a yellow powder which was recrystallized from $CH_2Cl_2$ to afford analytically pure [**9**]$CF_3SO_3$ (430 mg, 90%) as yellow powder; m.p. 274–276 °C (dec.). $C_{19}H_{27}CoF_3NO_3S$ (465.42): calcd. C 49.03, H 5.85, N 3.01; found C 48.69, H 5.87, N 2.98. $^1H$ NMR (500 MHz, $CD_3CN$): $\delta$ = 1.41 (s, *t*Bu), 2.08 (s, 3-/4-Me), 2.26 (s, 2-/5-Me), 5.53 (s, Cp), 9.34 (s, N*H*) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CD_3CN$): $\delta$ = 10.9 (3-/4-Me), 12.0 (2-/5-Me), 26.7 (C*Me*$_3$), 70.9 (*C*Me$_3$), 89.2 (Cp), 94.7 (C-2,5), 100.4 (C-3,4), 97.3 (C-1) ppm; in $CD_2Cl_2$ solution some C atoms were not observed.[23]

**The System 5/($C_5H_5NH$)$CF_3SO_3$ in the NMR Tube:** A solution of **5** (22 mg, 0.095 mmol) in $CD_2Cl_2$ (0.8 mL) was added into an NMR tube containing [$C_5H_5NH$]$CF_3SO_3$ (21 mg, 0.095 mmol) at –80 °C. The reagents were mixed utilizing an ultrasonic bath at this temperature. $^1H$ NMR spectra were recorded after one, two, and three weeks at –80 °C. As some solid [$C_5H_5NH$]$CF_3SO_3$ had formed, the mixing process was repeated. After three weeks the product ratio was **5**:$6^+$:$7^+$:**1** = 0:93:5:2, and a good $^{13}C$ NMR spectrum of $6^+$ could be recorded from this reaction mixture.

**$^{13}C$ NMR Data for $6^+$:** $^{13}C\{^1H\}$ NMR (50.3 MHz, $CD_2Cl_2$, –80 °C): $\delta$ = 13.2 (4-Me), 17.2 (Me), 24.2 (Me), 35.6 (1-Me), 49.3 (C-4), 82.7 (C-2), 83.8 (Cp), 87.8 (C-1), 100.0 (C-3); pyridine: 128.0 (β-$C_{exo}$), 128.3 (β-$C_{endo}$), 143.1 (α-$C_{exo}$), 144.0 (γ-C), 147.7 (α-$C_{endo}$) ppm; tentative and partial assignments by analogy to the case of $7^+$.

**Addition of Pyridinium Triflate to the Hexatriene Complex 5 and Synthesis of [7]$CF_3SO_3$:** To a mixture of **5** (649 mg, 2.79 mmol) and ($C_5H_5NH$)$CF_3SO_3$ (640 mg, 2.79 mmol) was added pyridine (10 mL) and thereafter $CH_2Cl_2$ (15 mL). The reaction mixture was stirred for 1 h. Concentrating the solution and addition of $Et_2O$ precipitated the raw product, which was purified by re-precipitation from $CH_2Cl_2$ solution to give [**7**]$CF_3SO_3$ (1.21 g, 94%) as spectroscopically pure, red, microcrystalline powder, with $^1H$ NMR spectroscopic data identical to those for [**7**]$BF_4$.

**Pyridine/4-Picoline Exchange of [7]$BF_4$ and Synthesis of [10]$BF_4$:** A sample of the pyridinium derivative [**7**]$BF_4$ (112 mg, 0.28 mmol) was dissolved in $CH_2Cl_2$ (10 mL) and 4-picoline (1 mL) was added with stirring. After 20 min the solution was concentrated to a small volume and $Et_2O$ was added to precipitate the complex salts which were dried in a vacuum for 0.5 h. This procedure was repeated three more times to give a spectroscopically pure sample of [**10**]$BF_4$ (111 mg, 96%). $^1H$ NMR (200 MHz, $CD_2Cl_2$): $\delta$ = –0.36 (q, $J$ = 6.1 Hz, 4-H), 1.17 (d, $J$ = 6.1 Hz, 4-Me), 1.89 (s, 1-Me), 2.15 (s, 3-Me), 2.19 (s, 2-Me), 4.80 (s, Cp); 4-picoline: 2.48 (s, 4-Me), 7.27 (dd, $J$ = 6.22, 1.95 Hz, α-$H_{exo}$), 7.48 (dd, $J$ = 6.22, 1.46 Hz, β-$H_{exo}$), 7.75 (dd, $J$ = 6.22, 1.95 Hz, α-$H_{endo}$), 9.13 (dd, $J$ = 6.22, 1.46 Hz,

β-$H_{endo}$) ppm; assignments by analogy with the assignments for [7]$BF_4$.

**Nucleophilic Substitution of Pyridine in [7]$BF_4$ with Cyanide and Synthesis of (Cyclopentadienyl)[η⁴-(2*Z*,3*Z*,4*E*)-2,3,4-trimethylhexa-2,4-dienenitrile]cobalt (11):** A solution of [7]$BF_4$ (395 mg, 0.99 mmol) in $CH_2Cl_2$ (10 mL) was mixed with a solution of $(Bu_4N)CN$ (531 mg, 1.98 mmol) in $CH_2Cl_2$ (10 mL) at –80 °C. The mixture was stirred and warmed to ambient temperature within 24 h. Then all volatiles were removed. The residue was extracted several times with a hexane/ether (4:1) mixture. The combined extracts were filtered through a layer of alumina (2 cm). Removal of the volatiles and crystallization from $CH_2Cl_2$/hexane at –80 °C yielded **11** (218 mg, 85%) as dark red crystalline solid; m.p. 90–91 °C, dec. 126 °C. $C_{14}H_{18}CoN$ (259.23): calcd. C 64.86, H 6.99, N 5.40; found C 64.92, H 7.08, N 5.37. $^1$H NMR (500 MHz, $CD_2Cl_2$): $\delta$ = 1.33 (d, $J$ = 6.1 Hz, 5-Me), 1.43 (s, 2-Me), 1.84 (q, $J$ = 6.1 Hz, 5-H), 2.06 (s, 4-Me), 2.15 (s, 3-Me), 4.61 (s, Cp) ppm. $^{13}$C{$^1$H} NMR (126 MHz, $CD_2Cl_2$): $\delta$ = 15.6 (4-Me), 16.2 (3-Me), 19.7 (5-Me), 24.2 (C-2), 25.7 (2-Me), 51.2 (C-5), 83.2 (Cp), 88.4 (C-3), 95.0 (C-4), 125.5 (C-1) ppm.[23] IR ($CH_2Cl_2$): $\tilde{\nu}$(CN) = 2183.0 cm$^{-1}$.

**Synthesis of [(1-Amino-2,3,4,5-tetramethylcyclopentadienyl)(cyclopentadienyl)cobalt] Salts:** a) Trifluoroacetic acid $CF_3CO_2H$ (25 μL, $d$ = 1.48 g·mL$^{-1}$, 0.33 mmol) was added to a solution of the nitrile complex **11** (30 mg, 0.11 mmol) in $CD_2Cl_2$ (0.7 mL). The color of the reaction mixture rapidly changed from dark red to lemon-yellow. Removal of the volatiles and precipitation from aqueous solution (10 mL) with $NH_4PF_6$ (57 mg, 0.33 mmol) gave, after recrystallization from $CH_2Cl_2$/$Et_2O$, [**12**]$PF_6$ (42 mg, 90%) as a yellow powder. b) A solution of $HBF_4$ in $Et_2O$ (87 μL, 54%, $d$ = 1.18 g·mL$^{-1}$, 0.636 mmol) was added to a solution of the nitrile complex **11** (55 mg, 0.212 mmol) in $CH_2Cl_2$ (10 mL). The color immediately changed to lemon-yellow and a precipitate formed within seconds. Ether (30 mL) was added to complete the precipitation. The solid was collected on a frit, thoroughly washed with diethyl ether, and reprecipitated several times from acetone/ether to yield [**12**]$BF_4$ (69 mg, 94%) as a yellow powder. $C_{14}H_{19}BCoF_4N$ (347.05): calcd. C 48.45, H 5.52, N 4.04; found C 48.39, H 5.59, N 4.13.

**Data for [12]$PF_6$:** $^1$H NMR (500 MHz, $CD_2Cl_2$): $\delta$ = 1.98 (s, 3-/4-Me), 1.99 (s, 2-/5-Me), 4.25 (s, NH), 4.97 (s, Cp) ppm. $^{13}$C{$^1$H} NMR (126 MHz, $CD_2Cl_2$): $\delta$ = 9.5 (3-/4-Me), 10.4 (2-/5-Me), 79.7 (C-2/-5), 85.6 (Cp), 92.4 (C-3/-4), 122.7 (C-1) ppm.[23]

**Reaction of [7]$CF_3SO_3$ with Excess $CF_3CO_2H$ and Formation of the Carbenoid Cation 13⁺:** In an NMR tube a solution of [7]$CF_3SO_3$ (93 mg, 0.20 mmol) in $CD_2Cl_2$ (0.7 mL) was combined with $CF_3CO_2H$ (109 μL, $d$ = 1.48 g·mL$^{-1}$, 1.41 mmol) at ambient temperature and kept for several minutes. NMR spectra were then measured with a 500 MHz spectrometer at –20 °C. $^1$H NMR (500 MHz, –20 °C, $CD_2Cl_2$): $\delta$ = 1.80 (s, 2-Me), 2.37 (d, $J$ = 6.6 Hz, 4-Me), 2.53 (s, 1-Me), 2.56 (s, 3-Me), 3.13 (q, $J$ = 6.6 Hz, 4-H), 5.36 (s, Cp) ppm. $^{13}$C{$^1$H} NMR (126 MHz, –20 °C, $CD_2Cl_2$): $\delta$ = 11.5 (2-Me), 17.5 (3-Me), 20.0 (C-5 = 4-Me), 31.3 (1-Me), 77.6 (C-4), 88.7 (Cp), 100.3 (C-2), 117.3 (C-3), 288.4 (C-1) ppm.[23]

**Synthesis of (Cyclopentadienyl)[(2–5-η)-(3*Z*,4*E*)-3,4-dimethylhexa-1,2,4-triene]cobalt (14):** A large excess of $CF_3CO_2H$ (3.1 mL, 40 mmol) was added to [7]$BF_4$ (2.02 g, 5.06 mmol) in $CH_2Cl_2$ (20 mL) at 0 °C. The mixture was stirred for 30 min and then added slowly to a slurry of alumina (ca. 30 g) in $NEt_3$/hexane (22 mL/80 mL) at 0°. After stirring for 30 min the orange-red solution was filtered with the help of a plug of alumina (2–3 cm). Removal of the volatiles in a vacuum left a red oil which was crystallized from a minimal amount of hexane at –80 °C overnight to give the hexatriene complex **14** (0.668 g, 57%) as red crystalline material; m.p. 30 °C. $C_{13}H_{17}Co$ (232.21): calcd. C 67.24, H 7.38; found C 67.01, H 7.26. $^1$H NMR (500 MHz, $CD_2Cl_2$): $\delta$ = 0.50 (q, $J$ = 6.45 Hz, 5-H), 1.31 (d, $J$ = 6.47 Hz, 5-Me), 1.86 (s, 3-Me), 2.18 (s, 4-Me), 4.63 (s, Cp), 4.72 (d, $J$ = 2.08 Hz, 1-$H_{anti}$), 4.88 (d, $J$ = 2.08 Hz, 1-$H_{syn}$) ppm. $^{13}$C{$^1$H} NMR (126 MHz, $CD_2Cl_2$): $\delta$ = 14.0 (4-Me), 16.9 (3-Me), 19.2 (5-Me), 49.6 (C-5), 72.4 (C-3), 83.2 (Cp), 97.2 (C-4), 97.3 (C-1), 171.9 (C-2) ppm.[23]

**Synthesis of Bis(cyclopentadienyl)[μ-2(1–3-η):1(4,5-η)-(1*Z*,2*Z*,3*Z*)-1,2,3-trimethylpenta-2,4-dien-1-ylidene-1κ(*C*¹)]dicobalt(*Co–Co*)] (15):** A solution of **5** (694 mg, 2.98 mmol) in toluene (15 mL) was heated to 110 °C for 4 d. Then all volatiles were removed in a vacuum leaving a black oily residue which was chromatographed on alumina (35-cm column) using hexane as eluent. Removal of the solvent afforded spectroscopically pure **15** (487 mg, 91%) as black microcrystalline solid; m.p. 67 °C. $C_{18}H_{22}Co_2$ (356.23): calcd. C 60.69, H 6.22; found C 61.28, H 6.25. $^1$H NMR (500 MHz, $CD_2Cl_2$): $\delta$ = –0.43 (dd, $^2J_{5anti,5syn}$ = 1.1, $^3J_{4,5anti}$ = 10.01 Hz, 5-$H_{anti}$), 1.28 (s, 2-Me), 1.58 (dd, $^2J_{5anti,5syn}$ = 1.1, $^3J_{4,5syn}$ = 6.72 Hz, 5-$H_{syn}$), 2.00 (s, 3-Me), 2.59 (s, 1-Me), 3.05 (dd, $^3J_{4,5anti}$ = 10.01, $^3J_{4,5syn}$ = 6.72 Hz, 4-H), 4.60 [s, Cp(Co-2)], 4.87 [s, Cp(Co-1)] ppm. $^{13}$C{$^1$H} NMR (126 MHz, $CD_2Cl_2$): $\delta$ = 14.5 (2-Me), 23.0 (3-Me), 26.8 (C-5), 30.5 (1-Me), 55.0 (C-4), 69.5 (C-3), 81.7 [Cp(Co-2)], 85.0 [Cp(Co-1)], 87.1 (C-2), 161.1(C-1) ppm.[23]

**X-ray Crystal Structure Determinations:** Suitable crystals of **5** were obtained by slow vacuum sublimation (40–50 °C, 1–2 days) as orange-red platelets. Crystallization of [7]$CF_3SO_3$ from acetone/ether afforded well-shaped red rods. Geometry and intensity data were collected with ENRAF-Nonius CAD4 diffractometers

Table 1. Crystal data, data collection parameters, and convergence results for **5** and [7]$CF_3SO_3$.

| | **5** | [7]$CF_3SO_3$ |
|---|---|---|
| Empirical formula | $C_{13}H_{17}Co$ | $C_{19}H_{23}CoF_3NO_3S$ |
| Formula mass | 232.21 | 461.37 |
| Crystal system | orthorhombic | monoclinic |
| Space group | $P2_12_12_1$ (no. 19) | $P2_1/n$ (no. 14) |
| $a$ [Å] | 8.945(3) | 8.208(2) |
| $b$ [Å] | 9.2280(10) | 16.585(2) |
| $c$ [Å] | 13.732(2) | 15.663(4) |
| $\beta$ [°] | | 101.28(2) |
| $V$ [Å$^3$] | 1133.5(4) | 2091.0(8) |
| $Z$ | 4 | 4 |
| $d_{calcd.}$ [g/cm$^3$] | 1.361 | 1.466 |
| $F$(000) | 488 | 952 |
| μ [mm$^{-1}$] | 1.472 | 0.965 |
| Absorption correction | empirical | empirical |
| Max./min. transmission | 0.855/0.448 | 0.644/0.551 |
| θ range [°] | 2–27 | 2–27 |
| Temperature [K] | 223 | 223 |
| Scan mode | ω | ω-2θ |
| Crystal size [mm] | 0.65×0.50×0.11 | 0.7×0.7×0.5 |
| Reflections collected | 10810 | 12703 |
| Reflections unique | 2480 | 4565 |
| Refls observed $I > 2\sigma(I)$ | 1944 | 3763 |
| Variables | 131 | 257 |
| $R_1$[a], observed (all data) | 0.0679 (0.0844) | 0.0429 (0.0534) |
| $wR_2$[b], observed (all data) | 0.1601 (0.1670) | 0.1163 (0.1221) |
| GOF[c] | 1.049 | 1.052 |
| Max. resd. density (e/Å$^3$) | 2.772 (0.8 Å from Co) | 0.503 |

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2]$ and $P = [\max(F_o^2,0) + 2F_c^2]/3$. [c] GOF = $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma(n - p)]^{1/2}$

(graphite-monochromated Mo-$K_\alpha$). Crystal data, data collection parameters, and convergence results for the compounds **5** and [**7**]-$CF_3SO_3$ are listed in Table 1. Note that the crystal of **5** turned out to be an inversion twin. CCDC-251060 (for **5**) and CCDC-251061 (for [**7**]$CF_3SO_3$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.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