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Review

(Tetramethylcyclobutadiene)cobalt chemistry

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Abstract

Easy accessibility of $Cb^*Co(CO)_2I$ (**1**, $Cb^* = C_4Me_4$), which can be prepared in one-pot from $Co_2(CO)_8$ and 2-butyne, facilitates the development of chemistry of the Cb^*Co fragment. **1** can be used directly to prepare Cb^*Co complexes or can be converted into more reactive synthons, $[Cb^*Co(arene)]^+$ (arene = C_6H_6 (**3a**), C_6H_5Me (**3b**)) and $[Cb^*Co(MeCN)_3]^+$ (**4**). **4** is most suitable for the preparation of complexes

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with anionic ligands whereas for reactions with less reactive neutral compounds photochemical generation of the $[Cb^*Co]^+$ species from **3a**,**b** in CH_2Cl_2 is recommended. Sandwich, half-sandwich, triple-decker, metallacarborane and cluster compounds were obtained using these methods.

Keywords: Cobalt; Cyclobutadiene; Sandwich compounds; Triple-decker complexes; Metallacarboranes; Clusters

1. Introduction

The CbCo fragment (Cb = η^4-C_4H_4) is isolobal with CpM (M = Fe [1], Ru) leading to a close relationship between complexes of these fragments. However, the chemistry of (cyclobutadiene)cobalt complexes [2] is much less studied than that of CpFe and CpRu analogues. Derivatives of CbCoCp are the most widespread owing to their simple preparation by alkyne dimerization at the CpCo fragment. For example, the reaction of CpCo complexes (CpCo(cyclooctadiene) [3], $CpCo(CO)_2$ [4] or Cp_2Co [5]) with tolane gives the tetraphenylcyclobutadiene complex $(C_4Ph_4)CoCp$. Numerous tricyclic [6], cyclophane [7], multiply ethynylated [8] and even polymeric [9] derivatives of CbCoCp have been synthesized in a similar way. However, the inertness of the Cp ligand precludes transformation of such compounds into (cyclobutadiene)cobalt complexes with other ligands. In contrast, the (carbonyl)halide complexes $(C_4R_4)Co(CO)_2X$ (R = H, Me, Ph) proved to be suitable starting materials. The parent complex $CbCo(CO)_2I$ has been prepared by reaction of 3,4-dichlorocyclobutene with $Na[Co(CO)_4]$ and subsequent treatment of the intermediate binuclear complex $CbCo_2(CO)_6$ with iodine [10]. $CbCo(CO)_2I$ was used to prepare CbCo complexes with Me, PPh_3 [11], Cp [10] and boratabenzene [12] ligands. However, difficult accessibility of 3,4-dichlorocyclobutene hampers the development of chemistry of the unsubstituted CbCo fragment. Tetraaryl-substituted complexes $(C_4Ar_4)Co(CO)_2X$ (Ar = Ph, *p*-tolyl; X = Cl, Br, I) [13] have been synthesized by ligand-transfer reactions from $[(Ar_4C_4)PdX_2]_2$ and used to prepare $(C_4Ar_4)Co$ complexes with C_6F_5, PPh_3, arene and cycloheptatriene ligands. However, the chemistry of $(C_4Ar_4)Co$ did not gain ground owing to unattractiveness of the phenyl and tolyl substituents.

The methyl groups proved to be the most favorable substituents for ring ligands. For instance, the pentamethylcyclopentadienyl ligand (Cp*) is widely used in organometallic chemistry mainly owing to stabilization of complexes and reactive intermediates caused by strong electron-donating and steric effects of five methyl groups [14]. Analogously, the tetramethylcyclobutadiene ligand (Cb* = η^4-C_4Me_4) should be also very useful. It was proved to be the case for Cb*Co complexes, chemistry of which is reviewed in this paper with main emphasis on our recent results.

2. Starting materials

2.1. Synthesis of $Cb^*Co(CO)_2I$

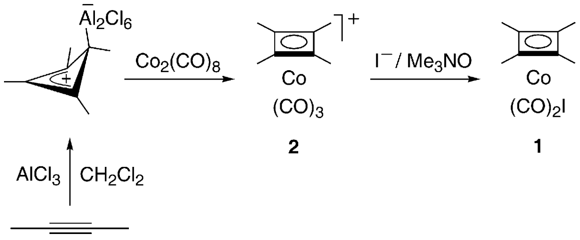
2.1.1. Synthesis by Cb* ligand transfer from nickel

The first cobalt derivatives of the Cb* ligand have been described by Bruce and Maitlis [15]. They prepared complex $Cb^*Co(CO)_2I$ (**1**), a key compound in Cb*Co chemistry, by reaction of $Co_2(CO)_8$ with the nickel iodide complex $[Cb^*NiI_2]_2$. However, similar reaction with the chloride $[Cb^*NiCl_2]_2$ affords the dicobalt complex $Cb^*Co(CO)_2Co(CO)_4$, probably because of the low stability of the chloride $Cb^*Co(CO)_2Cl$. Both reactions proceed through Cb* ring transfer from nickel to cobalt. The dicobalt complex reacts with I_2 to give the iodide **1**.

2.1.2. Synthesis from the (σ-cyclobutadiene)aluminium complex

Koster et al. [16] have found that 2-butyne reacts with $AlCl_3$ in CH_2Cl_2 to give the σ-cyclobutadiene complex $(\eta^1$-$C_4Me_4)AlCl_3$ which proved to be very useful in organic synthesis [17]. Hoberg and Riegel [18] have shown that $(\eta^1$-$C_4Me_4)AlCl_3$ reacts with Ni(0) complexes, $Ni(CO)_4$ or $Ni(cod)_2$, to give the Criegee's compound $[Cb^*NiCl_2]_2$. Yields are much higher in the presence of an additional equivalent of $AlCl_3$ (i.e. using the Al_2Cl_6 σ-cyclobutadiene complex $(\eta^1$-$C_4Me_4)Al_2Cl_6$). This suggests that the reaction proceeds via oxidation of Ni(0) to Ni(2+) by a strong oxidant, $AlCl_3/CH_2Cl_2$ ($E_{ox} \sim 1.6$ V versus SCE [19]), with subsequent transfer of the Cb* ligand from aluminium to nickel.

Pauson et al. [20] have extended this method for the preparation of Cb*Co complexes. The reaction of $(\eta^1$-$C_4Me_4)Al_2Cl_6$ with $Co_2(CO)_8$ was shown to give the tricarbonyl cation **2** which was isolated as a hexafluorophosphate salt in 59–68% yields (Scheme 1). Treatment of $\mathbf{2}PF_6$ with $[Bu_4N]I$ and Me_3NO (a mild CO-abstracting agent



Scheme 1. Synthesis of the (carbonyl)iodide complex **1**.

[21]) in CH_2Cl_2 affords the iodide complex **1** in 76% yield. A similar reaction with the use of K_2CO_3 instead of Me_3NO also gives **1** but in this case the yields were found to diminish rapidly when quantities larger than 1 mmol were used. Sodium amalgam reduction of **2** gives the dimeric complex $[Cb^*Co(CO)_2]_2$ (31%) which reacts with I_2 to give **1**.

2.1.3. *One-pot preparation*

Based on the reactions described by Pauson et al. [20] we developed a simple one-pot procedure [22] for the preparation of the (carbonyl)iodide complex **1**. After the reaction between $(\eta^1\text{-}C_4Me_4)Al_2Cl_6$ and $Co_2(CO)_8$ was over, the resulting mixture containing cation **2** was hydrolyzed by water and the aqueous phase was treated with $NaI{\cdot}2H_2O$ and $Me_3NO{\cdot}2H_2O$. Complex **1** precipitates slowly (overnight) and proved to be sufficiently pure for further applications. Although we previously reported a 37% yield, it was shown later that the yields depend on purity of the $Co_2(CO)_8$ and approach 60–65% if high-quality cobalt carbonyl is used. The one-pot procedure is less time-consuming and more economical than the two-step method described in the previous paragraph. It makes the key complex **1** easily accessible thus facilitating the development of Cb*Co chemistry. It is necessary to note that although **1** is reasonably air-stable for short periods of time (up to several days), an inert atmosphere is necessary for its prolonged storage.

2.2. *Synthesis of arene complexes $[Cb^*Co(arene)]^+$ from $Cb^*Co(CO)_2I$*

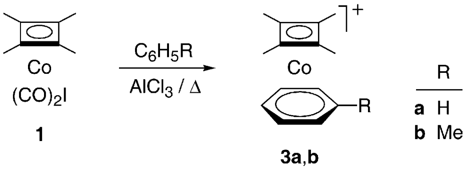
Pauson and coworkers [20b,23] have shown that heating the tricarbonyl cation **2** with arenes containing strongly electron-donating substituents (OR, NR_2) in the presence of Me_3NO yields arene complexes $[Cb^*Co(arene)]^+$ (**3**). However, the benzene complex **3a** is formed only in very low yield using this method. The method based on heating of the (carbonyl)iodide complex **1** with arenes in the presence of $AlCl_3$ was proved to be more general (Scheme 2). In particular, the benzene and toluene complexes **3a** and **3b** were obtained in 25 and 34% yields, respectively, using 3 eq. of $AlCl_3$ [20b]. We found that the yields can be increased up to ca. 60% if 10 eq. of $AlCl_3$ are used [22]. However, the preparation of complex **3a** in refluxing benzene is complicated by side-formation of the tricarbonyl complex **2**. In order to remove this impurity, little $NaI{\cdot}2H_2O$ and $Me_3NO{\cdot}2H_2O$ was added to the aqueous solution obtained by hydrolysis of the reaction mixture and the precipitated iodide **1** was filtered off. Subsequent addition of NH_4PF_6 precipitates pure complex **3a**PF_6. Alternatively, the formation of **2** can be largely suppressed by carrying out the reaction at higher temperature in a refluxing benzene/octane mixture. In the case of the preparation of the toluene complex **3b**, the product obtained in refluxing toluene is contaminated with arene complexes **3** having several Me groups in the benzene ring in consequence of transmethylation. Nevertheless, milder reaction conditions (refluxing in a toluene/hexane mixture) allow obtaining of **3b** in pure form.

2.3. *Synthesis of the acetonitrile complex $[Cb^*Co(MeCN)_3]^+$*

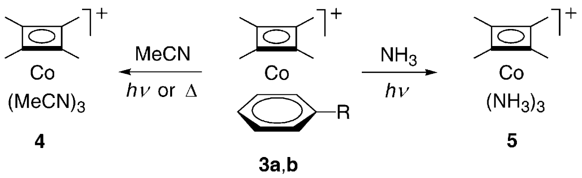
Labile solvate complexes of the general type $[L_xM(solv)_y]^{n+}$ (L = $MeNO_2$, CH_2Cl_2, THF, Me_2CO, MeCN) are widely used as synthons for organometallic fragments $[L_xM]^{n+}$. The first examples were the rhodium complexes $[(cod)Rh(THF)_x]^+$ [24] and $[Cp^*Rh(Me_2CO)_3]^{2+}$ [25]. Acetonitrile complexes are especially useful since they are sufficiently stable to be isolated and, at the same time, are still reactive.

The iron and ruthenium acetonitrile complexes $[CpFe(MeCN)_3]^+$ [26] and $[(C_5R_5)Ru(MeCN)_3]^+$ [27] (R = H [28], Me [29]) are formed by irradiation of the corresponding benzene complexes $[(C_5R_5)M(C_6H_6)]^+$ in MeCN. In accord with the isolobal analogy between CbCo and CpM (M = Fe, Ru), visible light irradiation of the cobalt arene complexes **3a**,**b** in MeCN affords the acetonitrile complex $[Cb^*Co(MeCN)_3]^+$ (**4**) (Scheme 3) [22,30]. Surprisingly, refluxing of **3a**,**b** in MeCN also gives **4**, in contrast to the iron and ruthenium benzene complexes which are thermally unreactive. Irrespective of the conditions, complex **4** is formed in almost quantitative yield. Photolysis of **3a** in liquid ammonia gives the triammine complex $[Cb^*Co(NH_3)_3]^+$ (**5**). Complex **4** is air-sensitive, especially in solution, and should be stored in an inert atmosphere. It is stable in MeCN, Me_2CO and $MeNO_2$ solution, however CH_2Cl_2 causes slow oxidation that is seen as a fast deterioration in the NMR spectra in this solvent.

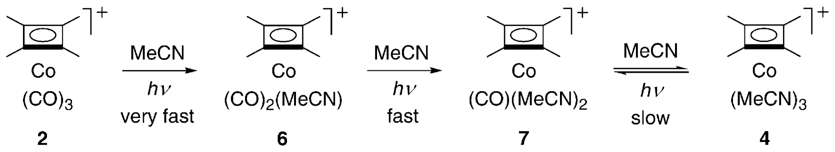
We also tried to prepare **4** directly from the tricarbonyl complex **2**. Pauson et al. [20b] have shown that in the presence of Me_3NO acetonitrile substitutes for only one carbonyl ligand in **2** giving the mono(acetonitrile) complex $[Cb^*Co(CO)_2(MeCN)]^+$ (**6**). We shown that UV-irradiation of **2** in MeCN leads to successive replacement of the CO ligands, each subsequent ligand being replaced slower than



Scheme 2. Synthesis of the arene complexes **3a**,**b**.



Scheme 3. Synthesis of the solvate complexes **4** and **5**.



Scheme 4. Photochemical replacement of the carbonyl ligands of cation **2** with acetonitrile.

the previous one (Scheme 4) [22]. The disubstitution product $[Cb^*Co(CO)(MeCN)_2]^+$ (**7**) was isolated in pure form. The replacement of the third CO group is possible provided that a slow stream of nitrogen or argon purges the solution in order to shift the equilibrium. However, even in this case the reaction proceeds very slowly and cannot be recommended as a preparative route. Complex **7** is analogous to the iron and ruthenium complexes $[(C_5R_5)Fe(CO)(MeCN)_2]^+$ [31] and $[CpRu(CO)(MeCN)_2]^+$ [32], and similar to the latter is useful as a source of the 14-electron $[Cb^*Co(CO)]^+$ fragment.

As it was mentioned in Section 2.2, the benzene complex **3a** obtained by reaction of the (carbonyl)iodide **1** with benzene in the presence of $AlCl_3$ is contaminated with the tricarbonyl complex **2**. If this impurity is not removed, visible light irradiation leads to the formation of 3 mol of the bis(acetonitrile) complex **7** per mole of **2** as a result of the metathesis between complexes **2** and **4** (Eq. (1)). The ^1H NMR signal of the residual protons of acetone-d$_6$ ($\delta = 2.07$ ppm [33]), in which the spectra of the benzene complex **3a** have been recorded earlier, practically coincides with the signal of complex **2** ($\delta = 2.075$ ppm [20b]) thus masking the presence of the impurity. It caused a series of misfortunes in our earliest attempts to obtain pure samples of **4**. Moreover, "purification" of the crude material in air afforded instead pure samples of the bis(acetonitrile) complex **7** due to its lower air-sensitivity as compared with **4**.

$$\underset{\mathbf{2}}{[Cb^*Co(CO)_3]^+} + 2\underset{\mathbf{4}}{[Cb^*Co(MeCN)_3]^+} \rightarrow 3\underset{\mathbf{7}}{[Cb^*Co(CO)(MeCN)_2]^+} \quad (1)$$

The structures of complexes **2** and **4** were determined by X-ray diffraction [22]. The Co···Cb* distance in the carbonyl complex **2** (1.769 and 1.785 Å for two independent cations, av. 1.777 Å) is longer than that in the acetonitrile complex **4** (1.680 and 1.670 Å for two conformers, av. 1.675 Å). This is evidently connected with much lower back donation from cobalt to the Cb* ring in the case of complex **2** as a result of strong acceptor ability of the carbonyl groups.

3. Half-sandwich Cb^*CoL_3 complexes

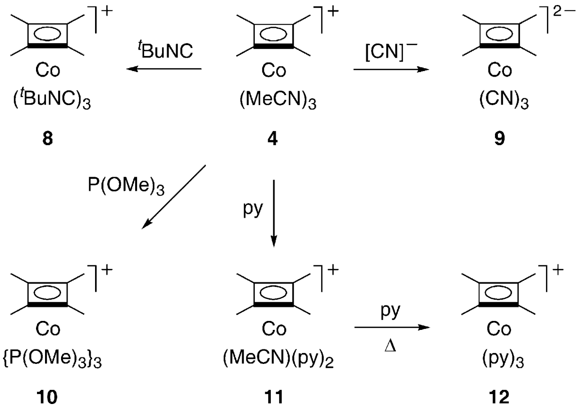
3.1. Ligand substitution reactions of $[Cb^*Co(MeCN)_3]^+$

The MeCN ligands in the tris(acetonitrile) complex **4** are substitutionally labile. They rapidly exchange with free MeCN as evidenced by line broading in the ^1H NMR spectra (acetone-d_6, 20 °C) on addition of acetonitrile-d_3 (decoalescence at −10 °C). The acetonitrile ligands can be replaced by other two-electron ligands L giving tris(ligand) complexes (Scheme 5) [22]. For instance, the strong carbon nucleophiles ^{t}BuNC and $[CN]^-$ readily effect substitution of all three acetonitrile ligands at room temperature to give complexes **8** and **9**. However, in the case of pyridine and the phosphorus ligands $P(OMe)_3$ and PMe_3, the third substitution step is slow. The phosphite complex **10** was obtained after 24 h standing of the solution of **4** in neat $P(OMe)_3$. Treatment of **4** with excess of pyridine at room temperature affords the disubstituted product $[Cb^*Co(MeCN)(py)_2]^+$ (**11**); substitution of the third acetonitrile ligand to give **12** requires prolonged heating at 40–50 °C.

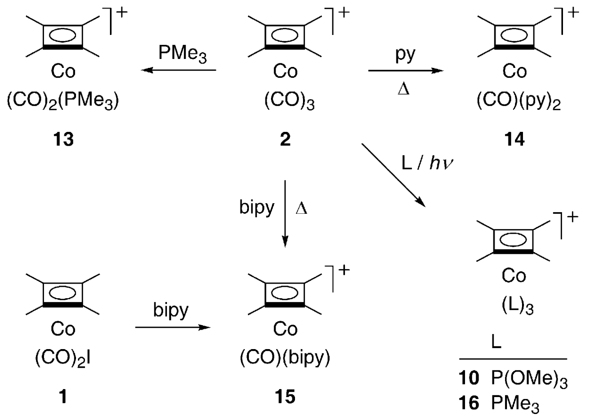
There are some obvious limitations to the method based on the replacement of the acetonitrile ligands in **4**. The ligand to be introduced should either bind strongly to the metal atom or should be less volatile than acetonitrile allowing to shift equilibrium by removal of MeCN from the reaction mixture. For instance, it is not possible to replace acetonitrile with dimethylsulfide.

3.2. Ligand substitution reactions of $[Cb^*Co(CO)_3]^+$ and $Cb^*Co(CO)_2I$

Easy availability of the carbonyl complex **2** makes it an attractive starting material. In favorable cases product formation is highly selective. For example, PPh_3 and dppm (dppm = $(Ph_2P)_2CH_2$) substitute for only one carbonyl ligand (in the presence of K_2CO_3, 20 °C) to give complexes



Scheme 5. Ligand substitution reactions of the acetonitrile complex **4**.



Scheme 6. Ligand substitution reactions of the carbonyl complexes **1** and **2**.

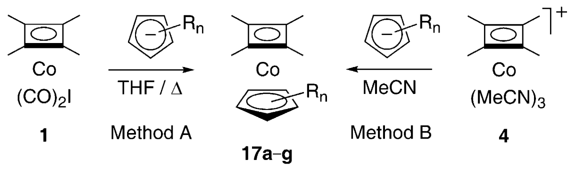
$[Cb^*Co(CO)_2(L)]^+$ (L = PPh_3, dppm) [20b]. The spontaneous room temperature reaction of **2** with PMe_3 also gives the monosubstitution product, $[Cb^*Co(CO)_2(PMe_3)]^+$ (**13**) (Scheme 6) [22]. On the contrary, in the case of the weaker donor ligand $P(OMe)_3$ warming to 40–50 °C was required to effect the reaction; this process shows little selectivity leading to both mono- and disubstitution products (according to ^1H NMR). Thermal reactions of **2** with pyridine (80 °C) [20b] and 2,2′-bipyridine (50–60 °C) [22] produce the disubstituted cations $[Cb^*Co(CO)(py)_2]^+$ (**14**) and $[Cb^*Co(CO)(bipy)]^+$ (**15**). The iodide salt of **15** can be obtained by reaction of the (carbonyl)iodide complex **1** with bipyridine [22]. The reaction of **1** with PPh_3 affords $Cb^*Co(CO)(PPh_3)I$ [15].

Photochemically induced ligand substitution reactions provide a synthetic alternative. Ultraviolet irradiation of **2** in CH_2Cl_2 in the presence of PMe_3 or $P(OMe)_3$ effects the stepwise replacement of one, two and, much more slowly, even of all three carbonyl groups giving cations $[Cb^*Co\{P(OMe)_3\}_3]^+$ (**10**) and $[Cb^*Co(PMe_3)_3]^+$ (**16**) as final products. In accordance with its equilibrium character, the process is accelerated by removal of CO from the reaction mixture by purging a slow stream of nitrogen or argon.

4. Complexes with five-electron ring ligands

4.1. Cyclopentadienyl complexes

Isolobal analogy of CbCo with CpFe suggests a close relationship between CbCoCp and ferrocene. It is supported, in particular, by ability of both compounds to undergo electrophilic substitution reactions [10,34,35]. Taking into account numerous fields of ferrocene application [36] it becomes clear that the cobalt analogues, including those containing the Cb* ring, are useful from the point of view of their practical application. It makes the development of methods for their synthesis specially important.



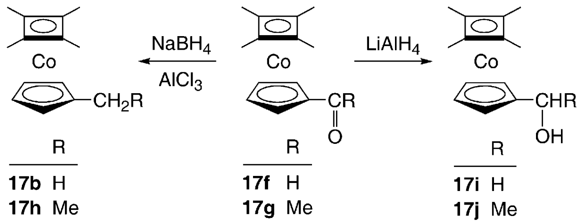
	R_n	Yield (%) A	Yield (%) B
a	H	74	74
b	Me	-	60
c	Me_5	0	41
d	$SiMe_3$	26	72
e	$(SiMe_3)_2$	0	60
f	C(O)H	40	86
g	C(O)Me	37	81

Scheme 7. Synthesis of cyclopentadienyl complexes **17** from **1** (method A) and **4** (method B).

The tetramethylcyclobutadiene complex Cb*CoCp (**17a**) was first prepared by reaction of **1** with CpNa at room temperature [15]; however, the yield was only 17%. Analogous reaction of **2** with CpNa gave **17a** in 32% yield [20b]. Refluxing of **1** with CpTl allowed to increase the yield up to 70% [37]. We shown that the reaction of **1** with sodium or lithium salts of monosubstituted cyclopentadienide anions, including those containing C(O)H, C(O)Me and $SiMe_3$ groups, affords complexes **17** in moderate yields after refluxing for several hours in THF (Scheme 7) [38]. However, this method (method A) proved to be inapplicable for the preparation of complexes with more sterically hindered ligands, Cp* and 1,3-$C_5H_3(SiMe_3)_2$.

The acetonitrile complex **4** is much more electrophilic than **2** owing to its positive charge and lability of the MeCN ligands. Its reactions with cyclopentadienide anions (method B) readily occur in acetonitrile at room temperature. In most cases lithium and sodium salts are equally effective. However, the Cp* complex **17c** was obtained only in very low yield starting from Cp*Li; the yield can be considerably increased using Cp*K apparently owing to its higher reactivity. Method B is more general and gives the products in higher yields. The most convenient method generates **4** from the arene complexes **3a**,**b** in solution (see Section 2.3) and uses it without isolation. However, complexes **3a**,**b** are formed from **1** in ca. 60% yield, thus making overall yields of the cyclopentadienyl compounds **17d**,**f**,**g** close to those in method A. Therefore it is expedient to use method B only when method A is inapplicable, e.g. to prepare **17c**,**e**.

Complex **17b** obtained by reaction of **4** with $[C_5H_4Me]^-$ contains ca. 5% impurity of **17a** arising from the presence of dicyclopentadiene impurity in commercially available methylcyclopentadiene dimer. Unfortunately, **17b** cannot be purified either by sublimation or by column chromatography. Nevertheless, we succeeded in preparing **17b** in pure form by reduction of the formyl derivative **17f** by $NaBH_4$ in the presence of $AlCl_3$ (Scheme 8). Similar reaction of the acetyl derivative **17g** yields the ethyl-substituted

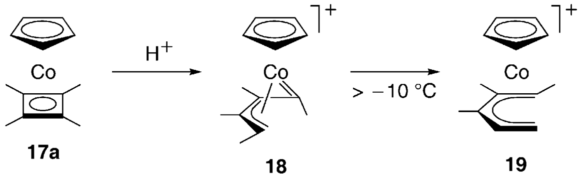


Scheme 8. Reduction of the carbonyl groups in **17f** and **17g**.

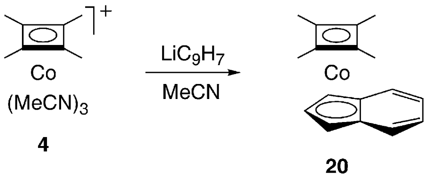
complex **17h**. Reduction of **17f**,**g** with $LiAlH_4$ gives the corresponding alcohols **17i**,**j**. It should be emphasized that these reactions occur essentially in the same conditions as analogous reactions for ferrocene derivatives [39] thus giving additional evidence of close relationship between CbCoCp and ferrocene.

However, in spite of many similarities between CbCo and CpFe complexes, the principal difference consists of the much easier ability of the coordinated cyclobutadiene ligand (as compared with Cp) to convert into other ligands. It is clearly demonstrated by recently described protonation of complex **17a** [40]. Thus, treatment of a CH_2Cl_2 solution of this complex with CF_3CO_2H or $HBF_4{\cdot}Et_2O$ at low temperature immediately gives the allyl carbene complex $[CpCo(\sigma,\eta^4\text{-}C_4HMe_4)]^+$ (**18**) with a five-electron butadienyl ligand [41] (Scheme 9). DFT calculations on the protonation of the monomethyl cyclobutadiene complex $CpCo(C_4H_3Me)$ show that protonation preferentially takes place from the *endo* side and is followed by a stereospecific ring-opening reaction to give the corresponding carbenoid complex $[CpCo(\sigma,\eta^4\text{-}C_4H_4Me)]^+$ with the same *anti* stereochemistry as found in **18**. Above −10 °C the cation **18** rearranges to produce the half-open cobaltocenium cation $[CpCo(\eta^5\text{-}C_5H_4Me_3)]$ (**19**).

The Co···Cb* distance in the acetylcyclopentadienyl complex **17g** (1.684 Å) [38] is very close to the corresponding values for the parent and tetraphenyl-substituted compounds, CbCoCp (1.681 Å) [42] and $(C_4Ph_4)CoCp$ (1.679 Å) [43], demonstrating insignificant substituent effects. At the same time, this distance is considerably shorter than that for the carbonyl complex **2** (av. 1.777 Å) in accord with strong donor ability of Cp^- leading to greater back donation from cobalt atom to the Cb* ring. The Co–C(Cb) bonds for **17g** (av. 1.97 Å) are ca. 0.1 Å shorter than the Co–C(Cp) bonds (av. 2.07 Å) similar to the parent compound (av. 1.96 and 2.03 Å) and $(C_4Ph_4)CoCp$ (1.98 and 2.05 Å, respectively), in accordance with predicted by Longuet-Higgins and Orgel [44] stronger metal bonding with the Cb ring than with Cp.



Scheme 9. Ring-opening and subsequent rearrangement under protonation of complex **17a**.

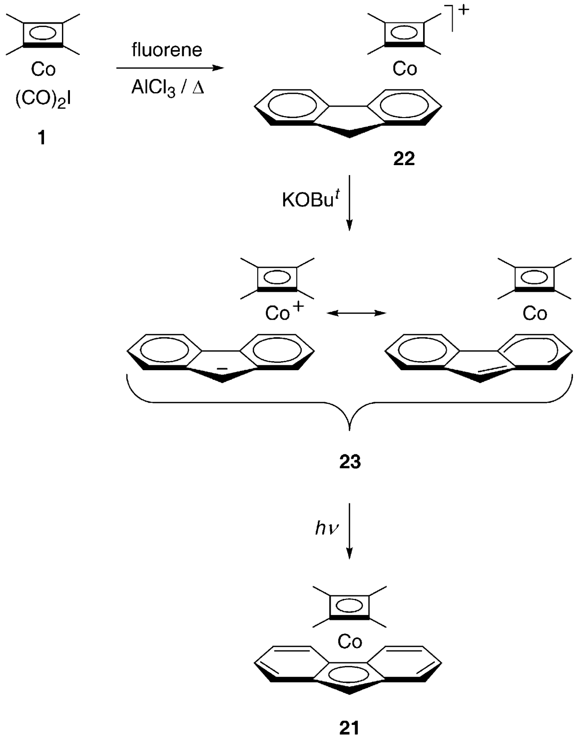


Scheme 10. Synthesis of the indenyl complex **20**.

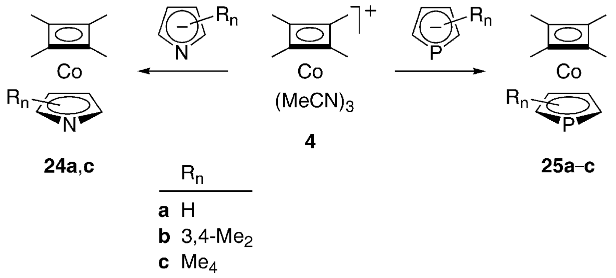
4.2. Indenyl and fluorenyl complexes

The indenyl complex $Cb^*Co(\eta^5\text{-}C_9H_7)$ (**20**, Co···Cb*, 1.679 Å) was obtained in high yield by reaction of **4** with lithium indenide (Scheme 10) [38]. However, similar reaction with lithium fluorenide gives a mixture of the fluorenyl complex $Cb^*Co(\eta^5\text{-}C_{13}H_9)$ (**21**) and fluorene in ca. 1:1 ratio, probably as a result of a side reaction of proton transfer from **4** to the fluorenide anion. The low stability of **21** complicates its isolation from the mixture.

In order to prepare **21** in pure form, we used the following method. The reaction of **1** with fluorene in the presence of $AlCl_3$ gives the cationic fluorene complex $[Cb^*Co(\eta^6\text{-}C_{13}H_{10})]^+$ (**22**) (Scheme 11), similar to the preparation of the benzene and toluene complexes **3a**,**b**. Subsequent deprotonation by $KOBu^t$ leads to the η^6-fluorenyl complex $Cb^*Co(\eta^6\text{-}C_{13}H_9)$ (**23**) which is depicted by zwitterionic and neutral limiting structures, analogously to the



Scheme 11. Synthesis of fluorenyl complexes.



Scheme 12. Synthesis of pyrrolyl and phospholyl complexes.

iron complex $\mathrm{CpFe}(\eta^6\text{-}C_{13}H_9)$ [45]. Visible light irradiation of this compound induces the $\eta^6 \rightarrow \eta^5$ haptotropic rearrangement [46] to give the target product **21** [38].

4.3. Complexes with five-electron heterocyclic ligands

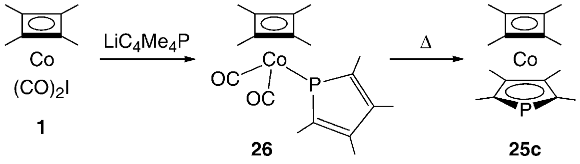
4.3.1. Pyrrolyl and phospholyl complexes

We were able to prepare the pyrrolyl complexes **24a**,**c** by reaction of the acetonitrile complex **4** with the corresponding potassium pyrrolides (Scheme 12) [38]. The yield of complex **24a** having the unsubstituted pyrrolyl ring was 60%. However, the tetramethylated analogue **24c** was obtained in a lower yield (35%); tetramethylpyrrole was also isolated in this case suggesting proton transfer side reaction. It should be mentioned that complexes **24a**,**c** cannot be prepared using the (carbonyl)iodide complex **1** instead of **4**.

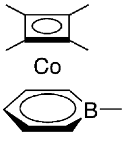
The reaction of the acetonitrile complex **4** with lithium phospholides was effectively used for the preparation of Cb*Co phospholyl derivatives [38]. Complexes **25b**,**c** with methylated phospholyl ligands were obtained in high yields (ca. 60%). Unfortunately, the yield of compound **25a** with the unsubstituted C_4H_4P ring was only 20%. It is interesting to note that in contrast to pyrrolyl analogues **24a**,**c**, complexes **25b**,**c** can be prepared also starting from complex **1** (Scheme 13). However, heating is necessary in this case and the yields are much lower than using complex **4**. The room temperature reaction of LiC_4Me_4P with **1** was shown to afford the σ-phospholyl complex **26** which transforms into **25c** when refluxed in THF. The $\mathrm{Co}\cdots\mathrm{Cb}^*$ distance in **25c** (1.689 Å) is only slightly longer than that in **17g** (1.684 Å).

4.3.2. Boratabenzene complexes

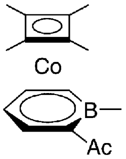
Several reviews on metal derivatives of boratabenzene anion $[C_5H_5BH]^-$ have been published [47]. The (boratabenzene)cobalt complexes $\mathrm{Cb^*Co}(C_5H_5BMe)$ (**27a**) and $\mathrm{Cb^*Co}(C_5H_5BPh)$ have been prepared by reaction of **1** with anions $[C_5H_5BR]^-$ [48]. CF_3CO_2D effects H/D-exchange in the α-position of the boratabenzene ring in **27a** within a few minutes at ambient temperature and in the γ-position within several hours. Interesting results were obtained from acetylation studies of **27a**. Treatment with AcCl in the presence of the mild catalyst $AsCl_3$ affords the 2-acetyl derivative **27b**. With $SnCl_4$ the 2,6-diacetyl derivative **27c** was obtained as a main product. The more active catalyst $AlCl_3$ effects boron replacement (termed as ring-member substitution [49]) to give the cationic arene complexes **3b** and $[\mathrm{Cb^*Co}(2\text{-}MeC_6H_4Ac)]^+$ (**3c**). Complexes **3b**,**c** are also formed from the acetyl derivatives **27b**,**c** in superacidic media (CF_3SO_3H or CF_3CO_2H/BCl_3). Vilsmeier formylation of **27a** gives its 2-formyl derivative.



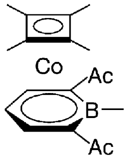
Scheme 13. Reaction of complex **1** with LiC_4Me_4P.



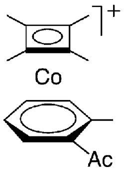
27a



27b

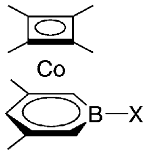


27c



3c

The B-dimethylamino-boratabenzene complex $\mathrm{Cb^*Co}(3,5\text{-}Me_2C_5H_3BNMe_2)$ (**28a**) was obtained recently by Herberich et al. [50] using the reaction of the acetonitrile complex **4** with $[\mathrm{Li(TMEDA)}][3,5\text{-}Me_2C_5H_3BNMe_2]$. Substitution reactions at the boron atom were studied in detail. Methanolysis of **28a** affords the methoxy derivative **28b**. The latter reacts with MeLi or BCl_3 to give the B-methyl and B-chloro compounds **28c** and **28d**, respectively. The chloro compound **28d** reacts with ${}^iBu_2AlH$, TlF or $LiSnMe_3$ to afford the hydrido, fluoro and trimethylstannyl derivatives **28e**, **28f** and **28g** ($\mathrm{Co}\cdots\mathrm{Cb}^*$, 1.703 Å), respectively. The B–O–B-linked dinuclear complex $[\mathrm{Cb^*Co}(3,5\text{-}Me_2C_5H_3B)]_2O$ (**28h**, $\mathrm{Co}\cdots\mathrm{Cb}^*$, 1.686 Å) was formed as a by-product in the preparation of **28g** owing to interaction with traces of air. The amino compound **28a** undergoes quaternization with iodomethane to produce $[\mathrm{Cb^*Co}(3,5\text{-}Me_2C_5H_3BNMe_3)]^+$ (**28i**) which possesses a borabenzene-trimethylamine ligand. When treated with $[Bu_4N]CN$ in CH_2Cl_2 nucleophilic substitution of the NMe_3 group takes place to give the B-cyanoboratabenzene complex **28j**.



28a–j

	X
a	NMe_2
b	OMe
c	Me
d	Cl
e	H
f	F
g	$SnMe_3$
h	$O_{1/2}$
i	NMe_3^+
j	CN

5. Arene exchange in $[Cb^{*}Co(arene)]^{+}$

Many examples of arene exchange reactions proceeding under thermal conditions are known [51]. However, photochemical arene exchange has been described earlier only for the iron complexes $[CpFe(arene)]^{+}$ [52] which are on the contrary unreactive thermally. The cobalt arene complexes $[Cb^{*}Co(arene)]^{+}$ proved to be unique since they are capable of reacting both under irradiation and heating.

5.1. Photochemical arene exchange

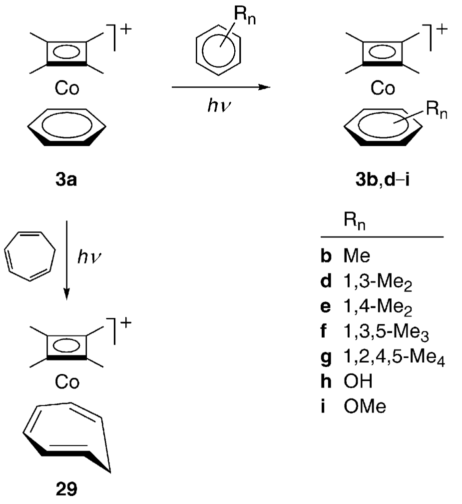
We found that visible light irradiation of the cobalt benzene complex **3a** in CH_2Cl_2 in the presence of other arenes results in arene exchange to give complexes **3b**,**d–i** (Scheme 14) [53]. Benzene derivatives containing Me, OH and OMe groups were successfully used in this reaction. However, in the case of C_6Me_6 the reaction is very slow, evidently owing to steric hindrance caused by six methyl groups. The reaction of **3a** with cycloheptatriene gives complex **29**. The toluene complex **3b** can be used instead of **3a** with a slight decrease of the reaction rate.

Comparative study of the reactions of the benzene complexes **3a** and $[CpFe(C_6H_6)]^{+}$ with mesitylene (in CH_2Cl_2) shows that the rate of arene exchange for **3a** is approximately two orders of magnitude lower than in the case of the iron analogue. Nevertheless, the rate of the reaction for the cobalt complexes is sufficiently high, provided that a powerful visible light source is used. It is recommended to use widely spread high pressure mercury vapor lamps with phosphor coated bulbs.

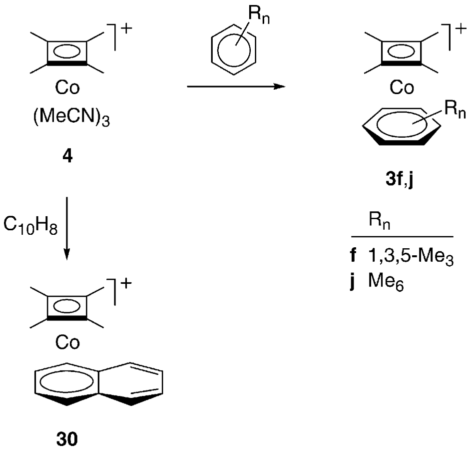
The rate of the reaction in acetone is much higher than in CH_2Cl_2 indicating that the first stage is nucleophilic replacement of benzene from the photochemically excited cation **3a** by solvent molecules and/or the counter ion; subsequent reaction with a substituted benzene affords a new arene complex **3**. It is additionally supported by a high rate of the reaction of **3a**,**b** with acetonitrile leading to the isolable solvate complex **4** (see Section 2.3) and by ability of the latter to react with arenes giving arene complexes **3** (see Section 5.2). It should be emphasized, however, that irradiation of **3a**,**b** in CH_2Cl_2 allows to generate the 12-electron species $[Cb^{*}Co]^{+}$ in the most active form due to a very low coordinating ability of this solvent. The photochemical method was successfully used further to prepare $Cb^{*}Co$ containing triple-decker complexes, metallacarboranes and transition metal clusters.

5.2. Thermal arene exchange

The benzene ligand in **3a** can be replaced by acetonitrile either photochemically or thermally (see Section 2.3). Therefore it was proposed that arene exchange under thermal conditions will be also possible. Indeed, refluxing of **3a** in $MeNO_2$ in the presence of mesitylene leads to complex **3f** as a result of arene exchange [53]. However, the rate of the reaction is considerably lower than under irradiation. In accord with the ability of donor solvents to catalyze arene exchange [51a,b], the reaction was greatly accelerated by addition of a catalytic amount of MeCN. It is explained by easier replacement of benzene by acetonitrile than by nitromethane. The reaction could be suggested to proceed via an intermediate formation of the solvate complexes of the type $[Cb^{*}Co(MeCN)_x(MeNO_2)_{3-x}]^{+}$ ($x \leq 3$). The ability of such solvates to react with arenes was proved while studying reactivity of the acetonitrile complex **4** towards arenes. The acetonitrile ligands in this complex are replaced by arenes (mesitylene, naphthalene) even at room temperature (Scheme 15). The reaction of **4** with C_6Me_6 in refluxing $MeNO_2$ allows to prepare complex $[Cb^{*}Co(C_6Me_6)]^{+}$ (**3j**) which is difficult to obtain by photochemical arene exchange in **3a**. It should be emphasized that arene exchange (photochemical or thermal) in **3a** can be used only to prepare complexes with arenes having stronger donor ability than benzene, which is related to the equilibrium character of the process. This limitation is absent in the reaction with the acetonitrile complex **4**. For instance, the method



Scheme 14. Photochemical arene exchange in complex **3a**.



Scheme 15. Reactions of the acetonitrile complex **4** with arenes.

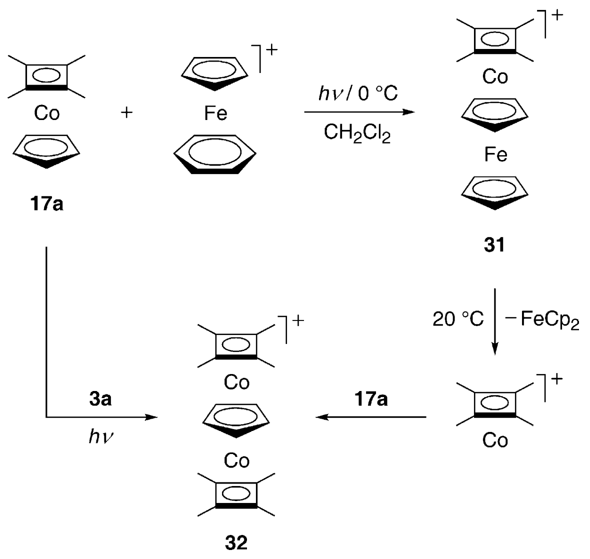
was successfully used to prepare the naphthalene complex **30** which is inaccessible by other methods.

The Co· · · Cb* distances in the benzene, naphthalene and cycloheptatriene complexes **3a** (1.707 Å), **30** (1.709 Å) and **29** (1.728 Å) [53] are longer than those in the acetylcyclopentadienyl and indenyl complexes, **17g** (1.684 Å) and **20** (1.679 Å) [38], but shorter than that in the tricarbonyl complex **2** (av. 1.777 Å) [22].

6. Triple-decker complexes

6.1. *μ-Cyclopentadienyl complexes*

Cationic triple-decker complexes are usually synthesized by electrophilic stacking reactions of sandwich compounds with cationic half-sandwich fragments [54]. In particular, triple-decker complexes with bridging cyclopentadienyl [54a,55], phospholyl [56], pentaphospholyl [57] and boratabenzene [58] ligands have been prepared using the fragments $[(C_5R_5)M]^+$ (M = Fe, Ru; R = H, Me). For example, the electrophilic stacking of ferrocene with $[CpFe]^+$, generated in situ by visible light irradiation of the benzene complex $[CpFe(C_6H_6)]^+$, leads to the thermally unstable parent diiron triple-decker complex $[CpFe(\mu\text{-}Cp)FeCp]^+$ [55c]. The similar reaction of the cobalt complex **17a** with the same fragment proved to be especially interesting (Scheme 16). The attack of the metalloelectrophile was shown to proceed regioselectively at the cyclopentadienyl ring to give the FeCo cationic triple-decker complex **31** as a primary product. This complex can be isolated in pure form if the reaction is conducted at 0 °C. At a higher temperature (20 °C) complex **31** decomposes with elimination of ferrocene molecule and generation of the highly reactive 12-electron cationic $[Cb^*Co]^+$ species. The stacking reaction of the latter with the starting compound **17a**, which is present in the reaction mixture, affords the Co_2 triple-decker complex **32**. To prepare **32** in pure form, the reactants **17a** and $[CpFe(C_6H_6)]PF_6$ should be taken in a molar ratio of ≥2:1 [55c].



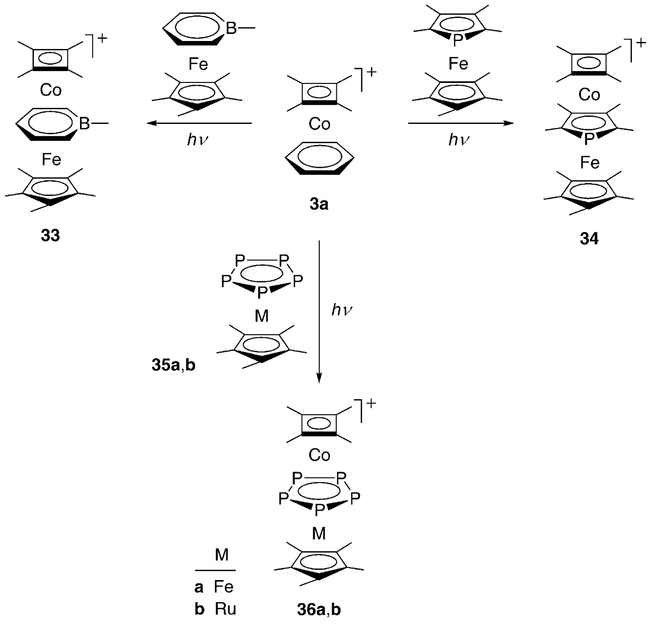
Scheme 16. Synthesis of the μ-cyclopentadienyl triple-decker complexes **31** and **32**.

The formation of the triple-decker cation **32** from the labile complex **31** occurs through exchange of sandwich compounds, viz. of ferrocene for **17a**, similar to arene exchange in complex **3a** (see Section 5.1), sandwich compounds acting as six-electron ligands similar to benzene.

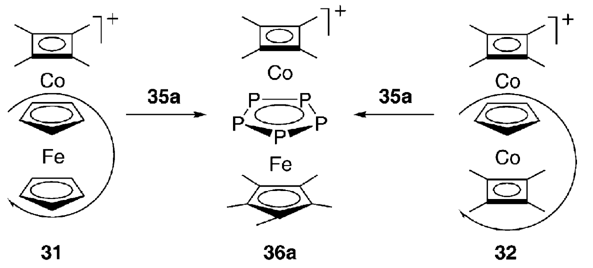
The dicobalt complex **32** can be also obtained by straightforward stacking reaction of **17a** with the $[Cb^*Co]^+$ fragment, photochemically generated in situ from **3a**, however preparation of **32** using $[CpFe(C_6H_6)]^+$ seems to be more favorable owing to easy accessibility of the iron complex. The ability of **17a** to substitute for benzene confirms similarity of coordinating properties of these compounds.

6.2. *Complexes with bridging five-electron boron and phosphorus containing rings*

Electrophilic stacking of the sandwich compounds $Cp^*Fe(C_5H_5BMe)$, $Cp^*Fe(C_4Me_4P)$ and $Cp^*M(cyclo\text{-}P_5)$ (M = Fe (**35a**), Ru (**35b**)) with the fragment $[Cb^*Co]^+$ (photochemically generated from **3a**) affords the triple-decker complexes **33**, **34** and **36a**,**b** with bifacially bonded boratabenzene, phospholyl and pentaphospholyl ligands (Scheme 17) [53]. The structures of the FeCo complexes **33** (Co· · · Cb*, 1.697 Å), **34** (Co· · · Cb*, 1.705 Å) and **36a** (Co· · · Cb*, 1.745 Å) were confirmed by X-ray diffraction. The longest Co· · · Cb* distance for **36a** is in accord with higher acceptor properties of cyclo-P_5 as compared



Scheme 17. Synthesis of triple-decker complexes with bridging five-electron boron and phosphorus containing rings.



Scheme 18. Sandwich compound exchange in triple-decker complexes.

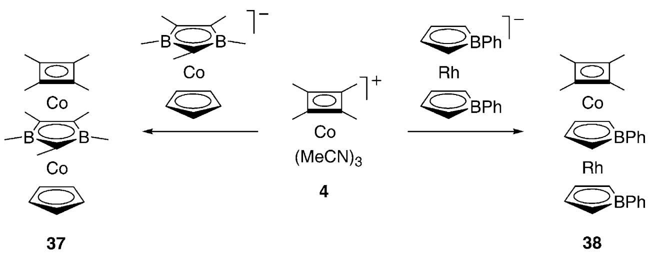
with boratabenzene and phospholyl rings. Complex **36a** is the most stable among the FeCo complexes owing to the better ability of the pentaphospholyl ring to back-bonding.

The formation of the Co_2 complex **32** from the FeCo complex **31** discussed above is an example of the synthesis of a stable triple-decker complex from a labile compound of this type. The reaction of **31** with the pentaphospholyl complex **35a** gives the triple-decker complex **36a** (Scheme 18). The dicobalt complex **32**, in spite of its higher stability as compared with **31**, also reacts with **35a** to give **36a**. Complex **36a** is formed from **31** and **32** as a result of exchange of sandwich compounds.

6.3. *Complexes with bridging three- and four-electron boron heterocycles*

Three- and four-electron boron heterocycles, 1,3-diborolyl [59] and borole [60], are known to possess very high propensity to bifacial bonding with metal atoms due to the favorable balance of their donor and acceptor properties. In order to obtain Cb*Co containing triple-decker complexes with these ligands, stacking reactions of the $[Cb^*Co]^+$ fragment with suitable sandwich complexes, $[CpCo(C_3B_2Me_5)]^-$ and $[Rh(C_4H_4BPh)_2]^-$ were studied. Negative charge makes these complexes sufficiently reactive towards the acetonitrile complex **4**.

The reaction of **4** with the anionic complex $[CpCo(C_3B_2Me_5)]^-$ affords the Co_2 μ-diborolyl triple-decker **37**, the structure of which was confirmed by X-ray diffraction (Co···Cb*, 1.693 Å) (Scheme 19) [61]. Similar reaction with $[Rh(C_4H_4BPh)_2]^-$ gives the CoRh μ-borole compound **38** [62]. The starting anionic complexes act as six-electron donors similar to Cp^-. It allows to consider the triple-decker complexes **37** and **38** as analogues of the cyclopentadienyl complexes **17**. Interestingly, the Co···Cb* distance in **37** is very close to that in complex **17g** (1.684 Å), suggesting similarity of the donor–acceptor properties of anions $[CpCo(C_3B_2Me_5)]^-$ and $[C_5H_4C(O)Me]^-$.



Scheme 19. Synthesis of triple-decker complexes with bridging three- and four-electron boron heterocycles.

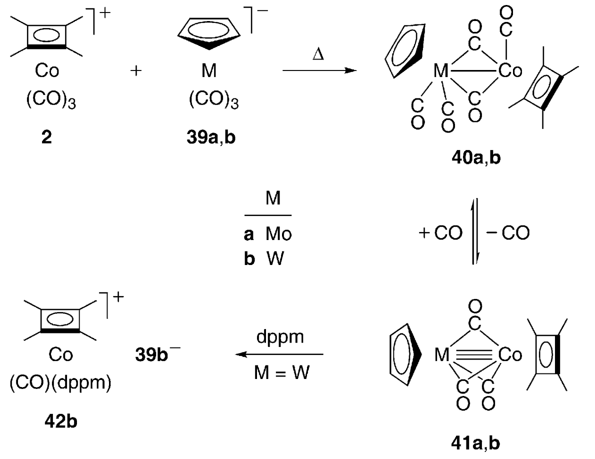
7. Complexes with metal–metal bonds

7.1. *Dimetal complexes*

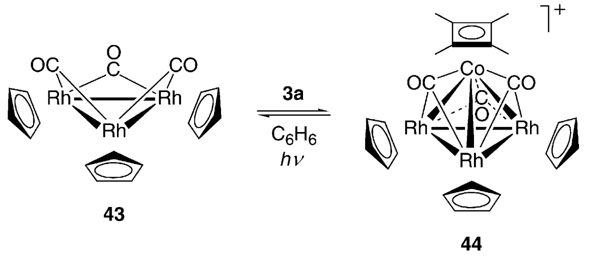
The tricarbonyl complex **2** reacts with the carbonylmetalates **39a**,**b** in refluxing THF to give the mixtures of the binuclear CoMo and CoW complexes **40a**,**b** and **41a**,**b**, which were separated by column chromatography (Scheme 20) [63]. Complexes **41a**,**b** containing the cobalt-metal triple bond (for **41b**: Co–W 2.356, Co···Cb*, 1.706 Å) are formed from **40a**,**b** by reversible CO elimination. Based on EH-MO calculations, complexes **41a**,**b** were described as structural analogues of the sandwich compound **17a** with anions **39a**,**b** acting as six-electron donor ligands isolobal with Cp^- [64]. However, the reaction of **41b** with dppm yielding salt $\mathbf{42b}^+\mathbf{39b}^-$ demonstrates greater cleavage ability of these compounds as compared with **17a**. Formation of dimetal compounds having carborane ligands is discussed in Section 8.2.1.

7.2. *Clusters*

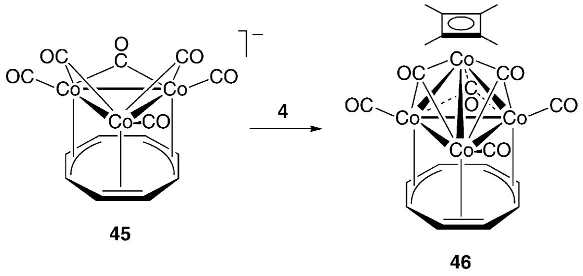
We have shown earlier that the triangular rhodium cluster $Rh_3Cp_3(\mu_2\text{-}CO)_3$ (**43**) having three μ_2-bridging carbonyl groups can act as a two- or six-electron ligand depending on the electronic requirements of an attacking metal containing species [65]. For instance, it donates two electrons to the fragments $[(Ph_3P)M]^+$ (M = Cu, Ag, Au) having one vacant frontier orbital (σ) of appropriate en-



Scheme 20. Synthesis and reactions of the dimetal complexes **40a**,**b** and **41a**,**b**.



Scheme 21. Reversible formation of the $CoRh_3$ cluster **44**.



Scheme 22. Synthesis of the Co_4 cluster **46**.

ergy [66] resulting in the formation of the Rh_3M clusters $[(Ph_3P)MRh_3Cp_3(\mu_2\text{-}CO)_3]^+$. In this case the CO groups retain their μ_2-bridging position suggesting that they are not involved in binding of **43** with the copper, silver or gold atom. With respect to the fragments $[(C_5R_5)M]^+$ (M = Fe, Ru; R = H, Me) having three vacant frontier orbitals (two of π- and one of σ-type) [67] compound **43** behaves as six-electron ligand similar to benzene. The resulting Rh_3M clusters $[(C_5R_5)MRh_3Cp_3(\mu_3\text{-}CO)_3]^+$ have three μ_3-bridging carbonyl groups indicating their participation in binding with the iron or ruthenium atom. Quite similar to $[CpFe]^+$ and $[(C_5R_5)Ru]^+$, the reaction of the $[Cb^*Co]^+$ fragment (generated in situ by irradiation of the benzene complex **3a**) with **43** results in the formation of the $CoRh_3$ cluster $[Cb^*CoRh_3Cp_3(\mu_3\text{-}CO)_3]^+$ (**44**) (Scheme 21) [68]. The structure of its analogue with one Me group in each Cp ring was confirmed by X-ray diffraction (Co···Cb*, 1.763 Å). Not only cluster **43** donates the same number of electrons as benzene to the $[(ring)M]^+$ fragments, but also conditions of these reactions are the same as for benzene and its derivatives (for example cf. Scheme 14). Moreover, the reactions between **43** and the arene complexes $[CpFe(C_6H_6)]^+$ and **3a** are reversible, i.e. cluster **43** and arenes can interchange in their complexes. It allows to consider the Rh_3 cluster **43** as metallocyclic analogue of benzene ligand, which was further supported by DFT calculations.

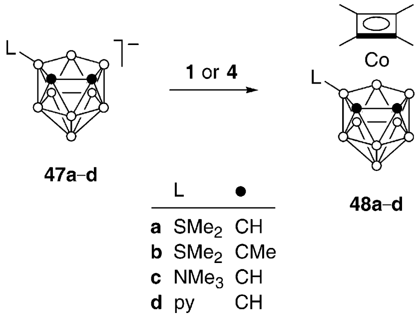
Wadepohl et al. [69] have shown that the anionic Co_3 cluster $[Co_3(CO)_3(\mu_2\text{-}CO)_3(\mu_3\text{-}C_8H_8)]^-$ (**45**) with a face-capping cyclooctatetraene ligand reacts with the ruthenium acetonitrile complex $[Cp^*Ru(MeCN)_3]^+$ to give the Co_3Rh cluster $Cp^*RuCo_3(CO)_3(\mu_3\text{-}CO)_3(\mu_3\text{-}C_8H_8)$. Similar reaction of **45** with the cobalt complex **4** affords the Co_4 cluster $Cb^*Co_4(CO)_3(\mu_3\text{-}CO)_3(\mu_3\text{-}C_8H_8)$ (**46**) (Scheme 22) [70]. This compound was also obtained by irradiation of salt $\mathbf{3a}^+\mathbf{45}^-$ which precipitates on mixing CH_2Cl_2 solutions of $[Et_4N]^+\mathbf{45}^-$ and $\mathbf{3a}^+PF_6{}^-$. X-ray diffraction study of **46** (Co···Cb*, 1.778 Å) reveals the $\mu_3\text{-}\eta^2{:}\eta^3{:}\eta^3$ bonding mode of C_8H_8, quite similar to the Co_3Ru analogue. However, a sharp singlet in the ^1H NMR spectrum of **46** (CD_2Cl_2, 20 °C) suggests a fast rotation of the eight-membered ring in solution. The examples described in this section demonstrate utility of the $[Cb^*Co]^+$ fragment for cluster chemistry.

8. Metallacarboranes

8.1. Cobaltacarboranes $Cb^*Co(L\text{-}C_2B_9H_{10})$ (L = two-electron ligand)

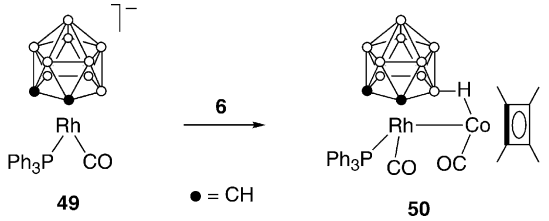
Many complexes with charge-compensated carborane monoanions of the type $[L\text{-}C_2B_9H_{10}]^-$ (L = two-electron ligand) are presently known [71]. The attractiveness of these ligands is connected with the similarity of their coordinating properties with those of the cyclopentadienide anion. (Cyclobutadiene)cobaltacarboranes **48a–d** were prepared by reaction of sodium derivatives of anions **47a–d** either with the (carbonyl)iodide complex **1** or with the acetonitrile complex **4** (Scheme 23) [30,72], the conditions of these reactions being practically the same as in the preparation of the related cyclopentadienyl complexes **17** (see Section 4.1). In the case of the reaction with the less reactive complex **1** the yields are lower than in analogous reaction with **4**. However, the yields can be considerably improved using thallium derivatives of the carborane anions instead of sodium derivatives.

The structures of complexes **48a** (Co···Cb*, 1.710 Å) and **48d** (Co···Cb*, 1.711 Å) were confirmed by X-ray diffraction. The Co···Cb* distances in these compounds are considerably longer than the corresponding distance in the acetylcyclopentadienyl complex **17g** (1.684 Å) in accord with lower back-donation from cobalt to the Cb* ring in consequence of greater acceptor ability of the carborane ligands.



	L	●
a	SMe_2	CH
b	SMe_2	CMe
c	NMe_3	CH
d	py	CH

Scheme 23. Synthesis of the cobaltacarboranes **48a–d**.



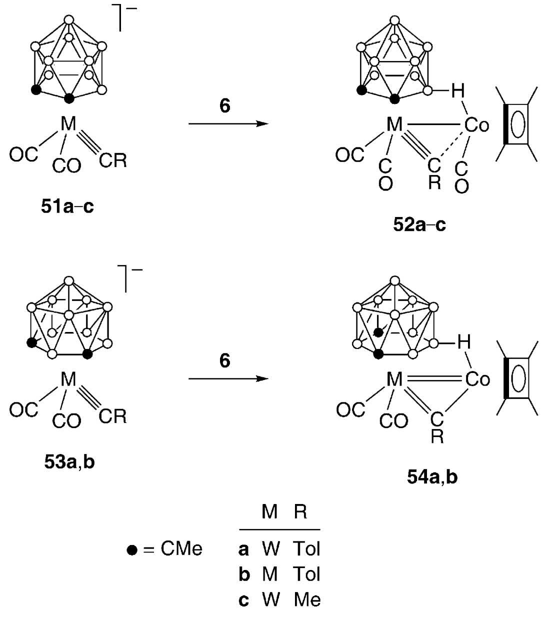
Scheme 24. Formation of the CoRh complex **50** from rhodacarborane **49**.

8.2. Electrophilic reactions of metallacarboranes with Cb^*Co containing species

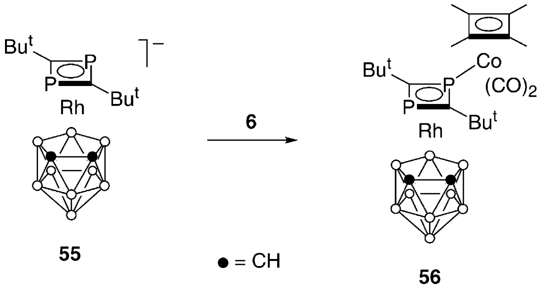
8.2.1. Formation of compounds with a metal–cobalt bond

Stone et al. [73] have shown that anionic metallacarboranes are able to react with metalloelectrophiles leading to heteronuclear dimetal compounds. In particular, the mono(acetonitrile) complex **6** was used as a metalloelectrophile. Its reaction with the rhodacarborane anion **49** affords the CoRh compound **50** (Co–Rh, 2.746; $Co\cdots Cb^*$, 1.765 Å) which contains a three-center two-electron B–H–Co bond (Scheme 24).

The alkylidyne–metal anions **51a–c** and **53a**,**b** (Scheme 25) were proved to be versatile reagents for preparing compounds containing heteronuclear metal–metal bonds [74]. The $C\equiv M$ linkages present in these anions readily add electrophilic metal–ligand fragments to give compounds in which an alkylidyne group bridges a bond between tungsten or molybdenum and another metal center. In particular, the reactions of these anions with the cobalt complex **6** afford the CoMo and CoW compounds **52a–c** and **54a**,**b**. All of the compounds have an exo-polyhedral B–H–Co bond. An alkylidyne group is fully bridging in compounds **54a**,**b** (for **54b**: μ-C–Mo, 1.914 Å; μ-C–Co, 1.915 Å; $Co\cdots Cb^*$, 1.745 Å) but only semibridging in **52a–c**, in accordance with different number of CO groups.



Scheme 25. Formation of dimetal complexes from (alkylidyne)metallacarboranes.

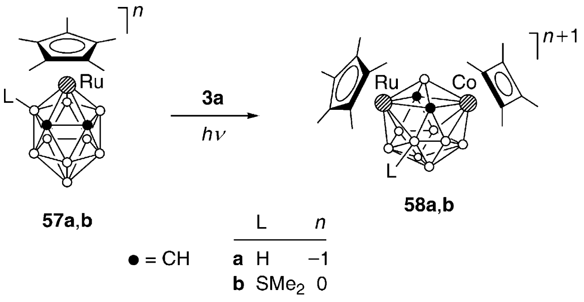


Scheme 26. Formation of the CoRh complex **56**.

In contrast to reactions with **49**, **51a–c** and **53a**,**b**, in the case of the (1,3-diphosphacyclobutadiene)rhodacarborane anion **55** the attack of electrophilic cobalt species proceeds at the phosphorus lone pair to give complex **56** ($Co\cdots Cb^*$, 1.760 Å) (Scheme 26) [75]. This compound can be considered as a zwitterionic analogue of the phosphine complex **13** (see Section 3.2, Scheme 6), the rhodacarborane anion **55** acting simultaneously as a phosphine ligand and a counter-ion with respect to the $[Cb^*Co(CO)_2]^+$ fragment.

8.2.2. Electrophilic insertion into 12-vertex metallacarboranes

We reported recently the first examples of direct electrophilic insertion into 12-vertex *closo*-metallacarboranes [76]. Metalloelectrophiles $[(ring)M]^+$ proved to be able to insert into sufficiently nucleophilic metallacarboranes of the type $CpM(C_2B_9H_{11})$. For example, insertion of the $[Cb^*Co]^+$ species into the ruthenacarboranes **57a**,**b** gives the 13-vertex cobaltaruthenacarboranes **58a** ($Co\cdots Cb^*$, 1.777 Å) and **58b** (Scheme 27). The rate of the reaction with the more nucleophilic anionic ruthenacarborane **57a** is much higher than with its neutral analogue **57b** having a charge-compensating substituent. In the case of **57a** it is even possible to use the (carbonyl)iodide complex **1**. Interestingly, the $[Cb^*Co]^+$ fragment is less active in electrophilic insertion reactions than $[Cp^*Ru]^+$, but is much more active than $[CpFe]^+$. Complexes **58a**,**b** belong to $2n$ electron (*hypercloso*) [77] systems (where n is the number



Scheme 27. Electrophilic insertion of the $[Cb^*Co]^+$ fragment into 12-vertex ruthenacarboranes.

of vertices), having two electrons less than required by the Wade's rules [78]. Nevertheless, they are thermally stable and chemically inert.

9. Conclusion

The development of chemistry of (tetramethylcyclobutadiene)cobalt complexes became possible owing to easy preparation of the carbonyl complexes $Cb^*Co(CO)_2I$ (**1**) and $[Cb^*Co(CO)_3]^+$ (**2**) starting from cobalt carbonyl and 2-butyne. Ligand substitution reactions of **2** afford half-sandwich complexes $[Cb^*Co(CO)_x(L)_{3-x}]^+$. Complex **1** proved to be especially useful. It reacts directly with sufficiently nucleophilic anionic cyclopentadienide and carborane ligands. The reaction of **1** with arenes in the presence of $AlCl_3$ affords the arene complexes $[Cb^*Co(arene)]^+$ (arene = C_6H_6 (**3a**), C_6H_5Me (**3b**)). Visible light irradiation of **3a**,**b** in CH_2Cl_2 generates the reactive $[Cb^*Co]^+$ species (apparently in form of labile associates with the solvent molecules and the counter-ion PF_6^-) as a result of replacement of an arene ligand. Arene exchange takes place in the presence of another arene. The photochemical method was successfully used to prepare triple-decker and cluster compounds. Insertion of the $[Cb^*Co]^+$ species into 12-vertex metallacarboranes affords 13-vertex dimetallacarboranes. Although we used mostly the benzene complex **3a** in our experiments, it was shown later that the toluene analogue **3b** is almost equally effective.

Another approach is based on the use of the substitutionally labile cationic acetonitrile complex **4** which can be easily prepared from **3a**,**b** either by photolytic or thermal ligand displacement in acetonitrile solution. Complex **4** is most suitable for reactions with anionic ligands, demonstrating much higher reactivity than the (carbonyl)iodide complex **1**. Such reactions enable, in particular, to obtain complexes with carbo- and heterocyclic ring ligands (Cp*, indenyl, pyrrolyl, phospholyl and boratabenzene) which cannot be prepared starting from **1**. The limitation of this method is connected with deprotonaton of **4** by extremely basic anions. Search for another synthon lacking this limitation is presently under way.

The methods described make Cb*Co complexes readily available allowing development of their application, similar to CpFe and CpRu congeners. For example, complexes **3** and **4** are perspective for catalytic application, similar to their iron and ruthenium analogues $[CpFe(arene)]^+$ [79] and $[CpRu(MeCN)_3]^+$ [80].

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