(Tetramethylcyclobutadiene)cobalt Complexes − Syntheses of Tris(ligand) Derivatives and Structures of $[(\mathrm{C_4Me_4})\mathrm{Co(CO)_3}]\mathrm{BF_4}$ and $[(\mathrm{C_4Me_4})\mathrm{Co(NCMe)_3}]\mathrm{PF_6}$

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Photolysis of $[\mathrm{Cb^{\star}Co(C_6H_6)}]\mathrm{PF_6}]$ (**6**) ($\mathrm{Cb^{\star} = C_4Me_4}$) in acetonitrile solution produces the red solvento complex $[\mathrm{Cb^{\star}Co(NCMe)_3}]\mathrm{PF_6}$ (**8**) in quantitative yield. Alternatively, heating of the acetonitrile solution to reflux temperature may effect the displacement of the benzene ligand. Photolysis of **6** in liquid ammonia gives $[\mathrm{Cb^{\star}Co(NH_3)_3}]\mathrm{PF_6}$ (**9**). Compound **8** is substitution-labile and reacts with a wide variety of Lewis bases to produce substitution products $[\mathrm{Cb^{\star}CoL_3}]\mathrm{PF_6}$ with L = $\mathrm{P(OMe)_3}$ (**10**), py (**11**), CN*t*Bu (**12**), and the related compound $(\mathrm{NEt_4})_2[\mathrm{Cb^{\star}Co(CN)_3}]$ (**13**). Thermal reaction of $[\mathrm{Cb^{\star}Co(CO)_3}]\mathrm{BF_4}$ (**7**) with $\mathrm{PMe_3}$ takes place spontaneously at ambient temperature and produces the monosubstitution product $[\mathrm{Cb^{\star}Co(CO)_2(PMe_3)}]\mathrm{BF_4}$ (**14**), while irradiation combined with a purging stream of $\mathrm{N_2}$ effects an exhaustive decarbonylation and affords $[\mathrm{Cb^{\star}Co(PMe_3)_3}]\mathrm{BF_4}$ (**16**). Irradiation of **7** in acetonitrile produces mixtures of the mono- and disubstitution products; if a purging stream of $\mathrm{N_2}$ is applied, $[\mathrm{Cb^{\star}Co(CO)(NCMe)_2}]\mathrm{BF_4}$ (**18**) is formed with a small admixture of $[\mathrm{Cb^{\star}Co(NCMe)_3}]\mathrm{BF_4}$. The iodide $\mathrm{Cb^{\star}CoI(CO)_2}$ reacts with 2,2′-bipyridine to produce the monocarbonyl complex $[\mathrm{Cb^{\star}Co(CO)(bipy)}]\mathrm{I}$ (**15**). Single-crystal structure determinations of $[\mathrm{Cb^{\star}Co(CO)_3}]\mathrm{BF_4}$ (**7**) with Co–Cb(ring plane) 1.777(2) Å (av.) and of $[\mathrm{Cb^{\star}Co(NCMe)_3}]\mathrm{PF_6}$ (**8**) with Co–Cb(ring plane) 1.68(1) Å (av.) are reported. Synthetic procedures for the preparation of $[\mathrm{Cb^{\star}Co(CO)_3}]\mathrm{BF_4}$ (**7**), $\mathrm{Cb^{\star}CoI(CO)_2}$ (**2**), and $[\mathrm{Cb^{\star}Co(C_6H_6)}]\mathrm{PF_6}$ (**6**) are also given. An electrochemical study of the compounds **8**, **10–13**, and **16** reveals chemically fully reversible oxidation reactions. Hard σ-donor ligands ($\mathrm{CN^-}$, py, NCMe) stabilize the corresponding 17e species much more so than soft donor ligands [$\mathrm{PMe_3}$, CN*t*Bu, and $\mathrm{P(OMe)_3}$].

Introduction

Electrophilic complex fragments or metallo-electrophiles of the general type $[\mathrm{L}_x\mathrm{M(solv)}_y]^{n+}$ are useful synthons in organometallic chemistry. Our interest in metallo-electrophiles developed during our quest for new triple-decker complexes.[1,2] Early examples of metallo-electrophiles are the 1,5-cyclooctadiene complex $[\mathrm{(COD)Rh(THF)}_x]^+$ [3] and the cation $[\mathrm{Cp^*Rh(OCMe_2)_3}]^{2+}$.[4] These species are usually generated from corresponding chlorides by dehalogenation with $\mathrm{Ag^+}$ or $\mathrm{Tl^+}$ salts with nonbasic anions such as $\mathrm{BF_4}^-$, $\mathrm{PF_6}^-$, or $\mathrm{CF_3SO_3}^-$. Weakly coordinating solvents such as nitromethane, dichloromethane, THF, acetone, or acetonitrile are used in the generation of the metallo-electrophiles to provide a maximum reactivity and a minimal stabilization. The number of coordinated solvent units is often unknown, especially in the cases of the most weakly bonded solvent molecules. On the other hand, the acetonitrile ligand provides sufficient stabilization to the electrophilic metal center to allow the isolation of less reactive, but well-defined compounds. The species $[\mathrm{CpFe(NCMe)_3}]^+$,[5,6] $[\mathrm{Cp^*Fe(NCMe)_3}]^+$,[7] $[\mathrm{CpRu(NCMe)_3}]^+$,[6,8] $[\mathrm{Cp^*Ru(NCMe)_3}]^+$,[9] and $[\mathrm{CpOs(NCMe)_3}]^+$ [10] are pertinent examples, and the more recently discovered species $[\mathrm{Cb^*Co(solv)}_x]^+$ ($\mathrm{Cb^* = C_4Me_4}$, solv = inter alia MeCN)[11] is related to these by virtue of the isolobal analogy.

Complex fragments of the (cyclobutadiene)cobalt type are well known in complexes with Cp counterligands, e.g. Cb*CoCp,[12] or $\mathrm{(C_4Ph_4)CoCp}$,[13] whereas comparatively little is known about (cyclobutadiene)cobalt complexes with counterligands other than Cp. There are several general reviews on (cyclobutadiene)metal complexes,[14] and also specialized reviews that center on the chemistry of (cyclobutadiene)cobalt complexes.[15]

In pioneering work Pauson et al.[16] have shown that the zwitterionic cyclobutenyl species $\mathrm{Me_4C_4AlCl_3}$ [17] readily re-

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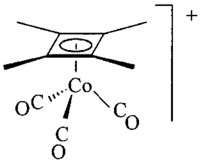
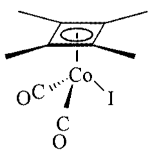
acts with $Co_2(CO)_8$ to form the cation $[Cb^*Co(CO)_3]^+$ (1^+). On this basis they developed syntheses of $Cb^*CoI(CO)_2$ (**2**), and $[Cb^*Co(C_6H_6)]^+$ (3^+). The goal of the present work is the further development of the chemistry of the (tetramethylcyclobutadiene)cobalt complex fragment and especially of the new metallo-electrophile $[Cb^*Co(NCMe)_3]^+$ (4^+). We also present the first structural characterizations of tris(ligand) species $[Cb^*CoL_3]^+$ with L = CO and MeCN.



1^+



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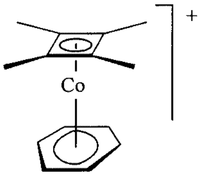
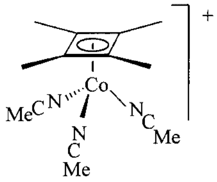


3^+



4^+

Results and Discussion

Starting Materials

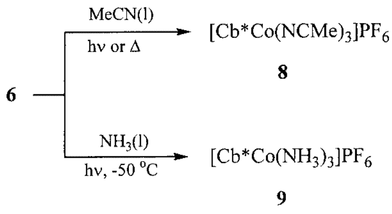
In the work of Pauson et al.[16] the salt $[Cb^*Co(CO)_3]PF_6$ (**5**) was isolated from the reaction of $Me_4C_4AlCl_3$ [17] and $Co_2(CO)_8$. In a second step, this salt was treated with Me_3NO/Bu_4NI in dichloromethane or with K_2CO_3/Bu_4NI in dichloromethane to afford the iodide **2**. In a further transformation the iodide **2** was heated with $AlCl_3$ in benzene, and the resulting cation 3^+ was isolated as hexafluorophosphate **6** [≡ (**3**)PF_6].[16]

In part of our work we used the tetrafluoroborate **7** [≡ (**1**)BF_4] which was synthesized by a straightforward adaptation of the published synthesis of the hexafluorophosphate **5**. The iodide **2** was prepared by a simplified procedure that combines the two steps of the original work into a single protocol. After hydrolysis of the primary reaction mixture, Me_3NO and NaI were added to the raw aqueous solution containing 1^+, producing the uncharged iodide **2** as a brown precipitate. This procedure gave a somewhat lower yield (37%; ref.[16] 45−52%), but requires less work.

When we repeated the synthesis of the benzene complex **6**, we found that some tricarbonyl cation 1^+ was also formed as was readily seen from the product IR spectrum or from ^1H NMR spectra in nitromethane or dichloromethane solution. It is recommendable to use a tenfold excess of $AlCl_3$, to add petroleum ether (octane fraction, 60% by volume), and to run the reaction at ca. 130 °C. Under these conditions the CO formed is removed more efficiently from the reaction mixture, and the formation of 1^+ is largely suppressed. The by-product may also be removed during workup of the reaction mixture, by adding a little Me_3NO and NaI to the aqueous solution. The yield of **6** varies somewhat erratically between 50 and 80% (ref.[16] 25%), presumably because traces of water seem to be favorable while larger amounts of water are detrimental.

Photolysis of $[Cb^*Co(C_6H_6)]PF_6$ (6) and Alternative Thermal Ligand Displacement

The sandwich cation 3^+ is rather light-sensitive, and solutions of **6** can be photolyzed with any light source at hand (cf. Exp. Sect.). In this context the most useful solvent is acetonitrile. During irradiation, the color changes from yellow to red, and subsequent removal of the volatiles affords the product $[Cb^*Co(NCMe)_3]PF_6$ (**8**) as red crystalline solid in quantitative yield. When acetonitrile solutions of **6** are heated, the benzene ligand is displaced almost completely. This thermal ligand displacement reaction may be forced to go to completion if the volatiles are largely pumped off and the reaction mixture is heated once more in fresh solvent (Scheme 1). The number of acetonitrile units in **8** was determined by elemental analysis and from the relative intensities of the ^1H NMR spectrum in [D_6]acetone; these were found to be 8.95:12 for the methyl signals of acetonitrile and Cb*, respectively. It was also finally confirmed by a single-crystal structure analysis (see below). The new compound **8** is sensitive to air, especially in solution. It undergoes slow oxidation by CH_2Cl_2 that is seen as a fast deterioration in the NMR spectra performed in the same solvent.



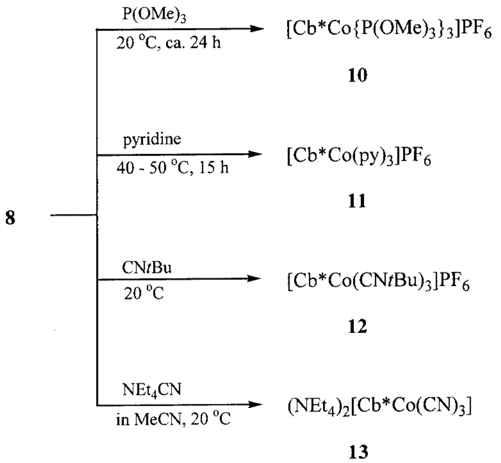
Scheme 1. Substitution reactions of $[Cb^*Co(C_6H_6)]PF_6$ (**6**)

^1H NMR spectra of **8** in [D_3]acetonitrile, measured at 200 MHz and at ambient temperature, show a single signal for the methyl groups of acetonitrile. An ^1H NMR spectrum in [D_6]acetone/[D_3]acetonitrile mixtures (with comparable quantities of free and coordinated acetonitrile), taken at 500 MHz, showed line-broadening at ambient temperature, decoalescence at −10 °C, and below two signals corresponding to a low-temperature exchange regime; at −84 °C, these two signals were sharp with chemical shifts of δ = 2.50 ppm for coordinated acetonitrile and of δ = 2.12 ppm for free acetonitrile.

The photolysis of **6** works equally well in liquid ammonia and affords the red crystalline salt $[Cb^*Co(NH_3)_3]PF_6$ (**9**). The crystals of **9** are sensitive to air and humidity and smell of ammonia; they melt at about 170 °C, apparently without decomposition. NMR spectra could be recorded in [D$_6$]acetone that was charged with gaseous NH_3.

Ligand Substitution Reactions of [Cb*Co(NCMe)$_3$]PF$_6$ (8)

Complex **8** readily undergoes ligand substitution reactions with a wide variety of neutral and anionic reagents. The in situ reaction with the carbaborane anion [9-(Me$_2$S)-7,8-C$_2$B$_9$H$_{10}$]$^-$ to give the metallacarbaborane Cb*Co[9-(Me$_2$S)-7,8-C$_2$B$_9$H$_{10}$] has been described in previous work,[11] and sandwich complexes with bora- and boratabenzene counter-ligands have been made with complex **8** as the starting material.[18] Herein we describe the new compounds **10−13** (Scheme 2). In the cases of pyridine and of the phosphorus ligands P(OMe)$_3$ and PMe$_3$, the third substitution step is slow, and gentle heating may be required to complete the substitution. We treated, for instance, compound **8** with an excess of PMe$_3$ at only ambient temperature. After removal of the volatiles under vacuum, the solid residue showed a virtual triplet for the protons of the *P*-methyl groups, thereby indicating the presence of two PMe$_3$ ligands. Similarly, treatment of **8** with excess pyridine at 20 °C for 3 h and subsequent removal of all volatiles left a red solid whose ^{1}H NMR spectroscopic data showed a pyridine/acetonitrile ratio of 2:1. Substitution of the third acetonitrile ligand required prolonged heating at temperatures of 40−50 °C. On the other hand, the slim and strong carbon nucleophiles CN*t*Bu and Et$_4$NCN readily effected substitution of all three acetonitrile ligands.



Scheme 2. Thermal ligand substitution reactions of [Cb*Co(NCMe)$_3$]PF$_6$ (**8**)

There are some obvious limitations to this method. The ligand to be introduced should either bind strongly to the metal atom or should be less volatile than acetonitrile. For instance, it is not possible to replace acetonitrile with dimethyl sulfide.

Ligand Substitution Reactions of [Cb*Co(CO)$_3$]BF$_4$ (7) and Cb*CoI(CO)$_2$ (2)

The cation **1**$^+$ is prone to thermal ligand substitution reactions. In favorable cases product formation is highly chemoselective. Thus, the tetrafluoroborate **7** reacts with trimethylphosphane in dichloromethane at ambient temperature with spontaneous evolution of CO to give the monosubstitution product [Cb*Co(CO)$_2$(PMe$_3$)]BF$_4$ (**14**) in good yield (Scheme 3). In contrast to this simple case, the analogous reaction with the weaker donor ligand P(OMe)$_3$ showed little selectivity. When **7** was treated with P(OMe)$_3$ in [D$_6$]acetone, warming to 40−50 °C was required to effect the reaction, and in ^{1}H NMR spectra signals of the mono- and the disubstitution product were observed besides those of the starting material. Thermal substitution of **1**$^+$ with 2,2′-bipyridine (bipy), at somewhat elevated temperatures, produced the cation [Cb*Co(CO)(bipy)]$^+$; the same cation can be obtained more conveniently from the reaction of the iodide **2** to give the iodide [Cb*Co(CO)(bipy)]I (**15**) (Scheme 4).

$$\mathbf{7} \xrightarrow[20\,^{\circ}\mathrm{C},\ 2\ \mathrm{h}]{\mathrm{PMe_3}} \underset{\mathbf{14}}{[\mathrm{Cb^*Co(CO)_2(PMe_3)]BF_4}}$$

$$\xrightarrow[h\nu,\ \mathrm{N_2\ purge}]{\mathrm{PMe_3}} \underset{\mathbf{16}}{[\mathrm{Cb^*Co(PMe_3)_3]BF_4}}$$

Scheme 3. Trimethylphosphane derivatives of [Cb*Co(CO)$_3$]BF$_4$ (**7**)

$$\underset{\mathbf{2}}{\mathrm{Cb^*CoI(CO)_2}} \xrightarrow[60\,^{\circ}\mathrm{C},\ 15\ \mathrm{h}]{\text{2,2'-bipyridine}} \underset{\mathbf{15}}{[\mathrm{Cb^*Co(CO)(bipy)]I}}$$

Scheme 4. An ionic 2,2′-bipyridine derivative of Cb*CoI(CO)$_2$ (**2**)

Photochemically induced ligand substitution reactions provide a synthetic alternative. Irradiation of **7** 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. For practical purposes it is necessary to purge the reaction mixture with a slow stream of dinitrogen. We used this method to produce the salt [Cb*Co(PMe$_3$)$_3$]BF$_4$ (**16**) by exhaustive decarbonylation (Scheme 3). The closely related trimethyl phosphite compound **10** can be prepared analogously; however, the synthesis from **8** described above seems more convenient.

We were especially interested in the replacement of the CO ligands of cation **1**$^+$ with acetonitrile. The first substitution step has already been described by Pauson et al.[16] to give the red salt [Cb*Co(CO)$_2$(NCMe)]BF$_4$ (**17**). Irradiation of an acetonitrile solution of **7** effects a slow second substitution and affords mixtures of **17** and the disubstitution product [Cb*Co(CO)(NCMe)$_2$]BF$_4$ (**18**). If a slow stream of dinitrogen purges the reaction mixture, the rates of these reactions are greatly increased. After a few hours, complex **17** is completely consumed, but the monocarbonyl complex **18** is now contaminated by an admixture of the tris(acetonitrile) complex $[Cb^*Co(NCMe)_3]BF_4$ (**19**) (typically 10%). The monocarbonyl complex **18** is highly reactive and rather sensitive to traces of air and humidity.

Structure Determinations

To the best of our knowledge no tris(ligand) complex of the Cb*Co fragment has yet been structurally characterized. Therefore, the structure of **7** was elucidated. Crystallization from acetone/THF gave small light-yellow crystals that turned out to be systematically twinned platelets. This situation is expected to limit the quality of the final structural model. The crystals possess the monoclinic space group *P*21/*m* with two very similar independent formula units in the elemental cell. Both cations and anions display crystallographic mirror symmetry. One of the cations (cation 1, all labels beginning with a leading 1) is shown in Figure 1.

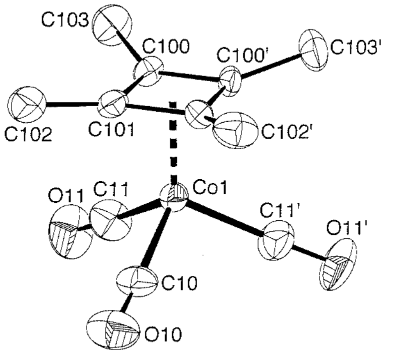


Figure 1. Structure of one of two independent cations $\mathbf{1}^+$ (PLATON plot, see ref.[19] at the 50% probability level) in the crystal of **7**; selected bond lengths [Å]: Co1−C10 1.826(13), Co1−C11/Co1−C11′ 1.852(10), Co1−C100/Co1−C100′ 2.061(8), Co1−C101/Co1−C101′ 2.048(8), Co2−C22 1.739(13), Co2−C21/Co2−C21′ 1.817(10), Co2−C200/Co2−C200′ 2.029(8), Co2−C201/Co2−C201′ 2.061(8)

The cation $\mathbf{1}^+$ possesses the expected piano-stool structure. The planes defined by the cyclobutadiene carbon atoms (plane C_4), the carbonyl carbon atoms (plane C_3), and the carbonyl oxygen atoms (plane O_3) are roughly parallel [largest deviation 3.8(6)° between the two carbon planes C_4 and C_3 of cation 1]. The metal-to-ring distance amounts to 1.769(2) for cation 1 and 1.785(2) Å for cation 2, and is remarkably long. In the family of CoCbCp complexes this distance ranges from 1.68 to 1.70 Å,[20a] and is 1.681 Å for the parent complex CoCbCp[20b] and 1.692 Å for $Co(C_4Ph_4)Cp$.[20a] With reference to the general bonding characteristics of (cyclobutadiene)metal complexes such as $Fe(CO)_3(C_4H_4)$,[21] we expect that the lower energy of the 2e valence orbital set of the $Co(CO)_3^+$ fragment, as compared to that of the uncharged CoCp fragment, results in an e MO set of more metal character and hence weaker Co−Cb bonding in the cation $\mathbf{1}^+$.

Crystals of **8**, that were suitable for a structural study, were obtained by crystallization of **8** from an acetonitrile/ether mixture. The structure determination of **8** (Figure 2) was hampered by disorder of the cyclobutadiene rings. In the final structural model this disorder is largely resolved showing two dispositions of the rings with almost equal (0.52 and 0.48) occupancies. The best ring planes C_4 (with the atoms C1, C2, C3, C4) and C_4B (with C1B, C2B, C3B, C4B; not shown in Figure 2) of the minor orientation display an interplanar angle of 6.8(16)°. The metal-to-ring distance amounts to 1.680(10) for the major disposition and to 1.670(10) Å for the minor disposition. In this case the weak π-acceptor property of the acetonitrile ligands allows for a much stronger Co−Cb interaction as compared to **7**.

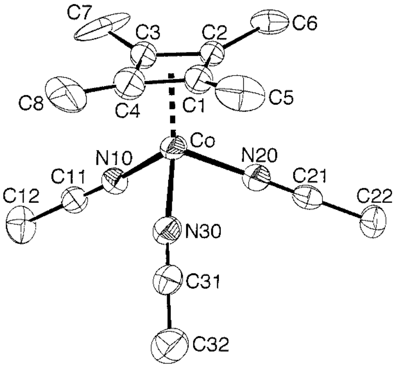


Figure 2. Structure of the major disposition of cation $\mathbf{4}^+$ (PLATON plot, see ref.[19] at the 30% probability level) in the crystal of **8**; for details of the disorder problem see text; selected bond lengths [Å]: Co−N10 1.943(6), Co−N20 1.951(7), Co−N30 1.957(7), Co−C1 1.95(4), Co−C2 2.043(12), Co−C3 1.989(13), Co−C(4) 1.856(19); the positional coordinates of C1 are most severely affected by the disorder of the Cb* ring

Electrochemical Studies

The redox behaviour of the complexes **8**, **10**−**13**, and **16** was studied by cyclic voltammetry. All these complexes show a chemically fully reversible oxidation. No reduction was found down to the solvent/electrolyte limit at about −2 V. Table 1 lists the electrochemical data obtained, with the compounds arranged in order of increasing oxidation potential. The data show that hard donor ligands tend to ease oxidation; in other words, hard donor ligands stabilize the $CbCo^{2+}$ fragment more than the soft donors PMe_3, CN*t*Bu, and $P(OMe)_3$. The 17e acetonitrile cation $\mathbf{4}^{2+}$ shows a second irreversible oxidation at about 0.8 V. The 17e monoanion $[Cb^*Co(CN)_3]^-$, derived from monoelectronic oxidation of **13**, is not further oxidized up to about 0.4 V, i.e. it exhibits a stability window of at least 1 V. The dianion of **13** is highly air-sensitive. However, the green air oxidation product seems to be different from the electrochemical oxidation product since it cannot be re-reduced electrochemically. Further investigation of the cyano compounds would seem desirable and rewarding.

The redox behaviour classifies the Cb^*Co^+ fragment as a relatively hard organometallic metallo-electrophile, similar to $CpFe^+$. This feature is illustrated by the fact that complexes $[Cb^*CoL_3]^{n+}$ could be prepared with ligands of predominant σ-donor character as well as with π-acceptor ligands. However, in both cases of Cb^*Co^+ and $CpFe^+$,

Table 1. Cyclovoltammetric data for **8**, **10−13**, and **16**

Electroactive species	Solvent	$E_{1/2}$/V vs. SCE	ΔE/mV	v/mV s^{-1}
$[Cb^*Co(CN)_3]^{2-}$ in **13**	acetonitrile	−0.616	146	50
$[Cb^*Co(py)_3]^+$ in **11**	acetonitrile	0.155	80	100
$[Cb^*Co(NCMe)_3]^+$ in **8**	acetonitrile	0.23	77	50
$[Cb^*Co(PMe_3)_3]^+$ in **16**	CH_2Cl_2	0.70	65	100
$[Cb^*Co(CNtBu)_3]^+$ in **12**	CH_2Cl_2	0.97	94	100
$[Cb^*Co\{P(OMe)_3\}_3]^+$ in **10**	CH_2Cl_2	1.02	74	100

ligands placed to the left of ammonia and acetonitrile in the spectrochemical series, such as water, lead to decomplexation of the carbocyclic ligand.

Conclusions

This paper documents an improved access to the (tetramethylcyclobutadiene)cobalt complexes $Cb^*CoI(CO)_2$ (**2**) and $[Cb^*Co(C_6H_6)]^+$ (**3**$^+$) (as hexafluorophosphate **6**) which may serve as versatile starting materials in this chemistry. Photolysis of the salt **6** in solution produces synthetically useful, reactive metallo-electrophiles of the type $[Cb^*Co(solv)_x]^+$. The generation of a very reactive species of this type in dichloromethane allowed the synthesis of triple-decker sandwich complexes with a bridging cyclopentadienyl ligand.[22] One main aim of this paper was the full characterization of the cation $[Cb^*Co(NCMe)_3]^+$ (**4**$^+$). This species is not only prepared from **3**$^+$ by the photolytic method, but also by thermal ligand displacement in acetonitrile solution. With the improved accessibility of Cb*Co complexes achieved in this work the metallo-electrophiles $[Cb^*Co(solv)_x]^+$ should from now on belong to the standard armory of the synthetic organometallic chemist.

Experimental Section

General Remarks: Reactions were carried out under dinitrogen by means of conventional Schlenk techniques. THF and Et_2O were distilled from sodium benzophenone ketyl, acetonitrile and CH_2Cl_2 from CaH_2. A 400-W Philips sodium lamp SON-T or the pyrex-filtered output of a 150-W mercury lamp were used in photolytic reactions. Elemental analyses were performed by Analytische Laboratorien Prof. Dr. H. Malissa und G. Reuter GmbH, 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 (^1H, 200 MHz. $^{13}C\{^1H\}$, 50.29 MHz. $^{31}P\{^1H\}$, 80.96 MHz) or, in special cases, with a Varian Unity 500 (^1H, 499.6 MHz. ^{13}C, 125.6 MHz) instrument. Chemical shifts are given in ppm; they were measured at ambient temperature and are referenced to internal TMS for ^1H 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.

$[Cb^*Co(CO)_3]BF_4$ (7): A suspension of anhydrous aluminium chloride (16.5 g, 124 mmol) in CH_2Cl_2 (40 mL) was cooled to 0 °C. A solution of 2-butyne (8.93 mL, 114 mmol) in dichloromethane (25 mL) was added dropwise while stirring for 30 min. After addition of more CH_2Cl_2 (35 mL), the mixture was allowed to warm to 20 °C and stirred for 1 h at 20 °C. Octacarbonyldicobalt (9.78 g, 28.6 mmol) was then added and stirring was continued for 80 h. The reaction mixture was hydrolyzed with cold water at 0 °C. The organic phase was removed and the water phase was filtered. $NaBF_4$ (8.0 g, 73 mmol) was added and the mixture was cooled to 0 °C overnight. The precipitate was collected and dried under vacuum. The raw product was dissolved in acetone, and the solution was passed through a 2-cm layer of alumina. Concentration of the filtrate and addition of ether gave **7** (6.67 g, 19.7 mmol, 35%) as a pale yellow powder. $C_{11}H_{12}CoF_4O_3$ (338.0): calcd. C 39.09, H 3.58; found C 39.09, H 3.60. $^{13}C\{^1H\}$ NMR (CD_3NO_2): δ = 9.9 (C_4Me_4), 106.6 (C_4Me_4), 197.8 (br, CO) ppm.

$Cb^*CoI(CO)_2$ (2): To the aqueous solution from a similar preparation [$AlCl_3$ (10.6 g, 80 mmol) in CH_2Cl_2 (40 mL), 2-butyne (5.74 mL, 73.5 mmol) in CH_2Cl_2 (25 mL), $Co_2(CO)_8$ (6.29 g, 18.4 mmol)] were added trimethylamine *N*-oxide $Me_3NO\cdot 2H_2O$ (1.99 g, 17.9 mmol) and NaI (18 g, 0.12 mol). The mixture was stirred for 15 h. The brown precipitate that formed was collected and dried under vacuum; the filtrate did not form any more product when further Me_3NO was added. The raw product was dissolved in CH_2Cl_2, and the solution was passed through a 4-cm layer of alumina. After concentration of the filtrate and addition of a sixfold volume of octane, the solution was kept at −30 °C for 15 h to give **2** (4.79 g, 37%) as dark brown crystals. $^{13}C\{^1H\}$ NMR ([D_6]acetone): δ = 10.2 (C_4Me_4), 94.2 (C_4Me_4) ppm; signals of CO groups not observed. For further data see ref.[16]

$[Cb^*Co(C_6H_6)]PF_6$ (6): A round-bottomed flask was charged with benzene (20 mL), octane (30 mL), iodide **2** (3.5 g, 10 mmol), and anhydrous aluminium chloride (13.4 g, 100 mmol). The mixture was stirred and heated under reflux at ca.130 °C for 8 h. After cooling to 20 °C, the reaction mixture was carefully hydrolyzed with ca. 100 mL of cold water. The organic phase was separated and the water phase was filtered. Addition of NH_4PF_6 (1.63 g, 10 mmol) to the filtrate gave a yellow precipitate. For further purification, the solution of the dry raw product was passed through a 2-cm layer of alumina. Concentration of the filtrate and addition of a large volume of ether gave **6** (2.44 g, 63%) as a pale yellow powder. $^{13}C\{^1H\}$ NMR ([D_6]acetone): δ = 10.1 (C_4Me_4), 94.7 (C_4Me_4), 99.8 (C_6H_6) ppm. For further data see ref.[16]

$[Cb^*Co(NCMe)_3]PF_6$ (8). By Photochemical Synthesis: A solution of **6** (390 mg, 1.00 mmol) in acetonitrile (20 mL) was irradiated with a sodium lamp at ambient temperature for 2 h. The color of the solution changed from yellow to red. Removal of the solvent under vacuum afforded **8** (434 mg, 100%) as an air-sensitive, red crystalline solid; m.p. 175 °C (dec.). $C_{14}H_{21}CoF_6N_3P$ (435.2): calcd. C 38.63, H 4.86, N 9.65; found C 38.51, H 4.83, N 9.66. **By Thermal Ligand Displacement:** A solution of **6** (392 mg, 1.00 mmol) in acetonitrile (20 mL) was heated to reflux temperature for 2.5 h. After removal of the volatiles, fresh acetonitrile (20 mL) was added, and the solution was re-heated for 1 h. The volatiles were pumped off to leave **8** (436 mg, 100%) as spectroscopically pure (^{1}H NMR) product. **Data:** ^{1}H NMR ([D$_6$]acetone): δ = 0.91 (s, Cb*), 2.41 (s, 3 Me) ppm. ^{13}C{^{1}H} NMR ([D$_6$]acetone): δ = 2.9 (*Me*CN), 8.9 ($\mathrm{C}_4\mathit{Me}_4$), 74.8 ($\mathit{C}_4\mathrm{Me}_4$), 124.6 (CN) ppm.

[Cb*Co(NH$_3$)$_3$]PF$_6$ (9): A Schlenk tube with a suspension of complex **6** (195 mg, 0.5 mmol) in liquid ammonia (20 mL) was irradiated with a sodium lamp, while the reaction mixture was stirred at −50 °C. The color of the reaction mixture changed to red and finally, when all the starting material had dissolved, it was a transparent solution (5−7 h). The ammonia was removed by allowing the system to slowly warm to ambient temperature, thus affording **9** (180 mg, 99%) as an air-sensitive, red crystalline solid; m.p. 170 °C, dec. 240 °C. $\mathrm{C_8H_{21}CoF_6N_3P}$ (363.2): calcd. C 26.46, H 5.83, N 11.57; found C 26.41, H 5.67, N 11.37. ^{1}H NMR ([D$_6$]acetone, saturated with NH$_3$): δ = 0.84 (s, Cb*), 1.44 (s, 3 NH$_3$) ppm. ^{13}C{^{1}H} NMR ([D$_6$]acetone, saturated with NH$_3$): δ = 8.9 ($\mathrm{C}_4\mathit{Me}_4$), 61.7 ($\mathit{C}_4\mathrm{Me}_4$).

[Cb*Co{P(OMe)$_3$}$_3$]PF$_6$ (10): Trimethyl phosphite (3 mL, 27 mmol) was added to the tris(acetonitrile) complex **8** (434 mg, 1 mmol) in acetonitrile (10 mL). The mixture was stirred at room temperature overnight. The solution was then concentrated in a gentle vacuum to ca. 3 mL, and stirring was continued for 24 h. Addition of ether (20 mL) precipitated a crystalline powder, which was collected on a frit, washed with ether (20 mL), and dried under vacuum to give **7** (680 mg, 100%) as a yellow powder; dec. 210−230 °C. $\mathrm{C_{17}H_{39}CoF_6O_9P_4}$ (684.3): calcd. C 29.84, H 5.74; found C 29.81, H 5.83. ^{1}H NMR ([D$_6$]acetone): δ = 1.51 (q, J_{PH} = 5.4 Hz, Cb*), 3.80 [m, 3 P(OMe)$_3$] ppm. ^{13}C{^{1}H} NMR ([D$_6$]acetone): δ = 9.4 [q, not well resolved, J_{PC} = 1.4 Hz, $\mathrm{C}_4\mathit{Me}_4$), 53.8 [vq, J_{PC} = 2.7 Hz, P(OMe)$_3$], 86.6 [q, not well resolved, J_{PC} = 2 Hz, $\mathit{C}_4\mathrm{Me}_4$] ppm. ^{31}P{^{1}H} NMR ([D$_6$]acetone): δ = −140.8 (sept, PF$_6^-$), 163.0 [s, P(OMe)$_3$] ppm.

[Cb*Co(py)$_3$]PF$_6$ (11): A solution of **8** (434 mg, 1 mmol) in pyridine (10 mL) was stirred at 40−50 °C overnight. The solution was then concentrated to 2−3 mL under vacuum at the same temperature. Addition of ether precipitated **11** in large crystal blocks, which were washed with ether (40 mL), and dried under vacuum to afford **11** (547 mg, 100%) as a dark red, crystalline solid; dec. 90 °C, very air-sensitive. Sharp NMR spectra could only be recorded when a trace of [D$_5$]pyridine was added. $\mathrm{C_{23}H_{27}CoF_6N_3P}$ (549.4): calcd. C 50.28, H 4.95, N 7.65; found C 49.83, H 5.08, N 7.55. ^{1}H NMR ([D$_6$]acetone with a drop of [D$_5$]pyridine): δ = 0.62 (s, Cb*), 7.41 (m, 6 H$_\beta$), 7.76 (tt, 3 H$_\gamma$), 8.79 (d, 6 H$_\alpha$) ppm. ^{13}C{^{1}H} NMR ([D$_6$]acetone with a drop of [D$_5$]pyridine): δ = 8.8 ($\mathrm{C}_4\mathit{Me}_4$), 70.4 ($\mathit{C}_4\mathrm{Me}_4$), 125.0 (C$_\beta$), 136.0 (C$_\gamma$), 150.6 (C$_\alpha$) ppm.

[Cb*Co(CN*t*Bu)$_3$]PF$_6$ (12): Preparation similar to that of **10**; with *tert*-butyl isocyanide (1.0 mL, 9 mmol) the reaction was completed in 2 h and gave **12** (560 mg, 100%) as a yellow crystalline solid; m.p. 178 °C, dec. 192 °C. $\mathrm{C_{23}H_{39}CoF_6N_3P}$ (561.5): calcd. C 49.20, H 7.00, N 7.48; found C 49.31, H 7.14, N 7.48. ^{1}H NMR ([D$_6$]acetone): δ = 1.56 (s, 3 *t*Bu), 1.57 (s, Cb*) ppm. ^{13}C{^{1}H} NMR ([D$_6$]acetone): δ = 9.6 ($\mathrm{C}_4\mathit{Me}_4$), 30.0 (C*Me*$_3$), 58.5 (*C*Me$_3$), 87.1 ($\mathit{C}_4\mathrm{Me}_4$), 155.8 (CN) ppm. IR (MeCN): $\tilde{\nu}$ = 2140, 2174 [ν(CN)] cm^{-1}.

(NEt$_4$)$_2$[Cb*Co(CN)$_3$] (13): A solution of **8** (515 mg, 1.18 mmol) in acetonitrile (20 mL) was added to a stirred solution of Et$_4$NCN (555 mg, 3.55 mmol) in acetonitrile (15 mL). The yellow color of the mixture indicates completion of the reaction immediately after mixing. The solvent was removed under vacuum to afford a brownish yellow crystalline material. The product was separated from Et$_4$NPF$_6$ by two recrystallizations from MeCN (0.5 mL)/dry acetone (10 mL), keeping the solution at −30 °C for 18 h, to give **13** (518 mg, 87%) as a spectroscopically pure, brownish-yellow, crystalline solid; m.p. 187 °C, dec. 194 °C, very air-sensitive. $\mathrm{C_{27}H_{52}CoN_5}$ (505.7): calcd. C 64.13, H 10.37, N 13.85; found C 63.6, H 10.0, N 14.1 (average of two determinations). ^{1}H NMR (CD$_3$CN): δ = 1.23 [tt, $^{3}J(^{1}\mathrm{H}\text{-}^{1}\mathrm{H})$ = 7.3, $^{3}J(^{14}\mathrm{N}\text{-}^{1}\mathrm{H})$ = 1.9 Hz, 8 Me], 1.27 (s, Cb*), 3.27 [q, br, $^{3}J(^{1}\mathrm{H}\text{-}^{1}\mathrm{H})$ = 7.3 Hz, 8 CH$_2$N] ppm. ^{13}C{^{1}H} NMR (CD$_3$CN): δ = 7.8 ($\mathit{C}\mathrm{H_3CH_2N}$), 10.9 ($\mathrm{C}_4\mathit{Me}_4$), 53.0 [t, $^{1}J(^{14}\mathrm{N}\text{-}^{13}\mathrm{C})$ = 3.0 Hz, CH$_2$N], 71.0 ($\mathit{C}_4\mathrm{Me}_4$), 165.1 (CN) ppm.

[Cb*Co(CO)$_2$(PMe$_3$)]BF$_4$ (14): A solution of PMe$_3$ in CH$_2$Cl$_2$ (1 M, 20 mL, 20 mmol) was added to **5** (342 mg, 1.01 mmol), and the mixture was stirred at room temperature until the spontaneous evolution of CO had completely ceased (ca. 2 h). The solution was concentrated in a gentle vacuum to ca. 2−3 mL. Addition of ether (10 mL) precipitated the raw product that was then collected on a frit, washed with ether (20 mL), and dried under vacuum. In a further purification step, the product was dissolved in CH$_2$Cl$_2$, passed through a 0.5-cm layer of alumina, and recovered by addition of ether to give **14** (270 mg, 69%) as a pale yellow, crystalline solid; dec. 245 °C. $\mathrm{C_{13}H_{21}BCoF_4O_2P}$ (386.0): calcd. C 40.45, H 5.48; found C 40.68, H 5.42. ^{1}H NMR ([D$_6$]acetone): δ = 1.73 (d, J_{PH} = 10.1 Hz, PMe$_3$), 1.89 (d, J_{PH} = 4.0 Hz, Cb*) ppm. ^{13}C{^{1}H} NMR ([D$_6$]acetone): δ = 9.5 (s, $\mathrm{C}_4\mathit{Me}_4$), 17.7 (d, J_{PC} = 31.1 Hz, PMe$_3$), 96.9 (s, $\mathit{C}_4\mathrm{Me}_4$) ppm. ^{31}P{^{1}H} NMR ([D$_6$]acetone): δ = 7.6 ppm. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 2025 and 2064 [ν(CO)] cm^{-1}.

[Cb*Co(CO)(bipy)]I (15): A solution of complex **2** (349 mg, 1.00 mmol) and 2,2′-bipyridine (156 mg, 1.00 mmol) in acetonitrile (5 mL) was stirred overnight at 50−60 °C. The product was precipitated by addition of ether (40 mL), washed with ether (40 mL), and dried under vacuum to afford **15** (471 mg, 99%) as a crystalline powder; dec. 130−140 °C. $\mathrm{C_{19}H_{20}CoIN_2O}$ (478.2): calcd. C 47.72, H 4.22, N 5.86; found C 47.79, H 4.29, N 6.05. ^{1}H NMR ([D$_6$]acetone): δ = 1.32 (s, Cb*), 7.86 (m, 4-/4′-H), 8.28 (m, 5-/5′-H), 8.81 (m, 6-/6′-H), 9.04 (m, 3-/3′-H) ppm. ^{13}C{^{1}H} NMR ([D$_6$]acetone): δ = 9.1 ($\mathrm{C}_4\mathit{Me}_4$), 89.6 ($\mathit{C}_4\mathrm{Me}_4$), 124.3 (C-6,6′), 127.9 (C-4,4′), 139.6 (C-5,5′), 154.8 (C-3,3′), 155.9 (C-2,2′). Assignments within the 2,2′-bipyridine ligand were made on the basis of COSY and HETCOR spectra. IR (KBr): $\tilde{\nu}$ = 1960.3 [ν(CO)] cm^{-1}.

[Cb*Co(PMe$_3$)$_3$]BF$_4$ (16): A solution of PMe$_3$ in CH$_2$Cl$_2$ (1 M, 20 mL, 20 mmol) was added to **14** (180 mg, 0.46 mmol) in a Schlenk tube, equipped with a capillary as a gas outlet, and irradiated with a mercury lamp at ambient temperature. A very slow stream of N$_2$ was passed through the solution for 5 h. Concentration of this solution to 5 mL and addition of diethyl ether (20 mL) afforded the raw product which was collected, washed with ether (20 mL) and dried under vacuum to give **16** (210 mg, 93%) as a deep yellow powder; dec. 150−160 °C. $\mathrm{C_{17}H_{39}BCoF_4P_3}$ (540.3): calcd. C 42.35, H 8.15; found C 42.15, H 8.05. ^{1}H NMR ([D$_6$]acetone): δ = 1.48 (q, J_{PH} = 3.1 Hz, Cb*), 1.50 (d, J_{PH} = 7.2 Hz, PMe$_3$) ppm. ^{13}C{^{1}H} NMR ([D$_6$]acetone): δ = 10.5 (s, $\mathrm{C}_4\mathit{Me}_4$), 21.6 (8 lines between 21.3 and 21.9, PMe$_3$), 78.5 (s, $\mathit{C}_4\mathrm{Me}_4$) ppm. ^{31}P{^{1}H} NMR ([D$_6$]acetone): δ = 7.3.

[Cb*Co(CO)(NCMe)$_2$]BF$_4$ (18): A sample of **7** (338 mg, 1.00 mmol) in a Schlenk tube, equipped with a capillary as a gas outlet, was dissolved in acetonitrile (20 mL). The solution was photolyzed while N$_2$ was passed through the solution for 8 h. Product formation was monitored by ^{1}H NMR spectroscopy in CD$_3$NO$_2$ on samples taken from the reaction mixture. The acetonitrile was removed completely under vacuum. The residue was dissolved in CH$_2$Cl$_2$, and the product was precipitated with ether and dried under vacuum; yield not determined. $\mathrm{C_{13}H_{18}BCoF_4N_2O}$ (364.0): calcd. C 42.89, H 4.98 N 7.70; found C 43.01, H 5.13, N 6.54. ^{1}H

NMR ([D$_6$]acetone): δ = 1.33 (s, Cb*), 2.50 (s, 2 Me) ppm. ^{1}H NMR ([D$_6$]MeNO$_2$): δ = 1.33 (s, Cb*), 2.39 (s, 2 Me) ppm. ^{13}C{^{1}H} NMR ([D$_3$]nitromethane): δ = 3.6 (*Me*CN), 9.2 (C_4*Me*$_4$), 92.2 (*C*$_4$Me$_4$), 128.9 (CN), 202.7 (CO) ppm.

X-ray Crystal Structure Determinations:[23] Diffraction intensity data were collected with ENRAF-Nonius CAD4 diffractometers, equipped with graphite monochromators. Crystal data, data collection parameters, and convergence results are listed in Table 2. Numerical absorption corrections[24] were applied before averaging symmetry-equivalent data. The structures were solved by direct methods[25] and refined on F^2.[26] Hydrogen atoms were calculated in standard geometry and treated as riding on the corresponding C atoms. In the case of **7** all crystals tested proved to be twinned. In the diffraction pattern reflections of the type *hkl*, $l = 0$ for both domains coincide, and reflections *hkl*, $l = 10$ show partial overlap and were omitted from the refinement. Despite this modest loss of information, the final completeness of the data set amounts to 0.94. The structure suffers from strongly anisotropic displacement parameters, especially for the methyl substituents on the Cb* rings and the BF_4^- anion; rigid bond[27] restraints and, in the case of the fluorine atoms, additional distance restraints were introduced to ensure a physically reasonable model. The Cb* ligand in **8** shows disorder; C atoms belonging to this moiety were assigned isotropic displacement parameters, and distance restraints were used to ensure a stable refinement of the alternative orientations.

Table 2. Crystal data, data collection parameters, and convergence results for **7** and **8**

	7	**8**
Empirical formula	$C_{11}H_{12}BCoF_4O_3$	$C_{14}H_{21}CoF_6N_3P$
Formula mass	337.95	435.24
Crystal system	monoclinic	monoclinic
Space group	$P2_1/m$	$C2/c$
Radiation (λ [Å])	Mo-K_α (0.71073)	Mo-K_α (0.71073)
a [Å]	10.057(3)	19.276(6)
b [Å]	11.402(5)	10.841(2)
c [Å]	12.2362(16)	19.621(2)
β [°]	93.476(19)	103.48(2)
V [Å^3]	1400.6(8)	3987(2)
Z	4	8
$d_{\text{calcd.}}$ [g/cm^3]	1.60	1.45
$F(000)$	680	1776
μ [mm^{-1}]	1.267	0.992
Absorption correction	numerical	numerical
Max./min. transmission	0.902/0.571	0.896/0.751
θ range [°]	3.1−26.0	2.7−26.0
Temperature [K]	213	213
Scan mode	ω−2θ	ω−2θ
Crystal size [mm]	0.67 × 0.48 × 0.10	0.25 × 0.23 × 0.12
Reflections collected	9436	8098
Reflections unique	3402	3915
Reflections observed	1391	1335
Criterion for observation	$I > 2\sigma(I)$	$I > 2\sigma(I)$
Variables	204	272
R_1[a], observed	0.084	0.079
wR_2 [b], all data	0.190	0.148
GOF[c]	0.832	0.872
Max. resd. density [e/Å^3]	2.27	0.60

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

Electrochemical Measurements: The redox behaviour of the complexes **8**, **10**−**13**, and **16** was investigated by cyclic voltammetry with an IJ Cambria Scientific CHI630A potentiostat at the Pt electrode in the solvents indicated in Table 1 using tetrabutylammonium hexafluorophosphate as the supporting electrolyte. Potentials are vs. SCE and have been standardized towards a ferrocene/ferrocenium potential vs. SCE of 0.400 V in either solvent.

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[23] CCDC-182899 [(**1**)BF_4] and -182900 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].
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