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(Tetramethylcyclobutadiene)cobalt Complexes with Five-Electron Carbo- and Heterocyclic Ligands[†]

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Tetramethylcyclobutadiene(cyclopentadienyl)cobalt complexes Cb*Co(C_5H_4R) (Cb* = η^4-C_4Me_4; R = H (**5a**), Me (**5b**), $SiMe_3$ (**5d**), C(O)H (**5f**), and C(O)Me (**5g**)) were obtained by reaction of cyclopentadienide anions either with the (carbonyl)iodide complex Cb*Co$(CO)_2$I (**1**) (method A) or with the more reactive acetonitrile complex $[Cb^*Co(MeCN)_3]^+$ (**2**) (method B). Analogous compounds Cb*CoCp* (**5c**), Cb*Co(1,3-$C_5H_3(SiMe_3)_2$) (**5e**), and Cb*Co(η^5-indenyl) (**6**) can be prepared only by method B. Treatment of **5f**,**g** with $NaBH_4/AlCl_3$ or $LiAlH_4$ affords the alkyl derivatives **5b** and **5h** (R = Et) or the alcohols **5i** (R = CH_2OH) and **5j** (R = CH(OH)Me), respectively. The reaction of **1** with fluorene/$AlCl_3$ yields complex [Cb*Co(η^6-fluorene)]$^+$ (**8**), which was deprotonated by $KOBu^t$ to give Cb*Co(η^6-fluorenyl) (**9**). Visible light irradiation of **9** induces $\eta^6 \rightarrow \eta^5$ haptotropic rearrangement to afford Cb*Co(η^5-fluorenyl) (**7**). The pyrrolyl and phospholyl complexes Cb*Co(C_4R_4N) (R = H (**10a**), Me (**10c**)) and Cb*Co(C_4R_4P) (R = H (**11a**), Me (**11c**); R_4 = H_2Me_2 (**11b**)) were obtained by reaction of **2** with the corresponding pyrrolide or phospholide anions. Improved procedures for the preparation of the starting materials **1** and **2** were developed. Using a one-pot procedure, the iodide **1** was obtained in high yield from 2-butyne and $Co_2(CO)_8$. Complex **2** was prepared by heating or irradiation of the toluene complex [Cb*Co(C_6H_5Me)]$^+$ (**4b**) in acetonitrile. Structures of **5g**, **6**, and **11c** were investigated by X-ray diffraction. Electrochemistry and joint UV−visible and EPR spectroelectrochemistry of complexes prepared were studied.

Introduction

The CbCo fragment (Cb = η^4-C_4H_4) is isolobal with CpFe[2] leading to a close relationship between ferrocene and CbCoCp. This is supported, in particular, by the ability of both compounds to undergo electrophilic substitution reactions.[3−5] Taking into account numerous fields of ferrocene application,[6] it becomes clear that the cobalt analogues could also be useful from a practical point of view. However, in contrast to ferrocene, the chemistry of CbCoCp is insufficiently studied.[7] Its first derivative, (C_4Ph_4)CoCp, has been prepared by dimerization of diphenylacetylene in the presence of a source of the CpCo fragment (CpCo(1,5-cyclooctadiene),[8] CpCo$(CO)_2$,[9] or Cp_2Co[10]). Numerous tricyclic,[11] cyclophane,[12] multiply ethynylated,[13] and even polymeric[14] derivatives have been synthesized in a similar way. Unfortunately,

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[†] (Tetramethylcyclobutadiene)cobalt Complexes, 2. Part 1: See ref 1.

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this simple method is inapplicable for the preparation of the parent compound CbCoCp and the methyl-substituted analogue Cb*CoCp (Cb* = η^4-C_4Me_4) since acetylene trimerization is the more favorable pathway for lower alkynes.[15,16]

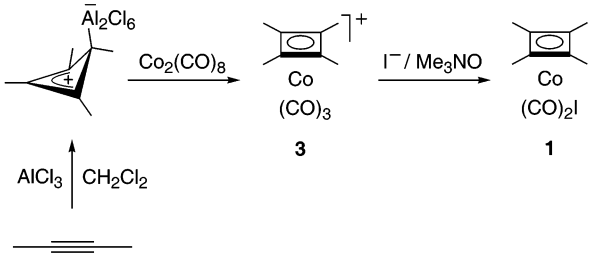
Pentamethylcyclopentadienyl ligand is widely used in organometallic chemistry mainly due to stabilization of complexes and reactive intermediates caused by strong electron-donating and steric effects of the five methyl groups.[17] By analogy, tetramethylcyclobutadiene ligand also proved to be very useful, in particular, in the case of cobalt.[18] The first cobalt derivatives of this ligand have been described by Bruce and Maitlis.[19] They have prepared the (carbonyl)iodide complex Cb*Co(CO)$_2$I (**1**), the key compound in Cb*Co chemistry, by reaction of $Co_2(CO)_8$ with [Cb*NiI$_2$]$_2$ proceeding via Cb* ring transfer from nickel to cobalt. A much more convenient way to **1** uses the (σ-cyclobutadiene)aluminum complex (η^1-C_4Me_4)Al_2Cl_6 (easily accessible by reaction of $AlCl_3$ with 2-butyne[20]) as a source of the Cb* ligand.[21] The reaction of **1** with CpNa was used to prepare Cb*CoCp.[19]

In cooperation with Herberich, we have described recently the acetonitrile complex [Cb*Co(MeCN)$_3$]$^+$ (**2**), which proved to be a very useful synthetic intermediate.[1] It was used, in particular, for the preparation of tris(ligand) derivatives [Cb*CoL$_3$]$^+$ (L = P(OMe)$_3$, py, and Bu^{t}CN) and [Cb*Co(CN)$_3$]$^{2-}$. Boratabenzene and carborane anions, [3,5-$Me_2C_5H_3BNMe_2$]$^{-}$[22] and [9-SMe$_2$-7,8-$C_2B_9H_{10}$]$^-$,[23] react with **2** to give the corresponding sandwich compounds. Herein we report the reactions of **2** with substituted cyclopentadienide anions leading to Cb*CoCp derivatives. This method is compared with an alternative method starting from **1**. Indenyl, fluorenyl, pyrrolyl, and phospholyl complexes of the Cb*Co fragment are also described. Redox behavior and structures of new compounds are discussed.

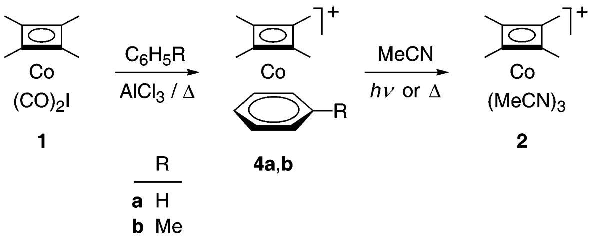
Results and Discussion

Starting Materials. The key compound **1** can be used directly as a synthon for the fragment Cb*Co or can be converted into other synthons. This compound has been prepared by Pauson et al.[21] in two steps. The reaction of (η^1-C_4Me_4)Al_2Cl_6 with $Co_2(CO)_8$ gives the tricarbonyl cationic complex [Cb*Co(CO)$_3$]$^+$ (**3**), which was isolated as a hexafluorophosphate salt in 59−68% yields (Scheme 1). Treatment of **3**PF$_6$ with [Bu$_4$N]I and Me$_3$NO (a mild CO-abstracting agent[24]) in CH_2Cl_2 affords the iodide complex **1** in 76% yield.

Scheme 1



Scheme 2



On the basis of these reactions, we developed a simple one-pot procedure for the preparation of **1**.[1] After the reaction between (η^1-C_4Me_4)Al_2Cl_6 and $Co_2(CO)_8$ was over, the resulting mixture containing cation **3** was hydrolyzed by water and the aqueous phase was treated with NaI·2H$_2$O and Me$_3$NO·2H$_2$O. Complex **1** precipitates slowly (overnight) and proved to be sufficiently pure for further applications. The previously reported yield was 37%; however, in the present work it was shown that the yield depends on the purity of the $Co_2(CO)_8$ and approaches 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. It makes complex **1** easily accessible, thus facilitating the development of Cb*Co chemistry.

Another very useful synthon for the fragment Cb*Co is the substitutionally labile cationic acetonitrile complex **2**, which was prepared from the benzene complex [Cb*Co(C_6H_6)]$^+$ (**4a**) either by photolytic or thermal ligand displacement in acetonitrile solution (Scheme 2).[1,25] The benzene complex **4a** was obtained by refluxing **1** in benzene in the presence of $AlCl_3$ in ca. 60% yield; however it is contaminated by the tricarbonyl complex **3**. To remove this impurity, a small amount of NaI·2H$_2$O and Me$_3$NO·2H$_2$O 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 **4a**PF$_6$.[26]

Taking into account the carcinogenity of benzene, we tried to use the toluene analogue **4b** instead of **4a**. As a matter of fact, **4b** proved to be almost equally effective for the preparation of **2**. Complex **4b** has been obtained by Pauson et al. by refluxing **1** in toluene in the presence of $AlCl_3$.[21] However, we noticed that the product obtained under such conditions is contaminated with arene complexes **4**, having several Me groups in the benzene ring as a consequence of transmethylation. Heating of the reagents in toluene at 80 °C results in

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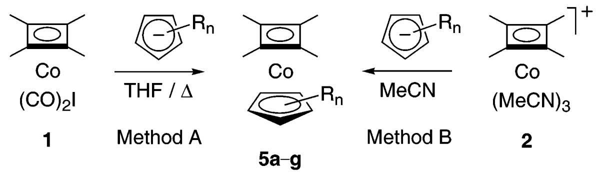
[25] All the cationic complexes described here were isolated as salts with the PF_6^- anion (the anions are omitted in the schemes).

[26] If the impurity of **3** is not removed, the subsequent reaction with MeCN leads to the formation of 3 mol of the bis(acetonitrile) complex [Cb*Co(CO)(MeCN)$_2$]$^+$ per mole of **3** as a result of the metathesis between **2** and **3**.

Scheme 3



	R_n	Yield (%) A	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

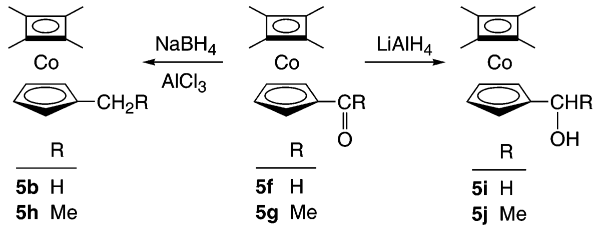
4b only in a several percent yield, the main product being the tricarbonyl cation **3**. Nevertheless, refluxing in a toluene/hexane mixture (1:1) results in pure **4b** in a reasonable yield (ca. 50%).[27] Apparently, refluxing promotes the removal of CO, thus facilitating the formation of **4b**.

Synthesis of Cyclopentadienyl Complexes. The cyclopentadienyl complex Cb*CoCp (**5a**) was first prepared by reaction of **1** with CpNa at room temperature; however the yield was only 17%.[19] Analogous reaction of **3** with CpNa gave **5a** in 32% yield.[21] Refluxing of **1** with CpTl in THF increased the yield up to 70%.[28] We have shown that the reaction of **1** with lithium or sodium salts of monosubstituted cyclopentadienide anions, including those containing $SiMe_3$, C(O)H, and C(O)Me groups, affords complexes **5** in moderate yields after refluxing for several hours in THF (Scheme 3). However, this method (method A) proved to be inapplicable for the preparation of complexes with more sterically hindered ligands, Cp* and 1,3-$C_5H_3(SiMe_3)_2$.

Taking into account the limited applicability of method A, we tried to develop a more general method. The (acetonitrile)iron complexes $[Cp'Fe(MeCN)_3]^+$ (Cp′ = C_5H_4-Me,[29] Cp*[30]) are known to react with cyclopentadienide anions to give asymmetrically substituted ferrocenes. Similar reaction of **2** (method B) leads to complexes **5a**−**g**. The reaction readily occurs in acetonitrile at room temperature. The most convenient procedure generates **2** from the arene complexes **4a**,**b** in solution (by visible light irradiation or refluxing in MeCN) and uses it without isolation. In most cases lithium and sodium derivatives of cyclopentadienide anions were successfully used. However, we were unable to prepare the Cp* complex **5c** starting from Cp*Li; it was obtained in a moderate yield using more reactive Cp*K.[31]

As can be seen from Scheme 3, method B is more general and usually gives the products in higher yields. However, precursors of **2**, the arene complexes **4a** and **4b**, are formed from **1** in ca. 45−60% yield, thus making overall yields of the cyclopentadienyl compounds **5d**,**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 **5c**,**e**. The more general applicability of method B as well as milder reaction conditions and higher yields of the products is undoubtedly connected with the greater electrophilicity of complex **2** (compared with **1**) due to its positive charge and lability of the acetonitrile ligands.

Scheme 4



Complex **5b** contains ca. 5% admixture of **5a** due to the presence of bis(cyclopentadiene) impurity[32] in commercially available bis(methylcyclopentadiene). Unfortunately, we were unable to purify **5b** either by sublimation or chromatography. Nevertheless, we succeeded in preparing **5b** in pure form by reduction of the formyl derivative **5f** by $NaBH_4$ in the presence of $AlCl_3$ (Scheme 4). Similar reaction of the acetyl derivative **5g** yields the ethyl-substituted complex **5h**. Reduction of **5f**,**g** with $LiAlH_4$ gives the corresponding alcohols **5i**,**j**.[33] It should be emphasized that these reactions occur essentially in the same conditions as analogous reactions for ferrocene derivatives, thus giving additional evidence of the close relationship between CbCoCp and ferrocene.[34] However, despite many similarities between them, the principal difference results from the much easier ability of the coordinated cyclobutadiene ligand (as compared with Cp) to convert into other ligands. This is clearly demonstrated by recently described protonation of complex **5a** to give the allyl carbene complex $[CpCo(\sigma,\eta^4\text{-}C_4HMe_4)]^+$ with a five-electron butadienyl ligand,[35,36] which rearranges to produce the half-open cobaltocenium cation $[CpCo(\eta^5\text{-}C_5H_4Me_3)]^+$.

Complexes **5a**−**j** are yellow-orange solids except for **5h**, which is a yellow oil. They are stable in air at least for several hours but are slowly oxidized during pro-

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[27] A trace of **3** was easily removed similar to that described for **4a**.

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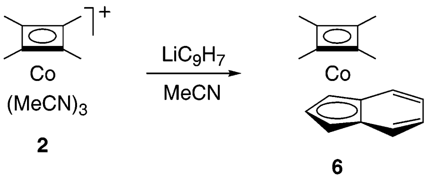
Scheme 5

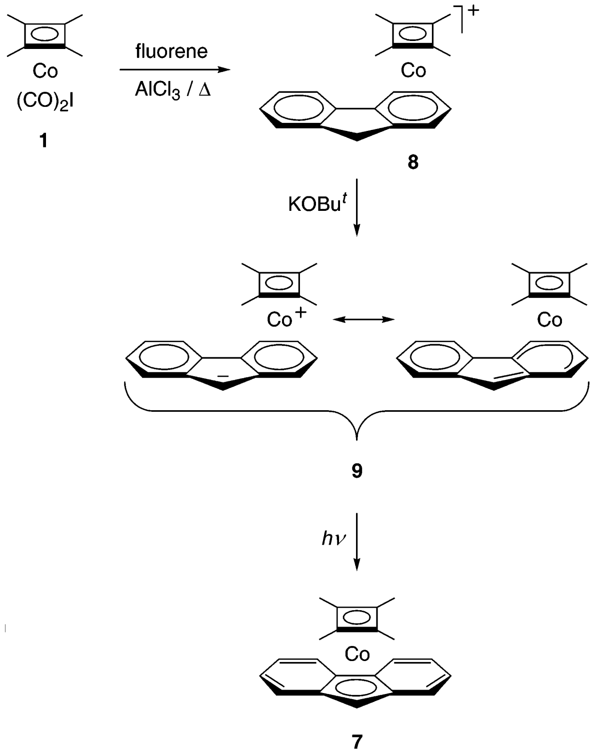


longed storage in air, probably as a result of a radical reaction with oxygen rather than electron transfer since their oxidation potentials are rather high (vide infra). The compounds prepared can be easily purified by sublimation in a vacuum except for the $SiMe_3$-substituted complexes **5d**,**e**, which are not volatile and were purified by column chromatography.

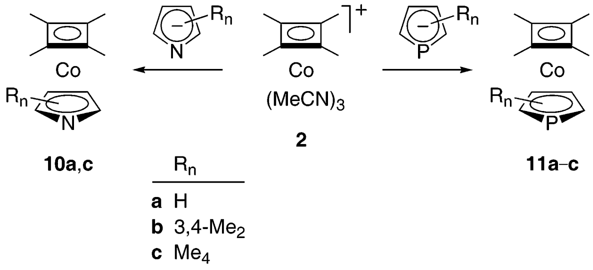
Synthesis of Indenyl and Fluorenyl Complexes. Gleiter et al.[37] have described tricyclic and cyclophane compounds containing the cyclobutadiene(indenyl)cobalt moiety. However, indenyl and fluorenyl complexes with simple substituents (H, alkyl, aryl) in the Cb ring were previously unknown. We have shown that the indenyl complex Cb*Co(η^5-indenyl) (**6**) can be obtained by reaction of lithium indenide with **2**, i.e., by method B (Scheme 5). Similar reactions of the ruthenium complexes $[(\eta\text{-}C_5R_5)Ru(MeCN)_3]^+$ (R = H, Me) with indenide[38] and fluorenide[39] anions have been used by us earlier to prepare compounds (η-C_5R_5)Ru(η^5-indenyl) and (η-C_5R_5)Ru(η^5-fluorenyl).

However, the reaction of **2** with lithium fluorenide gives a mixture of the fluorenyl complex Cb*Co(η^5-fluorenyl) (**7**) and fluorene in ca. 1:1 ratio, probably as a result of a side reaction of proton transfer from **2** to the fluorenide anion. The low stability of **7** complicates its isolation from the mixture. To prepare **7** in pure form, we used the following method (Scheme 6). The reaction of **1** with fluorene in the presence of $AlCl_3$ gives the cationic fluorene complex [Cb*Co(η^6-fluorene)]$^+$ (**8**), similar to the preparation of the benzene and toluene complexes **4a**,**b**. Subsequent deprotonation by KOBu^t leads to the η^6-fluorenyl complex Cb*Co(η^6-fluorenyl) (**9**), which is depicted by zwitterionic and neutral limiting structures, analogously to the iron compound CpFe(η^6-fluorenyl).[40] Visible light irradiation of **9** induces $\eta^6 \rightarrow \eta^5$ haptotropic rearrangement[41] to give the desired product **7**.

Scheme 6



Scheme 7



Synthesis of Pyrrolyl and Phospholyl Complexes. Cyclobutadiene(pyrrolyl)cobalt complexes were previously unknown. Mathey et al.[42] have described one example of a phospholyl analogue, (2,5-Bu$^t_2$$C_4H_2P$)Co(1,2-$C_4H_2Ph_2$). This compound was obtained as a result of thermal reaction between phenylacetylene and (2,5-Bu$^t_2$$C_4H_2P$)Co(1,5-cyclooctadiene).

We were able to prepare the pyrrolyl complexes **10a**,**c** by reaction of **2** with the corresponding potassium pyrrolides (Scheme 7).[43] The yield of complex **10a** having the unsubstituted pyrrolyl ring was 60%. However, the tetramethylated analogue **10c** was obtained in a lower yield (35%); tetramethylpyrrole was also isolated in this case, suggesting a proton transfer side reaction. It should be mentioned that complexes **10a**,**c** cannot be prepared using the (carbonyl)iodide complex **1** instead of **2**.

The reaction of the acetonitrile complex **2** with lithium phospholides was effectively used for the preparation of Cb*Co phospholyl derivatives. Complexes **11b**,**c** with methylated phospholyl ligands were obtained in high yields (ca. 60%). Unfortunately, the yield of compound **11a** with the unsubstituted C_4H_4P ring was only 20%. It is interesting to note that, in contrast to the pyrrolyl analogues **10a**,**c**, complexes **11b**,**c** can be prepared also starting from the iodide **1**. However, heating is necessary in this case and the yields are much lower than

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(37) Gleiter, R.; Pflästerer, G. *Organometallics* **1993**, *12*, 1886.

(38) (a) Kudinov, A. R.; Rybinskaya, M. I. *Metalloorg. Khim.* **1988**, *1*, 1429; *Organomet. Chem. USSR* **1988**, *1*, 781 (Engl. Transl.). (b) Kudinov, A. R.; Petrovskii, P. V.; Struchkov, Yu. T.; Yanovsky, A. I.; Rybinskaya, M. I. *J. Organomet. Chem.* **1991**, *421*, 91.

(39) Kudinov, A. R.; Shul'pina L. S.; Petrovskii P. V.; Rybinskaya M. I. *Metalloorg. Khim.* **1990**, *3*, 1391; *Organomet. Chem. USSR.* **1990**, *3*, 724 (Engl. Transl.).

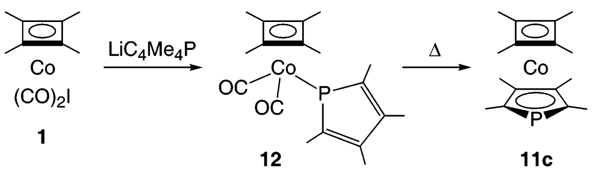
(40) Johnson, J. W.; Treichel, P. M. *J. Am. Chem. Soc.* **1977**, *99*, 1427.

(41) For haptotropic rearrangement of the related iron complex CpFe(η^6-fluorenyl) see: (a) Pomazanova, N. A.; Novikova, L. N.; Ustynyuk, N. A.; Kravtsov, D. N. *Metalloorg. Khim.* **1989**, *2*, 422; *Organomet. Chem. USSR.* **1989**, *2*, 210 (Engl. Transl.). (b) Kukharenko, S. V.; Strelets, V. V.; Ustynyuk, N. A.; Novikova, L. N.; Denisovitch, L. I.; Peterleitner, M. G. *Metalloorg. Khim.* **1991**, *4*, 299; *Organomet. Chem. USSR.* **1991**, *4*, 136 (Engl. Transl.).

(42) Caffyn, A. J. M.; Carmichael, D.; Mathey, F.; Ricard, L. *Organometallics* **1997**, *16*, 2049.

(43) Attempts to prepare **10a**,**c** using less reactive lithium pyrrolides were unsuccessful.

Scheme 8



using complex **2**. The room-temperature reaction of LiC$_4$Me$_4$P with **1** was shown to afford the σ-phospholyl complex **12**, which transforms into **11c** when refluxed in THF (Scheme 8).

The pyrrolyl and phospholyl complexes, except **11c**, are much more air sensitive than cyclopentadienyl analogues **5**, and an inert atmosphere is necessary for their isolation.

X-ray Diffraction Study. Structures of complexes **5g**, **6**, and **11c** were investigated by X-ray diffraction. The structures are shown in Figures 1−3, and selected bond lengths and angles are given in Tables 1−3. The compounds have a sandwich structure. The Cb* ring is nearly ideal square with a side 1.446−1.457 Å (av 1.452 Å) in **5g**, 1.460−1.471 Å (av 1.466 Å) in **6**, and 1.449−1.463 Å (av 1.454 Å) in **11c**. The planes of cyclic ligands are essentially coplanar (for **5g** the dihedral angle C$_4$/C$_5$ is equal to 5.0°, for **6** C$_4$/C$_5$ 2.9°, for **11c** C$_4$/C$_4$P 2.0°). The carbon atoms of the Cb* methyl groups are somewhat deviated from the ring planes away from the cobalt atom; the deviations amount to 0.08−0.17 Å for **5g**, 0.10−0.17 Å for **6**, and 0.16−0.17 Å for **11c**.

The cobalt atom is located over the center of the Cb* ring; the Co···Cb* distances in **5g** (1.683 Å) and **6** (1.679 Å) are very close to the corresponding values for the parent and tetraphenyl-substituted cyclopentadienyl complexes CbCoCp (1.681 Å)[44] and (C$_4$Ph$_4$)CoCp (1.679 Å),[45] demonstrating insignificant substituent effects. At the same time, these distances are considerably shorter than that for the carbonyl complex **3** (av 1.777 Å),[1] in accord with strong donor ability of Cp$^-$ leading to greater back-donation from the cobalt atom to the Cb* ring. The Co···Cb* distance in **11c** (1.689 Å) is only slightly longer than that in the cyclopentadienyl complexes, demonstrating insignificant effect of replacement of the CH fragment by a π-acceptor phosphorus atom.

To compare cobalt bonding with Cb and Cp rings, one should analyze the Co−C bond lengths rather than Co···ring distances, which are ring size dependent. The Co−C(Cb) bonds for **5g** (1.970−1.975 Å, av 1.97Å) are ca. 0.1 Å shorter than the Co−C(Cp) bonds (2.050−2.083 Å, av 2.07 Å), similar to the parent compound (av 1.96 and 2.03 Å, respectively)[44] and (C$_4$Ph$_4$)CoCp (1.98 and 2.05 Å, respectively), in accordance with stronger metal bonding with the Cb ring than with Cp, as predicted by Longuet-Higgins and Orgel.[46]

The Co···C$_5$ distance for the indenyl complex **6** (1.690 Å) is slightly longer than the corresponding distance in the acetylcyclopentadienyl analogue **5g** (1.679 Å), indicating weaker bonding of the C$_9$H$_7$ ligand compared with C$_5$H$_4$C(O)Me. The cobalt atom is not quite symmetrically coordinated with the C$_5$ ring, the distances from Co to the bridgehead C(4) and C(9) atoms (2.101 and 2.106 Å) being noticeably longer than other Co−C distances (2.062, 2.070, and 2.075 Å). However, a very small value of the elongation (ca. 0.03 Å) unambiguously confirms a η^5 bonding mode of the indenyl ligand.[47]

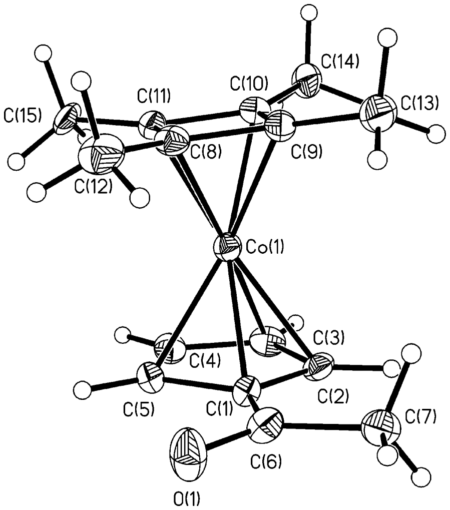


Figure 1. Structure of complex **5g**. Ellipsoids are shown at the 50% level.

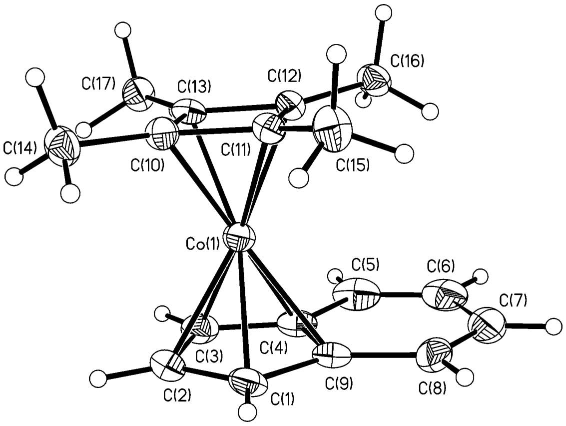


Figure 2. Structure of complex **6**. Ellipsoids are shown at the 50% level.

Electrochemistry and Joint UV−Visible and EPR Spectroelectrochemistry. The electrochemical behavior of the Co(I) sandwich complex **5a** is long known. In dichloromethane solution it undergoes a first one-electron oxidation, displaying features of chemical reversibility in the cyclic voltammetric time scale, followed in turn by further, ill-defined irreversible oxidation processes. In reality, during the longer times of macroelectrolysis the Co(II) monocation [**5a**]$^+$ is not completely stable, and its partial degradation leads to cobaltocenium ion as one of the final byproducts.[28]

As exemplified in Figure 4, which refers to the permethylated complex **5c**, the related Co(I) derivatives here studied follow a substantially similar redox pattern. In fact, the first oxidation, Figure 4a, displays features of chemical ($i_{pc}/i_{pa} = 1$) and substantial electrochemical ($\Delta E_p = 80$ mV at 0.05 V s^{-1}) reversibility.[48] Controlled potential coulometry ($E_w = +0.5$ V) confirmed the one-electron nature of such a process. A

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[44] Riley, P. E.; Davis, R. E. *J. Organomet. Chem.* **1976**, *113*, 157.

[45] Rausch, M. D.; Westover, G. F.; Mintz, E.; Reisner, G. M.; Bernal, I.; Clearfield, A.; Troup, J. M. *Inorg. Chem.* **1979**, *18*, 2605.

[46] Longuet-Higgins, H. C.; Orgel, L. E. *J. Chem. Soc.* **1956**, 1969.

[47] Westcott, S. A.; Kakkar, A. K.; Stringer, G. N.; Taylor, N. J.; Marder, T. B. *J. Organomet. Chem.* **1990**, *394*, 777.

[48] Zanello, P. *Inorganic Electrochemistry. Theory, Practice and Application*; Royal Society of Chemistry: Cambridge, 2003.

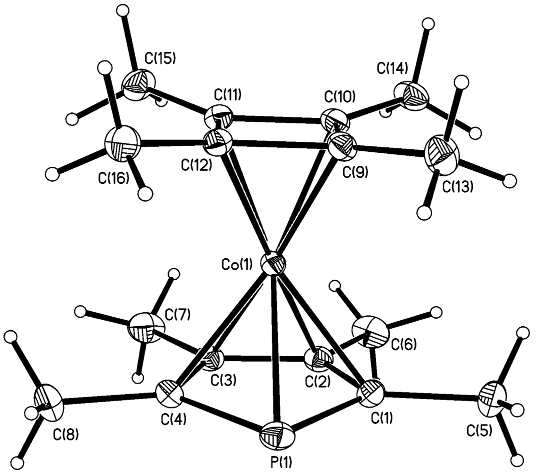

Figure 3. Structure of complex **11c**. Ellipsoids are shown at the 50% level.

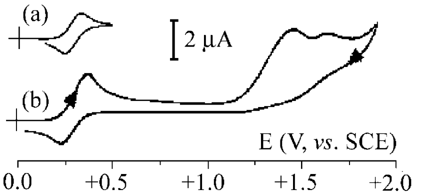

Figure 4. Cyclic voltammetric responses recorded at a platinum electrode in a CH_2Cl_2 solution of **5c** (1.3×10^{-3} mol dm^{-3}). $[NBu_4][PF_6]$ (0.2 mol dm^{-3}) supporting electrolyte. Scan rates: (a) 0.05 V s^{-1}; (b) 0.2 V s^{-1}.

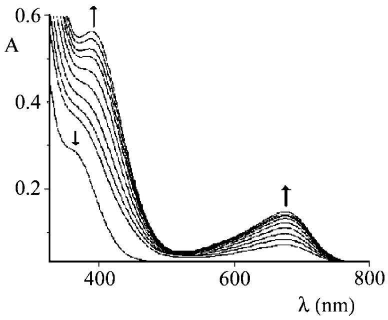

Figure 5. Visible spectral pattern accompanying the one-electron oxidation of **5c** in an OTTLE cell. CH_2Cl_2 solution.

second irreversible anodic process is present whose peak is somewhat higher than that of the first one at low scan rate ($i_{p(II)}/i_{p(I)} \approx 1.3$ at 0.2 V s^{-1}), Figure 4b, but tends to 1:1 at higher scan rates ($i_{p(II)}/i_{p(I)} \approx 1.1$ at 1.0 V s^{-1}). Such a trend indicates that the second oxidation is due to the monocation/dication irreversible electron transfer, rather than to the oxidation of byproducts arising from the eventual decomposition of the monocation. As shown, the lability of the dication is confirmed by the presence of a further spurious peak at high potential values, which disappears at high scan rates.

As a consequence of the exhaustive one-electron oxidation, the original yellow solution of **5c** turns light green. As a matter of fact, the pertinent spectroelectrochemical profiles recorded in an OTTLE (optically transparent thin-layer electrode) cell show that the original band at $\lambda_{max} = 361$ nm is progressively replaced by bands at 390 and 680 nm, respectively, Figure 5. It must be noted that, upon carrying out exhaustive oxidation at −20 °C, no appreciable degradation of $[\mathbf{5c}]^+$ takes place, as pointed out by the quite complementary cyclic voltammetric tests recorded on the low-temperature resulting solution, whereas, as exemplified in Figure 6, increasing the temperature causes appearance of minor byproducts in the voltammetric profile. On passing, we note that the expected degradation to decamethylcobaltocenium salt seems to be ruled out because of the lack of its reduction process around −1.5 V.[49]

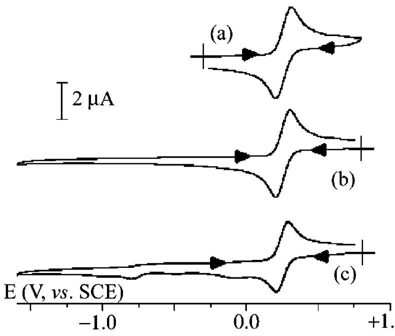

Figure 6. Cyclic voltammetric responses recorded at a gold electrode in a deaerated CH_2Cl_2 solution of **5c** (1.3×10^{-3} mol dm^{-3}): (a) before and (b) after exhaustive one-electron oxidation at −20 °C. (c) Cyclic voltammetric profile recorded under the same experimental conditions as (b), but increasing the temperature to +20 °C. $[NBu_4][PF_6]$ (0.2 mol dm^{-3}) supporting electrolyte. Scan rate 0.2 V s^{-1}.

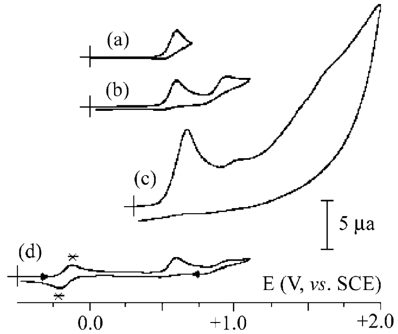

Figure 7. Cyclic voltammetric responses recorded at a gold electrode in a CH_2Cl_2 solution of: (a, b, c) **11b** (0.9×10^{-3} mol dm^{-3}); (d) after the addition of an equimolar amount of Cp^*_2Fe. $[NBu_4][PF_6]$ (0.2 mol dm^{-3}) supporting electrolyte. Scan rates (a, b, d) 0.2 Vs^{-1}; (c) 2.0 Vs^{-1}.

Quite different is the redox behavior of complexes **10a**,**c** and **11a**−**c**, in which the cyclopentadienyl ligand is replaced by P or N five-membered heterocycles. As a typical example, Figure 7 illustrates the cyclic voltammetric profile of **11b**. Also in this case, apparently two oxidation processes are displayed. However, not only do both processes look like they are coupled to fast chemical complications, but in reality the second process tends to disappear with an increase of the scan rate, Figure 7c. As a matter of fact, controlled potential coulometry corresponding with the first oxidation ($E_w = +0.7$ V) consumed 1.7 electrons *per* molecule, whereas a comparison with the one-electron oxidation of decamethylferrocene (starred peaks system), Figure 7d, proves that on the cyclic voltammetric time scale the first oxidation involves oxidation to the corresponding monocation. These data point out the notable instability of the monocation, which decomposes quickly to the byproduct responsible for the second anodic step.

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(49) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex 5g

Co(1)−C(1)	2.050(4)	C(1)−C(2)	1.431(6)
Co(1)−C(2)	2.075(4)	C(1)−C(5)	1.439(6)
Co(1)−C(3)	2.083(4)	C(2)−C(3)	1.421(6)
Co(1)−C(4)	2.074(4)	C(3)−C(4)	1.417(6)
Co(1)−C(5)	2.051(4)	C(4)−C(5)	1.415(6)
Co(1)−C(8)	1.974(4)	C(8)−C(9)	1.446(6)
Co(1)−C(9)	1.971(4)	C(8)−C(11)	1.457(5)
Co(1)−C(10)	1.975(4)	C(9)−C(10)	1.453(5)
Co(1)−C(11)	1.970(4)	C(10)−C(11)	1.455(6)
O(1)−C(6)	1.222(6)	C(1)−C(6)	1.470(6)
C(2)−C(1)−C(5)	108.0(4)	C(8)−C(11)−C(10)	89.7(3)
C(3)−C(2)−C(1)	107.6(4)	C(9)−C(10)−C(11)	89.9(3)
C(3)−C(4)−C(5)	109.0(4)	C(10)−C(9)−C(8)	90.3(3)
C(4)−C(3)−C(2)	108.2(4)	C(11)−C(8)−C(9)	90.1(3)
C(4)−C(5)−C(1)	107.2(4)		

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 6

Co(1)−C(1)	2.075(4)	C(1)−C(2)	1.411(6)
Co(1)−C(2)	2.062(4)	C(1)−C(9)	1.450(5)
Co(1)−C(3)	2.070(4)	C(2)−C(3)	1.419(6)
Co(1)−C(4)	2.101(4)	C(3)−C(4)	1.436(6)
Co(1)−C(9)	2.106(4)	C(4)−C(9)	1.438(5)
Co(1)−C(10)	1.972(4)	C(10)−C(11)	1.465(5)
Co(1)−C(11)	1.971(4)	C(10)−C(13)	1.464(5)
Co(1)−C(12)	1.982(4)	C(11)−C(12)	1.460(5)
Co(1)−C(13)	1.965(4)	C(12)−C(13)	1.471(5)
C(2)−C(1)−C(9)	107.1(3)	C(10)−C(13)−C(12)	89.9(3)
C(1)−C(2)−C(3)	110.1(4)	C(11)−C(12)−C(13)	89.8(3)
C(2)−C(3)−C(4)	107.2(3)	C(12)−C(11)−C(10)	90.3(3)
C(3)−C(4)−C(9)	108.0(3)	C(13)−C(10)−C(11)	89.9(3)
C(4)−C(9)−C(1)	107.5(3)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex 11c

Co(1)−C(1)	2.0732(11)	P(1)−C(1)	1.7790(12)
Co(1)−C(2)	2.0770(10)	P(1)−C(4)	1.7823(12)
Co(1)−C(3)	2.0758(11)	C(1)−C(2)	1.4186(15)
Co(1)−C(4)	2.0877(12)	C(2)−C(3)	1.4297(15)
Co(1)−P(1)	2.2762(5)	C(3)−C(4)	1.4172(16)
Co(1)−C(9)	1.9697(10)	C(9)−C(10)	1.4504(14)
Co(1)−C(10)	1.9851(11)	C(9)−C(12)	1.4633(14)
Co(1)−C(11)	1.9856(10)	C(10)−C(11)	1.4552(15)
Co(1)−C(12)	1.9705(10)	C(11)−C(12)	1.4486(15)
C(1)−P(1)−C(4)	89.67(5)	C(10)−C(9)−C(12)	89.86(8)
C(2)−C(1)−P(1)	112.66(8)	C(9)−C(10)−C(11)	90.07(8)
C(1)−C(2)−C(3)	112.51(9)	C(11)−C(12)−C(9)	89.82(8)
C(4)−C(3)−C(2)	112.32(9)	C(12)−C(11)−C(10)	90.25(8)
C(3)−C(4)−P(1)	112.74(8)		

Table 4 summarizes the formal electrode potentials for the first one-electron oxidation of the complexes studied, together with the related UV−visible spectrophotometric data. As seen, Table 4 also reports the electronic effects of the substituents present in the cyclopentadienyl ring through the field/inductive parameter F.[50] In fact, the formal electrode potentials for the Co(I)/Co(II) oxidation exhibit a weak linear correlation with such a parameter (correlation coefficient $R = 0.84$), which likely means that also resonance effects in part contribute to the location of the redox potential.

In view of the relative stability of the one-electron-oxidized derivatives, EPR investigations have been carried out on all the monocations electrogenerated at −20 °C. Representatively, Figure 8 shows the X-band EPR spectra (first and third derivative modes, respectively) of [**5c**]$^+$ in frozen CH_2Cl_2 solution ($T = 100$ K).

Table 4. Current Ratios, Formal Electrode Potentials (V, vs SCE), Peak-to-Peak Separations (mV), Visible Wavelengths (nm), and Field/Inductive Parameters for the Neutral/Monocation Oxidation of Complexes under Study (CH_2Cl_2 solution; $T = 293$ K)

complex	i_{pc}/i_{pa} [a]	$E°'_{0/+}$	ΔE_p [a]	λ_{max} neutral	λ_{max} monocation	ΣF
5a	1.00	+0.46	110	377 (yellow)	581 (gray-green)	0.00
	0.92[b,c]	+0.51[c]	75[b,c]			
5b	1.00	+0.43	99	372 (yellow)	576 (gray-green)	0.01
5c	1.00	+0.26	95	361 (yellow)	680 (green)	0.05
5d	1.00	+0.48	117	384 (yellow)	600 (brown-green)	0.01
5e	1.00	+0.45	85	386 (yellow)	598 (gray-green)	0.02
5f	0.71	+0.70	89	406 (yellow)	*d* (brown)	0.33
5g	0.69	+0.71	86	394 (yellow)	*d* (pale green)	0.33
6	0.96	+0.33	76	411 (yellow)	500, 739 (pale green)	
10a	0.0	+0.52[a,e]				
10b	0.0	+0.50[a,e]				
11a	0.0	+0.68[a,e]				
11b	0.3	+0.56[f]	75			
11c	0.2	+0.56[a,e]				
Cp_2Fe	1.0	+0.39	92	437 (yellow)	620 (blue-green)	

[a] Measured at 0.1 V s^{-1}. [b] Measured at 0.05 V s^{-1}. [c] From ref 28. [d] Significant degradation at room temperature. [e] Peak-potential values for processes complicated by fast chemical reactions. [f] Measured at 1 V s^{-1}.

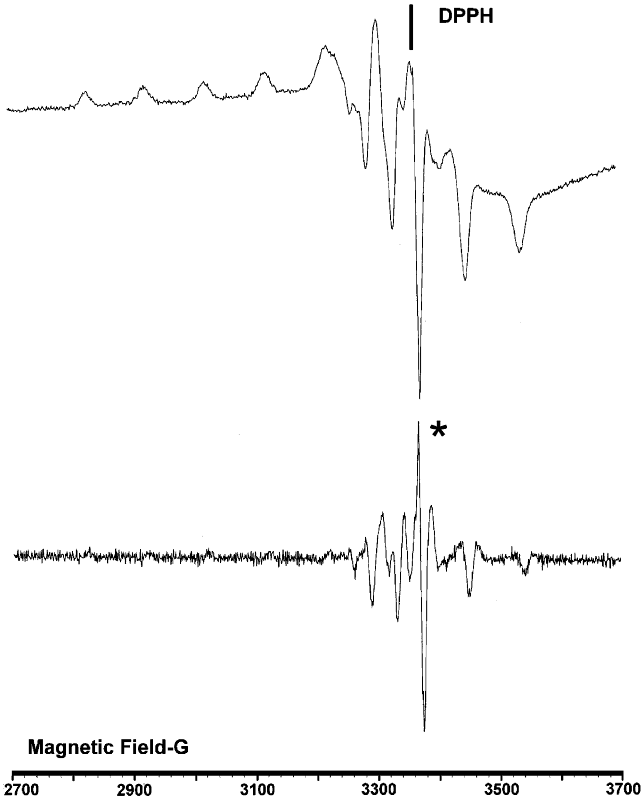

Figure 8. Liquid nitrogen ($T = 100$ K) X-band EPR spectrum of [**5c**]$^+$ in CH_2Cl_2 solution. (Top) First derivative mode. (Bottom) Third derivative mode (expanded window).

Excluding the narrow high-field signal (starred peak; $g_{av} = 1.992(8)$), which is assigned to an organic paramagnetic impurity, the spectral analysis can be suitably carried out in terms of the $S = 1/2$ low spin Co(II) electron spin Hamiltonian with resolution of the intense anisotropic line shape in well-separated axial absorptions ($g_{\|} > g_{\perp} > g_e = 2.0023$; $a_{\|}(Co) > a_{\perp}(Co)$; $I(^{59}Co) =$

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[50] Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

Table 5. X-Band EPR Anisotropic Parameters of the Co(II) Monocations under Study in CH_2Cl_2 Solution[a]

complex	$g_{\|}$	$g_{\perp}$	$\langle g\rangle$[b]	$\delta g_{\perp/\|}$	g_{iso}	$A_{\|}$	$a_{\perp}$	$\langle a\rangle$[c]	a_{iso}
[**5a**]$^+$	3.27(6)	1.95(6)	2.39(6)	1.32(6)		$\leq\Delta H_{\|}$	47(8)[d]	$\leq\langle\Delta H\rangle$	
[**5b**]$^+$	2.45(6)	1.96(6)	2.12(6)	0.49(6)		$\leq\Delta H_{\|}$	26(6)	$\leq\langle\Delta H\rangle$	
[**5c**]$^+$	2.116(8)	2.034(8)	2.061(8)	0.082(8)	2.060(8)	102(5)	15(5)	44(5)	44(8)
[**5d**]$^+$	2.76(6)	2.05(6)	2.29(6)	0.71(6)		$\leq\Delta H_{\|}$	44(5)[d]	$\leq\langle\Delta H\rangle$	
[**5e**]$^+$	3.26(6)	1.97(6)	2.40(6)	1.29(6)		$\leq\Delta H_{\|}$	15(5)	$\leq\langle\Delta H\rangle$	
[**5f**]$^+$	2.473(8)	2.044(8)	2.187(8)	0.429(8)		90(8)	48(8)[d]	62(8)	
[**5g**]$^+$	2.712(8)	2.005(8)	2.241(8)	0.707(8)		$\leq\Delta H_{\|}$	40(5)	$\leq\langle\Delta H\rangle$	
[**6**]$^+$	2.578(8)	2.015(8)	2.203(8)	0.561(8)		$\leq\Delta H_{\|}$	42(5) Co 16(5) H[d,e]	$\leq\langle\Delta H\rangle$ $\leq\langle\Delta H\rangle$	

[a] Anisotropic parameters: $T = 105$ K; isotropic parameters: $T = 298$ K; a_i in Gauss [b] $\langle g\rangle = (g_{\|} + 2g_{\perp})/3$. [c] $\langle a\rangle = (a_{\|} + 2a_{\perp})/3$. [d] Partial spectral resolution. [e] Superhyperfine splittings of ^1H.

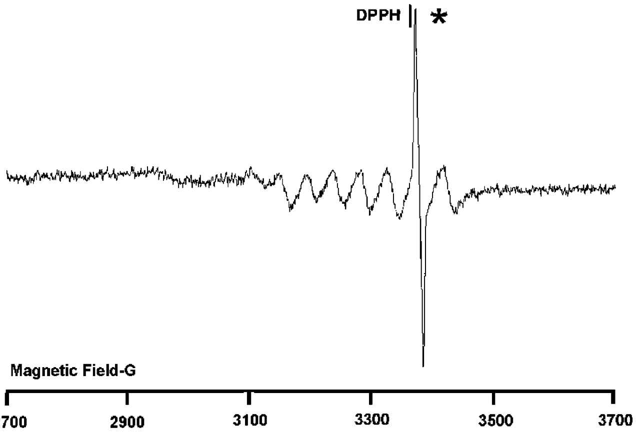

Figure 9. Room temperature ($T = 298$ K) X-band EPR spectrum of [**5c**]$^+$ in CH_2Cl_2 solution.

7/2, natural abundance = 100%). The two spectral regions are partially overlapped in the high-field position and display significant metal-centered anisotropic hyperfine (hpf) splittings, as a consequence of the strong Co(II) spin−orbit coupling (λ(Co) < 0).[51] The perpendicular region is completely resolved in the third derivative mode, the corresponding $g_{\perp}$ hpf signals being strongly enhanced and, correspondingly, the broad parallel multiplet quenched. There is no evidence for parallel or perpendicular superhyperfine (shpf) splittings of the methyl protons of the two ring ligands. The relevant anisotropic parameters are

$$g_{\|} = 2.116(8) \qquad a_{\|}(\mathrm{Co}) = 102(5)\ \mathrm{G}$$

$$g_{\perp} = 2.034(8) \qquad a_{\perp}(\mathrm{Co}) = 15(5)\ \mathrm{G}$$

$$\langle g\rangle = 2.061(8) \qquad \langle a\rangle(\mathrm{Co}) = 44(5)\ \mathrm{G}$$

$$\delta g = g_{\|} - g_{\perp} = 0.082$$

Raising the temperature, at the glassy−fluid transition ($T = 178$ K) the anisotropic spectral features collapse in the corresponding isotropic hpf signal, typical of $S = 1/2$ Co(II) species, Figure 9.

The line shape is totally resolved in the Co(II) hpf features, without detectable superhyperfine splittings (if any) of the ^1H of the two aromatic rings. As common for transition metal complexes, the isotropic features display the typical dependence of the overall isotropic line shape with T, H, and m_I.

The relevant isotropic parameters are

$$g_{iso} = 2.060(8)$$

$$a_{iso}(\mathrm{Co}) = 44(8)\ \mathrm{G}$$

$$\Delta H_{iso}(m_I = 7/2) = 25(8)\ \mathrm{G}$$

Such isotropic features testify to the nearly complete averaging of [**5c**]$^+$ original anisotropies in fast motion conditions ($T = 298$ K) and suggest the presence of an axial arrangement of the overall coordinating framework.[51,52] The temperature-dependent paramagnetic features indicate that the SOMO of [**5c**]$^+$ is mainly constituted by the cobalt 3d AOs, with minor contribution from the (s,p) AOs of the carbon and hydrogen atoms of the aromatic rings. Finally, the good fit of the $\langle g\rangle$ and g_{iso} as well as $\langle a\rangle$ and a_{iso} demonstrates that [**5c**]$^+$ substantially maintains its geometry in very different experimental conditions. Such a paramagnetic behavior substantially holds for all the electrogenerated Co(II) complexes with some significant differences strongly related to the nature of the second ligand. The pertinent EPR parameters are compiled in Table 5.

Inspection of the anisotropic g_i and a_i values points out significant differences among the monocations. The great variance of the g_i values can be accounted for by the parameter $\delta g_{\perp/\|} = |g_{\perp} - g_{\|}|$, which is diagnostic for structural anisotropies in Co(II) complexes.[51,52] In the present complexes $\delta g_{\perp/\|}$ ranges from 1.32 for [**5a**]$^+$ to 0.43 for [**5c**]$^+$, which means that, in the glassy state, the coordination sphere of [**5a**]$^+$ (as well as of [**5d**]$^+$, [**5e**]$^+$, and [**5g**]$^+$) is significantly distorted, whereas in [**5c**]$^+$ the cobalt center is buried in a high-symmetric environment. Such a trend is also reflected in the related $\langle g\rangle$ values.

The $g_{\|}$ regions of all the monocations are unresolved in both the hpf and shpf splittings ($a_{\|}$(Co, H) $\leq \Delta H_{\|}$), except for [**5c**]$^+$ and [**5f**]$^+$, which show hpf resolution. On the other hand, all the monocations exhibit hpf resolution of the $g_{\perp}$ region, except for [**5e**]$^+$, which is totally unresolved.[53] These magnetic effects testify to the active repulsion of the cyclopentadienyl HOMO's population on the $S = 1/2$ unpaired electron, thus inhibiting the electron delocalization on this ligand. In this connection, only [**6**]$^+$ displays significant shpf resolution in the presence of a correspondingly less

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intense $a_{\|}$(Co) value, which suggests a noticeable ^{1}H magnetic interaction with the unpaired electron, i.e., a significant delocalization of the $S = 1/2$ electron spin density on the indenyl ligand.

Chemical Oxidation. Koelle[28] has shown that chemical oxidation of **5a** with $AgOCOCF_3$ in CH_2Cl_2 gives cobaltocenium cation. We found that oxidation of **5a** with $AgBF_4$ in CH_2Cl_2 yields a mixture of $[Cp_2Co]^+$ (identified by ^{1}H NMR) with another cationic complex, which we were unable to identify. It was proposed that the formation of the latter is connected with the use of a silver salt since such salts can participate in reactions of other types.[49] Therefore we studied also oxidation of **5a** by acetylferrocenium cation $[CpFe(C_5H_4COMe)]^+$ (E = 0.73 V[49]); however the result was the same. The formation of $[Cp_2Co]^+$ suggests that the intermediately formed 17-electron monocation [**5a**]$^+$ eliminates the Cb* ligand to give the $[CpCo]^+$ fragment, which undergoes subsequent disproportionation. In this respect, the behavior of the Cb* ligand in [**5a**]$^+$ is similar to that of usual dienes in [CpCo(1,3-cyclohexadiene)]$^+$ and [CpCo(1,5-cyclooctadiene)]$^+$.[28,54]

In agreement with the electrochemical findings showing that the 17-electron permethylated monocation [**5c**]$^+$ is substantially stable in solution even at room temperature, we were able to isolate this cation as a hexafluorophosphate by chemical oxidation of **5c** by $[Cp_2Fe]^+$. The salt [**5c**]PF_6 was characterized by elemental analysis and ^{1}H NMR in CD_2Cl_2. Two rather sharp signals are observed at $\delta = -44.8$ (12H, $\Delta\nu = 156$ Hz) and +34.1 (15H, $\Delta\nu = 110$ Hz) ppm. The salt proved to be rather stable not only in the solid state but also in solution; only moderate broadening of the signals ($\Delta\nu = 307$ and 164 Hz, respectively) was observed after standing of the NMR tube for 3 days at room temperature. The cation [**5c**]$^+$ was reduced back to **5c** using $Cp^*{}_2Fe$ ($E = -0.13$ V; see Figure 7d). Much greater stability of cation [**5c**]$^+$ compared with [**5a**]$^+$ is connected with favorable electronic and steric effects of the methyl groups.

On the basis of the partial chemical reversibility of the **6**/[**6**]$^+$ electron transfer and the fate of [**5a**]$^+$, it was primarily thought that the 17-electron indenyl cation [**6**]$^+$ might convert to $[(\eta^5\text{-indenyl})_2Co]^+$. In reality, chemical oxidation of **6** with $[Cp_2Fe]^+$ yields a mixture of cationic complexes. Comparison of the ^{1}H NMR spectrum of this mixture with that of the authentic sample of $[(\eta^5\text{-indenyl})_2Co]^+$ indicates that the latter is absent among the oxidation products.

DFT Calculations. As mentioned above, X-ray data suggest stronger cobalt bonding with the Cb ring than with Cp. Nevertheless, oxidation of **5a** leads to the elimination of the Cb* ligand rather than Cp. To provide a possible explanation, we carried out the DFT calculations for CbCoCp.

Molecular orbital analysis of CbCoCp has been done previously using the INDO method in order to assign its photoelectron spectra bands.[55] However, due to obvious limitations of this method, only a general qualitative picture was obtained. The geometry of CbCoCp as a possible intermediate of the acetylene trimerization process has been calculated using the B3LYP functional, but no molecular orbital information has been published.[15]

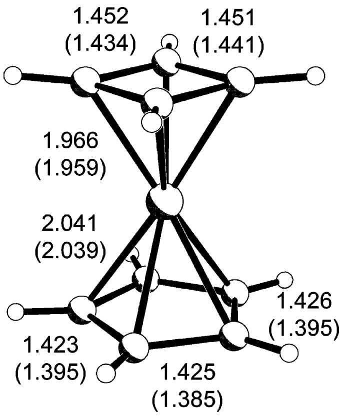

Figure 10. Optimized geometry of CbCoCp. Calculated bond distances are depicted near each bond with experimental values in parentheses.

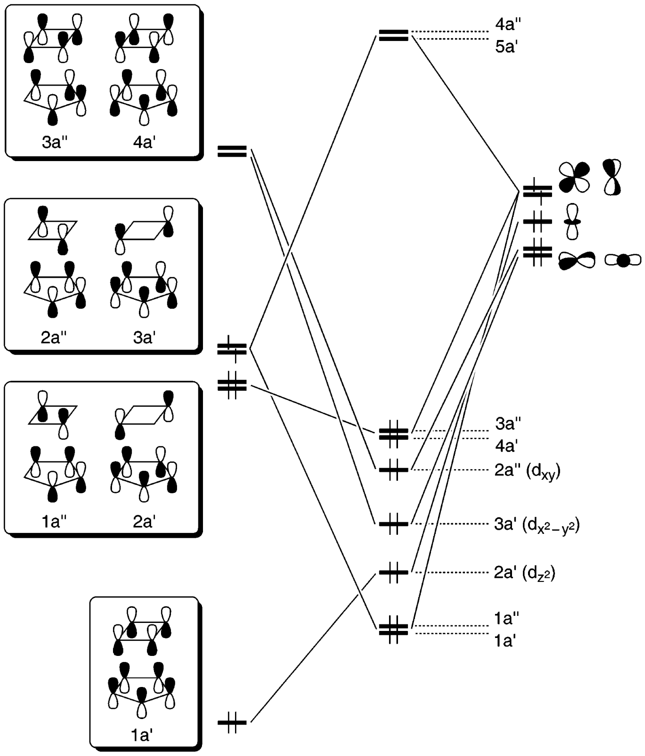

Figure 11. MO correlation diagram for CbCoCp. Only interactions resulting in significant contribution to the total bonding energy are shown.

The optimized geometry of this compound at the B3PW91/6-311G* level used in the present work displays better correlation with the experimental values (Figure 10, max. deviation = 0.04 Å, av deviation = 0.017 Å) than previous B3LYP calculations.[15] The maximum deviation from experimental geometry was observed for C−C(Cp) distances, possibly as a result of thermal motion and unrevealed disorder of the Cp ligand in the crystal. The calculated NBO charge for the Co atom in CbCoCp (+0.477) is significantly more positive than for the Fe atom in ferrocene (+0.204)[56] and less positive than for the Co atom in $[Cp_2Co]^+$ (+0.552).

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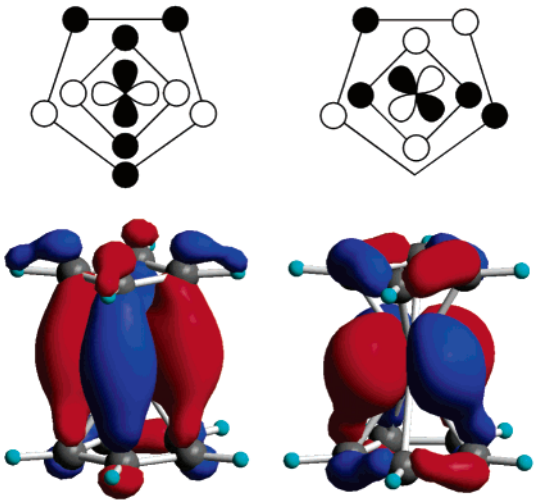

Figure 12. Back-donation in CbCoCp: qualitative pictures and plots for 3a′ HOMO−3 (left) and 2a″ HOMO−2 (right).

Table 6. Relative Energies (in eV) for Selected Orbitals of CbCoCp

orbital	energy	orbital	energy
LUMO+1	7.03	HOMO−3	1.29
LUMO	7.03	HOMO−4	0.75
HOMO	1.55	HOMO−5	0.00
HOMO−1	1.55	HOMO−6	0.00
HOMO−2	1.53		

The NBO total charges of the Cb and Cp ligands are −0.187 and −0.290, respectively. The lower negative charge of the Cb ligand is in accordance with a common description of cyclobutadiene as a neutral ligand.

The molecular orbital correlation diagram of CbCoCp is shown in Figure 11, and the relative orbital energies are given in Table 6. The symmetry and general orbital picture is in agreement with previous INDO calculations, although the relative energy of some orbitals is different.

A main contribution to the metal−ligand bonding arises from the interaction between d_{xz}, d_{yz} metal orbitals and 2a″, 3a′ ligand π-orbitals resulting in 1a′ HOMO−5 and 1a″ HOMO−6 molecular orbitals, which are similar to the e_{1g} HOMO−5 and HOMO−6 of ferrocene.[56] At the same time, back-donation (accomplished by interaction between d_{xy}, $d_{x^2-y^2}$ metal orbitals and 3a″, 4a′ ligand δ-orbitals giving 2a″ HOMO−2 and 3a′ HOMO−3, Figure 12) is more important for CbCoCp than similar interaction in the case of ferrocene (e_{2g} HOMO and HOMO−1). However, only one of two resulting MOs, viz., HOMO−3, is bonding for both Cb and Cp ligands as a consequence of the Cb ligand symmetry. Another one, HOMO−2, is bonding for the Cp ligand and nonbonding for Cb.

Molecular orbitals 3a″ HOMO and 4a′ HOMO−1 (Figure 13), resulting from the covalent interaction between d_{xz}, d_{yz} metal orbitals and 2a′, 1a″ ligand π-orbitals, are bonding with respect to the Co−Cb interaction and antibonding with respect to Co−Cp. Therefore removal of one electron from HOMO orbital should lead to simultaneous weakening of the Co−Cb bond and strengthening of the Co−Cp bond, thus giving thermodynamical evidence for the elimination of the Cb* ligand under oxidation of the tetramethylcyclobutadiene complex **5a**. However, kinetic effects could also be important, as exemplified by oxidation of sterically hindered tricyclic derivatives of CbCoCp leading to elimination of a Cp ligand rather than Cb.[57]

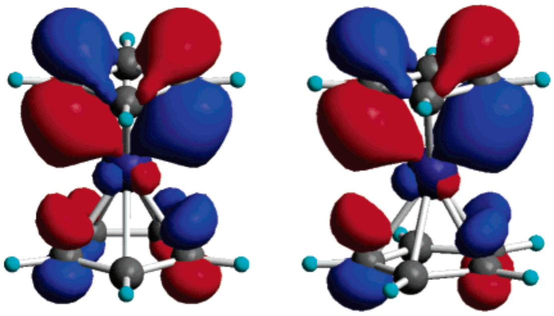

Figure 13. Plots for 3a″ HOMO (left) and 4a′ HOMO−1 (right) of CbCoCp.

Conclusion

(Tetramethylcyclobutadiene)cobalt complexes with five-electron ligands (cyclopentadienyl, indenyl, fluorenyl, pyrrolyl, and phospholyl) were prepared by reaction of the corresponding anions with the (carbonyl)iodide **1** or the acetonitrile complex **2**. The method using **2** (easily accessible by heating or irradiation of the benzene or toluene complex **4a**,**b**) is more general due to greater electrophilicity of this complex compared with **1**. However, this method has limitations connected with deprotonaton of **2** by extremely basic anions. The search for another synthon lacking this limitation is presently under way. The methods described make Cb*Co complexes readily available, allowing the development of their application, similar to CpFe congeners.

Experimental Section

General Remarks. All reactions were carried out under argon in anhydrous solvents which were purified and dried using standard procedures. The isolation of products was conducted in air unless otherwise stated. High-quality anhydrous aluminum chloride was used. Starting materials were prepared as described in the literature: $Co_2(CO)_8$,[58] $C_5H_5SiMe_3$, 1,3-$C_5H_4(SiMe_3)_2$,[59] C_4Me_4NH,[60] C_4H_4PPh, 3,4-$C_4H_2Me_2PPh$,[61] C_4Me_4PPh (using $LiAlH_4$ as a reducing agent instead of PBu_3),[62] $Na[C_5H_4C(O)H]$,[63] $Na[C_5H_4C(O)Me]$,[64] $K[C_4R_4N]$,[65] $Li[C_4R_4P]$,[62,66] and $AgBF_4{\cdot}3$dioxane.[67] 2-Butyne was prepared by dehydrohalogenation of 2,3-dibromobutane by $NaNH_2$ in liquid

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ammonia, similar to the preparation of propyne.[68] After the reaction was over, ammonia was absorbed by passing through the traps with water; subsequent gentle heating afforded the product, which was dried and distilled (bp 26 °C). Solutions of lithium cyclopentadienides and lithium indenide were prepared by treatment of cyclopentadienes or indene in THF with BuLi. Irradiation was conducted in a Schlenck tube using a high-pressure mercury vapor lamp with a phosphor-coated bulb (400 W). Both the tube and the lamp were placed into a vessel of an appropriate volume covered inside with aluminum foil; cooling was accomplished by running water. Column chromatography was performed on silica gel L 100/400 (0.5 × 10 cm) using petroleum ether as an eluent. The ^1H and ^{31}P NMR spectra were recorded with a Bruker AMX 400 spectrometer operating at 400.13 and 31.1 MHz, respectively. Materials and apparatus for electrochemistry and joint EPR spectroscopy have been described elsewhere.[69] X-Band EPR spectra were recorded with an ER 200-D-SCR spectrometer operating at $\nu = 9.4$ GHz. Simulation of EPR spectra was carried out according to literature programs.[69b] The UV–vis spectroelectrochemical measurements were carried out using a Perkin-Elmer Lambda 900 UV–vis spectrophotometer and an OTTLE cell equipped with a Pt minigrid working electrode (32 wires/cm), Pt minigrid auxiliary electrode, Ag wire pseudoreference, and CaF_2 windows.[70] The electrode potential was controlled during electrolysis by an Amel potentiostat 2059 equipped with an Amel function generator 568. Nitrogen-saturated solutions of the compounds under study were used with $[NBu_4]PF_6$ (0.2 mol dm^{-3}) as supporting electrolyte. Working potential was kept fixed at the peak potential of the process studied, and spectra were progressively collected after each 2 min electrolysis. All potential values are referred to the Saturated calomel electrode (SCE).

Cb*Co(CO)$_2$I (1). A solution of 2-butyne (6.0 mL, 4.1 g, 76 mmol) in CH_2Cl_2 (25 mL) was added dropwise to a stirred suspension of anhydrous aluminum chloride (10.6 g, 79.5 mmol) in CH_2Cl_2 (40 mL) at 0 °C. An additional portion of CH_2Cl_2 (35 mL) was added, and the reaction mixture was stirred at room temperature for 1 h. $Co_2(CO)_8$ (6.3 g, 18.4 mmol) was then added in one portion, and stirring was continued for 80 h. The reaction mixture was carefully hydrolyzed with cold water. The aqueous phase was separated, filtered, and stirred with $Me_3NO{\cdot}2H_2O$ (4.0 g, 36 mmol) and $NaI{\cdot}2H_2O$ (7.0 g, 37.6 mmol) overnight (the prolongation of this operation should be avoided since it may result in noticeable formation of paramagnetic impurities, which cause signal broading in the ^1H NMR spectrum). The brown solid was filtered off, washed thoroughly with water, and dried in a vacuum. The product is sufficiently pure and can be used for subsequent syntheses without purification. Yield: 7.7–8.3 g (60–65%). IR (KBr, cm^{-1}): ν(CO) 2055, 2016. ^1H NMR (acetone-d_6): δ 1.90 (s, Cb*). Anal. Calcd for $C_{10}H_{12}CoIO_2$: C, 34.31; H, 3.46. Found: C, 34.19; H, 3.37. If necessary, the product can be purified by elution with CH_2Cl_2 through a short layer of Al_2O_3 (ca. 4 cm) with subsequent concentration in a vacuum and addition of a 5-fold volume of petroleum ether. After standing overnight at −15 °C, red-brown crystals were filtered off and dried in a vacuum. An alternative purification procedure consists in dissolution in acetone, filtration, and subsequent precipitation by water. Complex **1** is reasonably air-stable for short periods of time (up to several days); however an inert atmosphere is necessary for its prolonged storage.

[Cb*Co(C$_6$H$_6$)]PF$_6$ (4aPF$_6$). A mixture of **1** (3.5 g, 10 mmol), anhydrous aluminum chloride (13.3 g, 100 mmol), and benzene (70 mL) was vigorously stirred under reflux for 8 h. After cooling, the reaction mixture was carefully hydrolyzed with cold water. The aqueous phase was separated, filtered, and stirred with $Me_3NO{\cdot}2H_2O$ (ca. 0.2 g, 1.2 mmol) and $NaI{\cdot}2H_2O$ (ca. 0.4 g, 2 mmol) for 4 h. A brown precipitate of **1** was filtered off. Addition of an aqueous solution of NH_4PF_6 (1.6 g, 10 mmol) to the filtrate afforded a yellow precipitate, which was filtered off, washed with water, and dried in a vacuum. The product was reprecipitated by ether from acetone as a yellow solid. Yield: 2.3–2.5 g (60–65%). ^1H NMR (acetone-d_6): δ 6.72 (s, 6H, C_6H_6), 1.70 (s, 12H, Cb*).

[Cb*Co(C$_6$H$_5$Me)]PF$_6$ (4bPF$_6$). A mixture of **1** (3.5 g, 10 mmol), anhydrous aluminum chloride (13.3 g, 100 mmol), toluene (50 mL), and hexane (50 mL) was vigorously stirred under reflux for 6 h. The workup procedure was carried out as described for **4a**PF$_6$ to produce a yellow solid. Yield: 1.8–2.0 g (45–52%). ^1H NMR (acetone-d_6): δ 6.63–6.55 (m, 5H, C_6H_5), 2.47 (s, 3H, Me), 1.66 (s, 12H, Cb*). Anal. Calcd for $C_{15}H_{20}CoF_6P$: C, 44.57; H, 4.99. Found: C, 44.39; H, 4.91.

[Cb*Co(MeCN)$_3$]PF$_6$ (2PF$_6$). Photochemical Procedure. A solution of **4a**PF$_6$ (0.5 g, 1.3 mmol) or **4b**PF$_6$ (0.5 g, 1.2 mmol) in acetonitrile (15 mL) was irradiated for 4 h, resulting in color change from yellow to red. The solvent was removed in a vacuum to give a red microcrystalline solid in almost quantitative yield. Complex **2**PF$_6$ is highly air-sensitive. ^1H NMR (acetone-d_6): δ 2.05 (s, 9H, Me), 0.96 (s, 12H, Cb*).

Thermal Procedure. A solution of **4a**PF$_6$ (0.5 g, 1.3 mmol) or **4b**PF$_6$ (0.5 g, 1.2 mmol) in acetonitrile (30 mL) was refluxed for 6 h in the case of **4a**PF$_6$ and 12 h in the case of **4b**PF$_6$. The solvent was removed in a vacuum to give the product in almost quantitative yield.

General Procedures for the Preparation of Cb*Co Complexes with Five-Electron Carbo- and Heterocyclic Ligands. Method A (Starting from 1). A solution of sodium or lithium derivative of the corresponding cyclopentadienide or phospholide anion (0.32 mmol) in THF (ca. 3 mL) was added dropwise to a stirred solution of **1** (100 mg, 0.29 mmol) in THF (5 mL) at 0 °C. The temperature was allowed to rise to ambient, and the reaction mixture was then stirred under reflux for 6 h in the case of cyclopentadienide anions and 20 h in the case of phospholide anions. The solvent was removed in a vacuum, and the residue was extracted with petroleum ether. Filtration and removal of the solvent left a crude product, which was purified as specified below. ^1H NMR data for complexes **5a**–**j**, **10a**,**c**, and **11a**–**c** are given in Table 7.

Cb*CoCp (5a). The product was sublimed at 50–60 °C (12 mmHg) as a yellow-orange solid. Yield: 49 mg (74%).

Cb*Co(C$_5$H$_4$SiMe$_3$) (5d). The product was chromatographed and then recrystallized from pentane at −78 °C as a yellow-orange solid. Yield: 23 mg (26%). Anal. Calcd for $C_{16}H_{25}CoSi$: C, 63.13; H, 8.28. Found: C, 63.35; H, 8.26.

Cb*Co(C$_5$H$_4$C(O)H) (5f). The product was sublimed at 75–80 °C (12 mmHg) as a yellow-orange solid. Yield: 31 mg (40%). IR (KBr, cm^{-1}): ν(CO) 1670. Anal. Calcd for $C_{14}H_{17}OCo$: C, 64.62; H, 6.64. Found: C, 64.62; H, 6.59.

Cb*Co(C$_5$H$_4$C(O)Me) (5g). The product was recrystallized from pentane at −78 °C as a yellow-orange solid. Yield: 29 mg (37%). IR (KBr, cm^{-1}): ν(CO) 1678. Anal. Calcd for $C_{15}H_{19}OCo$: C, 65.69; H, 6.98. Found: C, 65.92; H, 7.16.

Cb*Co(3,4-C$_4$H$_2$Me$_2$P) (11b). The product was sublimed at 45 °C (0.01 mmHg) as a yellow-orange solid. All manipulations were carried out under argon. Yield: 6 mg (7%). ^{31}P NMR (acetone-d_6): δ −33.3. Anal. Calcd for $C_{14}H_{20}CoP$: C, 60.44; H, 7.25. Found: C, 60.40; H, 7.33.

Cb*Co(C$_4$Me$_4$P) (11c). The product was sublimed at 65 °C (0.01 mmHg) as a yellow-orange solid. Yield: 12 mg (14%). ^{31}P NMR (CDCl$_3$): δ −24.4. Anal. Calcd for $C_{16}H_{24}CoP$: C, 62.74; H, 7.90. Found: C, 62.91; H, 8.05.

Method B (Starting from 2PF$_6$). A solution or suspension of alkaline metal derivative of the corresponding anion (0.31 mmol) in THF (ca. 3 mL) was added to a frozen (−78 °C)

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Table 7. ^{1}H NMR Data (δ in ppm, J in Hz) for Complexes 5a–j, 10a,c, and 11a–c[a]

complex	C_4Me_4	$C_5H_{5-n}R_n$	R
5a	1.55	4.53 (s, 5H)	
5b	1.51	4.39 (t, 2.0; 2H)	1.95 (s, 3H)
		4.33 (t, 2.0; 2H)	
5c	1.29		1.78 (s, 15H)
5d	1.52	4.62 (t, 1.7; 2H)	0.19 (s, 9H)
		4.52 (t, 1.7; 2H)	
5e	1.45	4.56 (s, 2H, H4,5)	0.19 (s, 18H)
		4.47 (s, 1H, H2)	
5f	1.47	5.07 (t, 2.0; 2H)	9.62 (s, 1H)
		4.87 (t, 2.0; 2H)	
5g	1.44	5.06 (t, 2.0; 2H)	2.28 (s, 3H)
		4.77 (t, 2.0; 2H)	
5h	1.51	4.40 (t, 2.0; 2H)	2.32 (q, 7.6; 2H, CH_2)
		4.36 (t, 2.0; 2H)	1.14 (t, 7.6; 3H, Me)
5i	1.53	4.56 (t, 2.0; 2H)	4.33 (d, 5.6; 2H, CH_2)
		4.50 (t, 2.0; 2H)	1.37 (t, 5.6; 1H, OH)
5j	1.54	4.61 (m, 1H)	4.58 (m, 1H, CH)
		4.55 (m, 1H)	1.63 (d, 4.0; 1H, OH)
		4.46 (m, 2H)	1.44 (d, 6.4; 3H, Me)
10a	1.50	5.78 (s, 2H)	
		5.03 (s, 2H)	
10c	1.32		2.08 (s, 6H)
			1.80 (s, 6H)
11a	1.56	5.37 (t, 5.6; 2H, H_β)	
		4.63 (dd, 36.8 (PH), 5.6 (HH); 2H, H_α)	
11b	1.49	4.29 (d, 36.4 (PH); 2H)	2.03 (s, 6H)
11c	1.39		1.91 (s, 6H, Me_β)
			1.77 (d, 9.2 (PH); 6H, Me_α)

[a] In $CDCl_3$ except for **11b**, the spectrum of which was recorded in acetone-d_6.

solution of **2**PF_6 prepared by irradiation or refluxing of **4a**PF_6 or **4b**PF_6 (0.26 mmol) in acetonitrile (3 mL) as described above. The temperature was allowed to rise to ambient, and stirring was continued overnight. The solvent was removed in a vacuum, and the residue was extracted with petroleum ether. Filtration and removal of the solvent resulted in a crude product. Complexes **5a**,**d**,**f**,**g** and **11b**,**c** were purified as described above.

Cb*CoCp (5a). Yield: 45 mg (74%).

Cb*Co(C_5H_4Me) (5b). The product was chromatographed and then sublimed at 60 °C (12 mmHg) as a yellow-orange solid. Yield: 38 mg (60%). According to ^{1}H NMR, the product contains 5% admixture of **5a**.

Cb*CoCp* (5c). A suspension of KCp*, prepared by refluxing potassium with a slight excess of pentamethylcyclopentadiene in THF until disappearance of the metal (ca. 4 h), was used. The product was chromatographed and then sublimed at 60 °C (0.01 mmHg) as a yellow-orange solid. Yield: 32 mg (41%). Anal. Calcd for $C_{18}H_{27}Co$: C, 71.50; H, 9.00. Found: C, 71.71; H, 9.15.

Cb*Co($C_5H_4SiMe_3$) (5d). Yield: 57 mg (72%).

Cb*Co(1,3-$C_5H_3(SiMe_3)_2$) (5e). The product was chromatographed followed by recrystallization from pentane at −78 °C as a yellow-orange solid. Yield: 59 mg (60%). Anal. Calcd for $C_{19}H_{33}CoSi_2$: C, 60.60; H, 8.83. Found: C, 60.83; H, 9.01.

Cb*Co($C_5H_4C(O)H$) (5f). Yield: 58 mg (86%).

Cb*Co($C_5H_4C(O)Me$) (5g). Yield: 58 mg (81%).

Cb*Co(η^5-indenyl) (6). The product was chromatographed as an orange solid. Yield: 53 mg (72%). ^{1}H NMR (benzene-d_6): δ 7.35 (2H, H4,7) and 7.01 (2H, H5,6) (multiplets characteristic of A and B parts of AA′BB′ spin system), 5.08 (d, $^3J = 2.4$ Hz, 2H, H1,3), 4.83 (t, $^3J = 2.6$ Hz, 1H, H2), 1.29 (s, 12H, Cb*). Anal. Calcd for $C_{17}H_{19}Co$: C, 72.34; H, 6.78. Found: C, 72.58; H, 6.96.

Cb*Co(C_4H_4N) (10a). The product was sublimed at 25 °C (0.01 mmHg) as a yellow-orange solid. All manipulations were carried out under argon. Yield: 39 mg (64%). Anal. Calcd for $C_{12}H_{16}CoN$: C, 61.80; H, 6.92. Found: C, 61.54; H, 7.04.

Cb*Co(C_4Me_4N) (10c). The product was sublimed at 90 °C (0.01 mmHg) as a yellow-orange solid. All manipulations were carried out under argon. Yield: 26 mg (35%). Anal. Calcd for $C_{16}H_{24}CoN$: C, 66.42; H, 8.36. Found: C, 66.46; H, 8.53.

Cb*Co(C_4H_4P) (11a). The product was sublimed at 45 °C (0.01 mmHg) as a yellow-orange solid. All manipulations were carried out under argon. Yield: 13 mg (20%). ^{31}P NMR ($CDCl_3$): δ −26.3. Anal. Calcd for $C_{12}H_{16}CoP$: C, 57.61; H, 6.45. Found: C, 57.50; H, 6.46.

Cb*Co(3,4-$C_4H_2Me_2P$) (11b). Yield: 46 mg (63%).

Cb*Co(C_4Me_4P) (11c). Yield: 52 mg (65%).

Reduction of the Carbonyl Group in Cb*Co(C_5H_4C(O)R) (5f,g). Cb*Co(C_5H_4Me) (5b). Anhydrous aluminum chloride (260 mg, 1.92 mmol) was very slowly added to a stirred suspension of **5f** (100 mg, 0.38 mmol) and $NaBH_4$ (220 mg, 5.76 mmol) in THF (10 mL) at 0 °C, leading to a color change from yellow to dark red. The reaction mixture was stirred at 0 °C until it became light yellow (ca. 30 min). The mixture was carefully hydrolyzed with water (20 mL) and extracted with CH_2Cl_2 (20 mL). The organic phase was separated, washed with water, and dried over $MgSO_4$. The solvent was removed in a vacuum, and the crude product was chromatographed and then sublimed at 60 °C (12 mmHg) as a yellow-orange solid. Yield: 51 mg (55%). Anal. Calcd for $C_{14}H_{19}Co$: C, 68.29; H, 7.78. Found: C, 68.38; H, 7.88.

Cb*Co(C_5H_4Et) (5h). Complex **5h** was prepared by reduction of **5g** (100 mg, 0.36 mmol) as described above for the preparation of **5b**. The crude product was purified by chromatography with subsequent distillation at 60 °C (12 mmHg) to give a light yellow oil. Yield: 63 mg (67%). Anal. Calcd for $C_{15}H_{21}Co$: C, 69.22; H, 8.13. Found: C, 69.23; H, 8.30.

Cb*Co($C_5H_4CH_2OH$) (5i). $LiAlH_4$ (14 mg, 0.38 mmol) was added to a solution of **5f** (200 mg, 0.76 mmol) in Et_2O (10 mL). The reaction mixture was stirred at room temperature for 1 h and then was refluxed for 2 h. The mixture was treated at 0 °C with ethyl acetate (3 mL) and then with an aqueous solution of NH_4Cl. After filtration, the organic phase was separated, washed with water, and dried over $MgSO_4$. The solvent was removed in a vacuum, and the residue was sublimed at 80 °C (12 mmHg) as a yellow-orange solid. Yield: 110 mg (55%). Anal. Calcd for $C_{14}H_{19}CoO$: C, 64.12; H, 7.30. Found: C, 64.13; H, 7.24.

Cb*Co($C_5H_4CH(OH)Me$) (5j). Complex **5j** was prepared by reduction of **5g** (200 mg, 0.72 mmol) as described above for the preparation of **5i**. The product was sublimed at 85 °C (12 mmHg) as a yellow-orange solid. Yield: 101 mg (51%). Anal. Calcd for $C_{15}H_{21}CoO$: C, 65.21; H, 7.66. Found: C, 65.21; H, 7.59.

[Cb*Co(η^6-fluorene)]PF_6 (8PF_6). A mixture of **1** (0.4 g, 1.15 mmol), anhydrous aluminum chloride (1.5 g, 11.5 mmol), fluorene (2.0 g, 11.5 mmol), and heptane (70 mL) was vigorously stirred under reflux for 4 h. The organic phase was decanted off, and the dark brown oil was carefully hydrolyzed with cold water (ca. 100 mL). The workup procedure was carried out as described for **4a**PF_6 to produce a yellow solid. Yield: 0.24 g (44%). Anal. Calcd for $C_{21}H_{22}CoF_6P$: C, 52.73; H, 4.64. Found: C, 52.83; H, 4.52. ^{1}H NMR data for complex **8**PF_6 as well as for **7** and **9** are given in Table 8.

Cb*Co(η^6-fluorenyl) (9). THF (10 mL) was added at 0 °C to a mixture of complex **8**PF_6 (200 mg, 0.42 mmol) and $KOBu^t$ (70 mg, 0.63 mmol). The dark red reaction mixture was stirred for 1 h. The solvent was removed in a vacuum, and the residue was extracted with petroleum ether (ca. 25 mL). Removal of the solvent in a vacuum gave a crude product, which was recrystallized twice from pentane at −40 °C as a red solid. All manipulations were carried out under argon. Yield: 100 mg (72%). Anal. Calcd for $C_{21}H_{21}Co$: C, 75.90; H, 6.37. Found: C, 75.91; H, 6.57.

Table 8. ^{1}H NMR Data (δ in ppm, J in Hz) for Complexes 7−9

complex	C_4-Me_4	H(1,4)	H(2,3)	H(5,8)	H(6,7)	H(9)
7[a,b]	0.95	7.79 (d, 8.0)	7.15 (t, 6.6)			5.44 (s)
		7.44 (d, 8.0)	7.09 (t, 7.2)			
8[c]	1.35	7.32 (d, 6.4)	6.75 (t, 6.0)	8.09 (m)	7.58 (t, 3.8)	4.14 (AB, 22.4)
		7.10 (d, 6.4)	6.69 (t, 6.0)	7.75 (m)	7.56 (t, 3.8)	
9[a]	0.82	6.40 (d, 6.4)	5.01 (t, 5.0)	8.21 (d, 8.0)	7.78 (d, 8.0)	6.41
		5.98 (d, 6.4)	4.93 (t, 5.0)	8.16 (d, 8.0)	7.34 (d, 8.0)	

[a] In benzene-d_6. [b] The protons H(1,4) and H(2,3) are equivalent to the protons H(5,8) and H(6,7), respectively. [c] In acetone-d_6.

Table 9. Crystallographic Data and Structure Refinement Parameters for 5g, 6, and 11c

	5g	**6**	**11c**
empirical formula	$C_{15}H_{19}CoO$	$C_{17}H_{19}Co$	$C_{16}H_{24}CoP$
molecular weight	274.23	282.25	306.25
cryst color, habit	orange plate	dark orange needle	light red prism
cryst size (mm)	0.05 × 0.50 × 0.50	0.30 × 0.40 × 0.60	0.29 × 0.25 × 0.24
cryst syst	triclinic	monoclinic	
space group	$P1$	$P2_1$	$P2_1/c$
a (Å)	7.536(3)	7.093(1)	9.799(2)
b (Å)	8.458(4)	7.901(1)	11.217(2)
c (Å)	11.715(5)	12.462(2)	14.735(3)
α (deg)	92.396(9)		
β (deg)	103.839(9)	102.582(4)	105.77(3)
γ (deg)	113.186(9)		
V (Å^3)	658.6(5)	681.7(2)	1558.6(5)
Z	2	2	4
D_{calcd} (g cm^{-3})	1.383	1.375	1.305
θ range (deg)	1.81−27.88	3.05−29.99	2.16−45.12
abs coeff, μ(Mo Kα) (cm^{-3})	12.84	12.37	11.85
T_{max} and T_{min}	0.862 and 0.288	0.928 and 0.548	
no. of collected reflns	4713	5684	17 702
no. of indep reflns	2969 (R_{int} = 0.0455)	3436 (R_{int} = 0.0300)	12 869 (R_{int} = 0.0329)
no. of obsd reflns ($I > 2\sigma(I)$)	2411	2683	7073
no. of params	154	163	163
R_1 (on F for obsd reflns)[a]	0.0675	0.0453	0.0450
wR_2 (on F^2 for all reflns)[b]	0.1884	0.1057	0.1003
F(000)	288	296	648
GOF	0.735	0.541	1.076
largest diff peak and hole (e Å^{-3})	1.388 and −1.952	1.432 and −0.460	0.659 and −1.601

[a] $R_1 = \sum||F_o| - |F_c||/\sum(F_o)$ for observed reflections. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{0.5}$ for all reflections.

Cb*Co(η^5-fluorenyl) (7). Complex **9** (100 mg, 0.3 mmol) was dissolved in petroleum ether (10 mL) and irradiated for 5 h, resulting in a color change from dark red to orange. The solvent was removed in a vacuum, and the product was recrystallized from pentane at −78 °C and then sublimed at 80 °C (0.01 mmHg) as a yellow-orange solid. All manipulations were carried out under argon. Yield: 54 mg (54%). Anal. Calcd for $C_{21}H_{21}Co$: C, 75.90; H, 6.37. Found: C, 73.90; H, 5.47. High air sensitivity of the product precludes obtaining satisfactory elemental analysis data.

Cb*Co(η^1-C_4Me_4P)(CO)$_2$ (12). A solution of LiC_4Me_4P (0.31 mmol) in THF (ca. 3 mL) was added to complex **1** (100 mg, 0.28 mmol) in THF (5 mL), and the mixture was stirred at room temperature for 20 h. The solvent was removed in a vacuum, and the residue was extracted with pentane. After filtration, the product was recrystallized from pentane at −10 °C as orange needles. All manipulations were carried out under argon. Yield: 45 mg (44%). IR (KBr, cm^{-1}): ν(CO) 2028, 1993. ^{1}H NMR ($CDCl_3$): δ 2.05 (d, $^3J_{PH}$ = 10.8 Hz, 6H, Me_α), 1.99 (d, $^4J_{PH}$ = 1.1 Hz, 6H, Me_β), 1.75 (d, $^4J_{PH}$ = 1.6 Hz, 12H, Cb*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −1.1. Anal. Calcd for $C_{18}H_{24}CoO_2P$: C, 59.67; H, 6.68. Found: C, 59.85; H, 6.68.

[Cb*CoCp*]PF$_6$ (5cPF$_6$). A mixture of **5c** (62 mg, 0.2 mmol) and $[Cp_2Fe]PF_6$ (68 mg, 0.2 mmol) in CH_2Cl_2 (10 mL) was stirred overnight, resulting in a dark green solution. A small volume of ether (ca. 3 mL) was added, leading to precipitation of a black solid, which was removed by filtration. Subsequent addition of a big volume of ether (ca. 20 mL) precipitated a green solid, which was filtered off, washed with ether, and dried in a vacuum. All manipulations were carried out under argon. Yield: 59 mg (65%). ^{1}H NMR (CD_2Cl_2): δ 34.10 (s, 15H, $\Delta\nu$ = 110 Hz, Cp*), −44.80 (s, 12H, $\Delta\nu$ = 156 Hz, Cb*). Anal. Calcd for $C_{18}H_{27}CoF_6P$: C, 48.33; H, 6.09. Found: C, 48.17; H, 5.94.

Reduction of [Cb*CoCp*]PF$_6$ (5cPF$_6$). A mixture of **5c**PF$_6$ (36 mg, 0.08 mmol) and Cp*$_2$Fe (24 mg, 0.07 mmol) in CH_2Cl_2 (10 mL) was stirred overnight. The solvent was removed in a vacuum, and the residue was extracted with petroleum ether. Removal of the solvent in a vacuum and subsequent sublimation at 60 °C (0.01 mmHg) afforded **5c** as a yellow-orange solid. Yield: 14 mg (67%). ^{1}H NMR ($CDCl_3$): δ 1.78 (s, 15H, Cp*), 1.29 (s, 12H, Cb*).

Oxidation of Cb*CoCp (5a). A mixture of **5a** (44 mg, 0.19 mmol) and $AgBF_4$·3dioxane (86 mg, 0.19 mmol) in CH_2Cl_2 (5 mL) was stirred overnight. The solution was filtered, and the volume of the filtrate was reduced to ca. 0.5 mL in a vacuum. Addition of ether (ca. 20 mL) precipitated a yellow solid, which was filtered off and dried in a vacuum. Yield: 24 mg. The ^{1}H NMR spectrum (acetone-d_6) contains a signal at δ 5.92 (s), which was assigned to $[Cp_2Co]^+$.[71] In addition, there is a group of signals that can be assigned to a single compound which was not identified.

Computational Details. All calculations were carried out using the Gaussian 98 package.[72] The geometry of CbCoCp was optimized at the B3PW91/6-311G* level of theory[73] with tightened convergence criteria (SCF = Vtight, Opt = Tight, and Int = UltraFine options). X-ray diffraction geometry with C_s symmetry was used as a starting point for optimization (calculations without symmetry constraints or with a different conformation of Cb ligand gave essentially the same results). Frequency calculations were performed to confirm the global minimum. Natural bond order (NBO) analyses were carried out using the NBO scheme included in the Gaussian 98 package.

X-ray Crystallography. Crystals suitable for X-ray diffraction were grown up by slow evaporation of pentane solutions at room temperature (for **5g** and **6**) or at −10 °C (for **11c**). X-ray diffraction measurements were carried out on a Bruker SMART 1000 CCD area detector, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å, ω-scans with

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a 0.3° step in ω and 10 s per frame exposure) at 110 K. Low temperature of the crystals was maintained with a Cryostream (Oxford Cryosystems) open-flow N_2 gas cryostat. Reflection intensities were integrated using SAINT software[74] and the SADABS semiempirical method.[75] The structures were solved by direct methods and refined by full-matrix least-squares against F^2 in anisotropic approximation for non-hydrogen atoms. All hydrogen atoms were placed in geometrically calculated positions and included in the final refinement using the "riding" model with the $U_{iso}(H)$ parameters equal to $1.2U_{eq}(C_i)$ or $1.5U_{eq}(C_{ii})$, where $U(C_i)$ and $U(C_{ii})$ are respectively the equivalent thermal parameters of the methyne and methyl carbon atoms to which the corresponding H atoms are bonded. The absolute structure of **6** was determined on the basis of the comparison of equivalent reflections (Flack method[76]), the Flack absolute structure parameter being equal to 0.00(3). Crystallographic data and structure refinement parameters for **5g**, **6**, and **11c** are given in Table 9. All calculations were performed on an IBM PC/AT using SHELXTL software.[77]

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC 237596 for **5g**, CCDC 237597 for **6**, and CCDC 237881 for **11c**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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Supporting Information Available: Details of crystallographic experiments for complexes **5g**, **6**, and **11c** (tables of crystal data collection, refinement parameters, atomic coordinates, anisotropic displacement parameters, bond distances, and bond angles) and details of DFT calculations for CbCoCp (atomic coordinates for optimized geometry, summary of natural population analysis, and plots for selected orbitals). This material is available free of charge via the Internet at http://pubs.acs.org.

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