$C_{14}H_{11}N_2Re$: C, 42.74; H, 2.82. Found: C, 42.70; H, 3.10.

Irradiation of **5b** in toluene for 2 days as above afforded a mixture of **5a** and **5b** (ratio 1:2, determined by ^1H NMR). Complete conversion to **5a** was effected when the toluene solution of **5b** was heated to 90 °C for 3 days.

Crystal Structure Analysis of 1a. Dark red crystals of **1a** were obtained from solutions of **1a** in Et_2O at −60 °C. A platelet of suitable size was mounted in a glass capillary under nitrogen. Intensity data were collected on a CAD4 four-circle diffractometer (Enraf-Nonius, Delft, The Netherlands). Some decay (0.06%/h, total 9%) was observed; the decay correction[38] had little influence on the structural parameters. The structures were solved and refined by means of standard heavy-atom methods, alternating least-squares refinements, and difference Fourier calculations. All non-hydrogen atoms were refined anisotropically. No attempt was made to localize the hydrogen atoms experimentally; they were placed in calculated positions (d(C–H) = 95 pm, $B_{eq} = 5.0 \times 10^4$ pm^2). All calculations were performed on a VAX 11/730 computer using the SDP program system.[38] The maximum residual electron density in the final difference Fourier map was $<0.7 \times 10^{-6}$ e pm^{-3} outside the Re atom (distance from Re, $d >$ 140 pm).

Crystal Structure Analysis of 1b. Dark red crystals of **1b** were grown from benzene solutions by slow evaporation at ambient temperature. The data collection was done as in the case for **1a**. No decay or intensity fluctuations were observed. The structure was solved by standard methods as above. Calculations were performed on a PDP 11/45 computer. Units weights were used during refinement; more sophisticated weighting schemes were not tested, largely because of limitations of the computing facility. The final maximum residual electron density was $<0.5 \times 10^{-6}$ e pm^{-3} outside the Re atom ($d >$ 110 pm).

Acknowledgment. Support of this work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Registry No. **1a**, 12092-03-4; **1b**, 12092-02-3; **2a**, 109279-69-8; **2b**, 12701-30-3; **3a**, 109011-49-6; **3b**, 109063-32-3; **5a**, 109011-50-9; **5b**, 109063-33-4; DMAC, 762-42-5; DCA, 1071-98-3; Cp_2WH_2, 1271-33-6; Cp_2ReH, 1271-32-5.

Supplementary Material Available: Tables of positional parameters for **1a** and general temperature factor expressions for **1a**, **1b′**, and **1b″** (3 pages); listings of structure factors for **1a** and **1b** (31 pages). Ordering information is given on any current masthead page.

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An Unexpected Carbon–Carbon Bond Formation in the Reaction between $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$ and Hexafluorobut-2-yne. X-ray Crystal Structure of $[\{(\eta^5\text{-}C_5H_5)Co\}_2\{\mu\text{-}\eta^4,\eta^4\text{-}C_4(CF_3)_4C_{10}H_{12}C_4(CF_3)_4\}]\cdot 0.5CH_2Cl_2$

Miriam B. Gomes de Lima,[†] Jacques E. Guerchais,[†] Françoise J. Le Floch-Pérennou,[†]
Paul L'Haridon,[‡] François Y. Pétillon,*[†] and Jean Talarmin[†]

Laboratoire de Chimie, Electrochimie et Photochimie Moléculaires, Associé au CNRS No. 322, Faculté des Sciences, Université de Bretagne Occidentale, 29287 Brest-Cedex, France and Laboratoire de Chimie Minérale C, Associé au CNRS No. 254, Université de Rennes I, 35042 Rennes-Cedex, France

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Reaction of hexafluorobut-2-yne with $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$, in boiling toluene for 48 h, gives novel complexes $[(\eta^5\text{-}C_5H_5)Co\{\eta^4\text{-}C_4(CF_3)_4C_{10}H_{12}\}]$ and $[\{(\eta^5\text{-}C_5H_5)Co\}_2\{\mu\text{-}\eta^4,\eta^4\text{-}C_4(CF_3)_4C_{10}H_{12}C_4(CF_3)_4\}]$ resulting from cycloaddition of a cobaltacyclopentadiene intermediate to dicyclopentadiene. Decoordinations of the new ligands formed in the coordination sphere of the cobalt atoms are carried out by controlled-potential electrolyses. The dicobalt complex has been characterized by an X-ray diffraction study. Crystals are monoclinic of space group $P2/n$ with four molecules in a unit cell of dimensions a = 27.983 (7) Å, b = 9.248 (7) Å, c = 14.996 (9) Å, and β = 103.89 (3)°. The structure has been solved by direct methods and refined by full-matrix least squares to R (R') = 0.046 (0.062) for 2419 intensities.

Introduction

The ability of transition metals to promote cyclization reactions of alkynes with other organic molecules has attracted much attention in the last few years. In many cases, particularly with the low-valent metals, metallocyclopentadienes, formed by oxidative cyclization of two coordinated alkynes, are involved as intermediates.[1] In the course of our investigation of the (η^5-cyclopentadienyl)cobalt system,[2] we have found that the reaction of $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$ with hexafluorobut-2-yne gives novel high-membered rings bonded to cobalt centres. We propose a mechanism involving a cobaltacyclopentadiene as intermediate in the reaction.

Results and Discussion

$[Co(\eta^5\text{-}C_5H_5)(CO)_2]$ (**1**) (ca. 1.5 g) reacts with hexafluorobut-2-yne (ca. 2.8 g) in boiling toluene for 48 h to give complexes **3** (ca. 17%) and **4** (ca. 31%). Careful examination of the reaction mixture from which **3** and **4** were isolated (separation by column chromatography) revealed the presence of a third minor (ca. 3.5%) product (**2**) (Scheme I). More substantial yields of **2** are obtained

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[†] Université de Bretagne Occidentale.

[‡] Université de Rennes I.

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(2) Pétillon, F. Y.; Le Quéré, J. L.; Le Floch-Pérennou, F.; Guerchais, J. E.; L'Haridon, P. *J. Organomet. Chem.* **1985**, *281*, 305.

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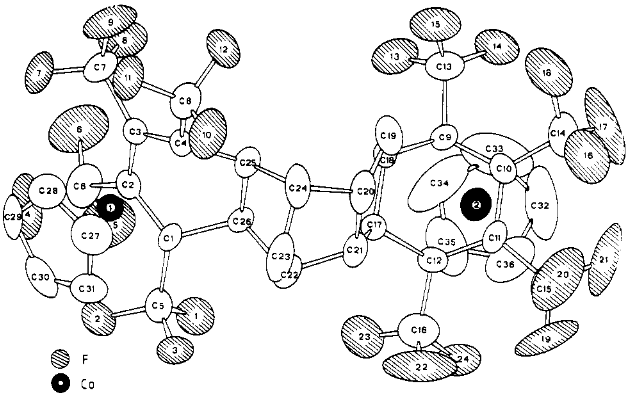
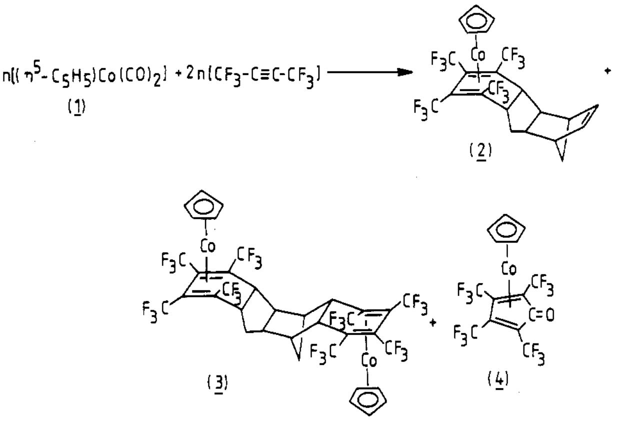


Figure 1. Molecular structure of $[\{(\eta^5\text{-}C_5H_5)Co\}_2\{\mu\text{-}\eta^4,\eta^4\text{-}C_4(CF_3)_4C_{10}H_{12}C_4(CF_3)_4\}]\cdot 0.5CH_2Cl_2$. Hydrogen atoms and Co–C bonds are omitted for clarity.

Scheme I

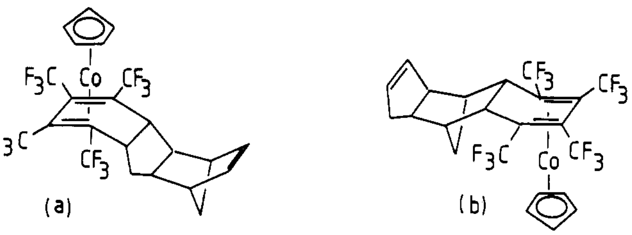


when the reactants are heated at lower temperatures (~80 °C) and for shorter reaction times. The reaction of $CF_3C{\equiv}CCF_3$ with dicarbonylcyclopentadienylcobalt has been previously reported to give only (η^5-cyclopentadienyl)[tetrakis(trifluoromethyl)cyclopentadienone]cobalt (**4**)[3] (ca. 50%) accompanied by a small amount (ca. 5%) of (η^5-cyclopentadienyl)[1,4-η-hexakis(trifluoromethyl)benzene]cobalt and traces of compound **3**, the structure of which was not determined.[4]

Our results and those reported previously[3,4] show clearly that alteration of reaction conditions such as reaction time, temperature, mole ratio of reactants, and solvent caused a significant variation in the number and nature of the products obtained.

Complex **3** was identified by an X-ray diffraction study as the dinuclear species shown in Figure 1 and Scheme I. It crystallizes in space group $P2/n$ with four complex molecules and two solvent (CH_2Cl_2) molecules per unit cell. The crystal structure of **3** consists of two $[(\eta^5\text{-}C_5H_5)Co\{C_4(CF_3)_4\}]$ groups which are bridged by a 1,3-perhydroethanopentalene unit. Positional parameters and selected bond distances and angles are listed in Tables I and II, respectively. Each cobalt atom attains an 18-electron configuration and displays distorted tetragonal-pyramidal coordination: the basal positions are occupied by the olefinic carbon atoms and the remaining site is occupied by a cyclopentadienyl ring. Each $[(\eta^5\text{-}C_5H_5)Co]$ moiety is within the bonding distance of four carbon atoms in a six-membered ring [R_1(Co(1)) and R_2(Co(2))]. The R_2 ring is cis fused to a five-membered ring (R_3) which, in turn, is cis fused to a seven-membered ring (R_4). The R_1 ring is itself cis fused to the R_4 ring. The C(1–4) and C(9–12) atoms are respectively coplanar. The "inner" carbon atoms C(2), C(3), C(10), and C(11) of the diene portions of the six-membered ring are equidistant, at about 1.95 Å, from the cobalt atoms. Significantly longer Co–C distances of ~2.03 Å are found for the "outer" carbon atoms C(1), C(4), C(9), and C(12) of the dienes. A similar trend has been observed for analogous structures.[5] The orientations of the $[(\eta^5\text{-}C_5H_5)Co]$ groups with respect to the butadiene planes P_1(C(1–4)) and P_2(C(9–12)) are such that one $[(\eta^5\text{-}C_5H_5)Co]$ group, $[(\eta^5\text{-}C_5H_5)Co(1)]$, lies above the plane P_1, while the other $[(\eta^5\text{-}C_5H_5)Co(2)]$, lies below the plane P_2.

Scheme II



Pertinent ^1H, ^{13}C, and ^{19}F NMR data are listed in the "Experimental Section". The NMR data of **3** are consistent with the structure determined by the X-ray diffraction study. The room-temperature ^{19}F NMR spectrum exhibits two multiplets at 50.1 (A) and 52.2 (B) ppm and two quartets at 54.8 (C) and 56.0 (D) ppm (relative intensities 6/12/3/3). The X-ray data show that four CF_3 groups (C(6)F_3, C(7)F_3, C(14)F_3, C(15)F_3) are quasi-equivalent; therefore the signal at 52.2 ppm is assigned to these fluorine groups. The multiplet (A) is split at low temperature which suggests its assignment to the C(5)F_3 and C(8)F_3 groups. The two remaining signals (C and D) are consequently due to the C(13)F_3 and C(16)F_3 groups which have different chemical environments.

Compound **2** is formulated as the mononuclear species shown in Scheme I on the basis of elemental and mass analyses and by comparison of its NMR data with those of **3**. Its room-temperature ^{19}F NMR shows three pseudoquintuplets (relative intensities 3/3/6). The high-field (52.3 ppm) and low-field (51.7 and 49.2 ppm) signals are assigned to the "inner" and to the "outer" CF_3 groups, respectively. This ^{19}F NMR pattern supports the configuration **2a** which is less symmetrical than the configuration **2b** (Scheme II).

We suggest that the formation of complexes **2** and **3** from $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$ can be rationalized according to Schemem III A involving two processes: (i) formation of a cobaltacyclopentadiene (**5**) as an intermediate; (ii) a concerted (4 + 2) π_s cycloaddition process taking place within the coordination sphere of the cobalt atom. The presence of an *endo*-bicyclopentane unit in **3** lends support to this pathway. Moreover, the disappearing of **2** and the concomitant growing of the yield of **3**, when the reaction time increases, suggests strongly that **2** is a precursor to **3**. The main step of this process involves a cycloaddition of the cobaltacyclopentadiene **5** to the bicyclopentadiene **6** to give **2** with subsequent elimination of $[(\eta^5\text{-}C_5H_5)Co]$. Although we failed to isolate **5**, its formation during the course of the reaction seems very likely, it has been previously postulated as intermediate in metal-catalyzed cyclomerization of alkynes.[6] The dicyclopentene and the

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(5) Cotton, F. A.; Wilkinson, G. In *Advances Inorganic Chemistry*, 3rd ed.; Wiley-Interscience: New York, 1972; p 731.

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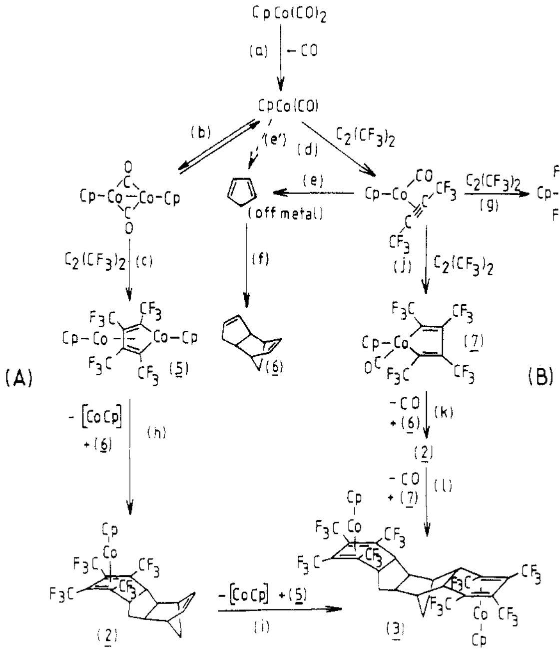
Scheme III



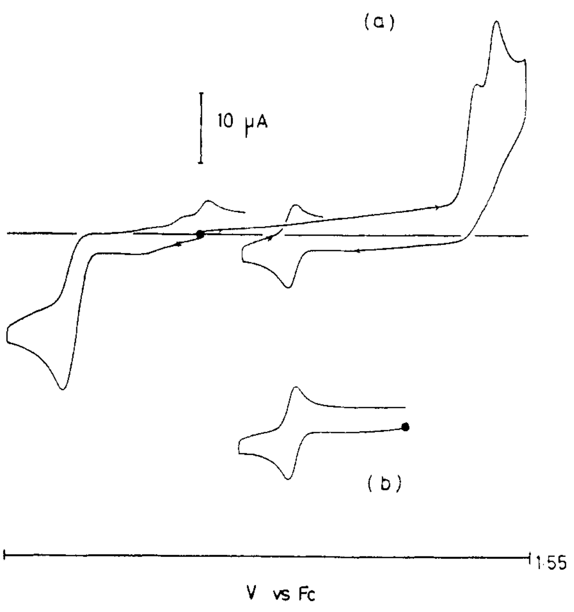
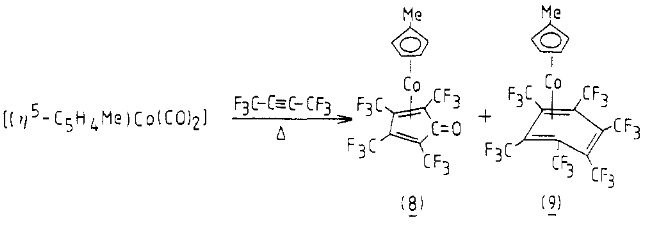


Figure 2. Cyclic voltammetry in CH_3CN–0.1 M $(Bu_4N)PF_6$: (a) complex **3**; (b) authentic sample of $[CpCo(CH_3CN)_3]^{2+}$ (scan rate = 0.2 V/s; ●, initial potential; vitreous carbon electrode).

Scheme IV



dicyclopentane groups, which are respectively present in **2** and **3**, are presumed to arise from an endo cycloaddition of two cyclopentadiene units which result from decomposition of some cyclopentadienylcobalt complexes. In an attempt to distinguish between the mechanistic possibilities, we carried out an experiment in which **4** was submitted to cycloaddition reaction conditions with dicyclopentadiene (in toluene solvent). Neither **2** nor **3** were formed, which excluded **4** as possible precursor to **2** or **3**. The a–c and a, d, and g steps have been previously postulated for the formation of **5** and **4**, respectively.[7]

An alternative pathway involving as intermediate a mononuclear cobaltacyclopentadiene complex, such as $[(\eta^5\text{-}C_5H_5)(CO)Co(C_4F_6)]$ (**7**), similar to those well investigated by Wakatsuki,[8] cannot be a priori ruled out (Scheme IIIB). Such a pathway is characterized by direct reaction of dicyclopentadiene with the metallole to give complex **2** which reacts with one further molecule of **7** to yield **3**. It is supported by the observation that $[Co(\eta^5\text{-}C_5H_4Me)(CO)_2]$ reacted with hexafluorobut-2-yne, under the same conditions as those under which $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$ reacted, and gave only (η^5-methylcyclopentadienyl)[tetrakis(trifluoromethyl)cyclopentadienone]cobalt (**8**) (ca. 55%) and (η^5-methylcyclopentadienyl)[1,4-η-hexakis(trifluoromethyl)benzene]cobalt (**9**) (ca. 17%) (Scheme IV). Indeed, the latter product is considered as resulting from further addition of alkyne to the seven-membered metallocycle.[8a] The lack of analogous complexes to **2** and **3** in the reaction (Scheme IV) could be due to the fact that the release of the (MeC_5H_4) group from $[Co(\eta^5\text{-}MeC_5H_4)(CO)]$ or $[Co(\eta^5\text{-}MeC_5H_4)(CO)(C_4F_6)]$ becomes very difficult owing to the presence of electron donor group on the cyclopentadienyl ring. If the (trifluoromethyl)cobalt complex **7** has not been characterized, the iridium analogue is known, but it appears to be inert to further reaction;[9] such a trend reduces the ability of the mononuclear cobaltacyclopentadiene species to act as intermediate in a mechanism such as B. Therefore it appears that at least two distinct mechanisms might be envisaged to rationalize the production of complexes **2** and **3** from the reaction of hexafluorobut-2-yne with $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$.

Related studies on reactions involving the condensation of cyclopentadiene and cobalt atoms with hexafluorobut-2-yne and leading to the production of multimetal complexes have been reported previously;[10] however, in these examples there are no more than two alkynes added to one cyclopentadiene ring. There are also some analogies between the reaction described here and the addition of hexafluorobut-2-yne to nickelocene,[11] both giving rise to cycloaddition reactions.

Attempts to decoordinate the novel cyclic ligands formed in **2** and **3** by heat or by a chemical way (Ce^{4+}, H^+) failed. Therefore, we investigated the possibility to liberate the organic moieties by electrochemical means.

Cyclic voltammetry (CV) of **2** and **3** in CH_3CN–0.1 M $[Bu_4N][PF_6]$ demonstrates that the oxidation of **3** occurs in two successive irreversible steps ($E_p(ox._1)$ = 1.15 V/Fc, $E_{p/2}$ = 1.08 V/Fc; $E_p(ox._2)$ = 1.31 V/Fc, $E_{p/2}$ = 1.26 V/Fc) (Figure 2), whereas **2** undergoes a single irreversible oxidation (E_p(ox.) = 1.28 V/Fc, $E_{p/2}$ = 1.19 V/Fc).[12] On the reverse and subsequent anodic scans of the CV's of both complexes, a reversible couple ($E_{1/2}$ = –0.18 V/Fc) and an irreversible reduction peak (E_p(red.) = –1.38 V/Fc, $E_{p/2}$ = –1.30 V/Fc) are observed. As shown by a comparison

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[7] Lee, W. S.; Brintzinger, H. H. *J. Organomet. Chem.* **1977**, *127*, 93.

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[11] Davidson, J. L.; Herak, R.; Manojlović-Muir, Lj.; Muir, K. W.; Sharp, D. W. A. *J. Chem. Soc., Chem. Commun.* **1973**, 865.

[12] The complexes are irreversibly reduced at E_p(red.) = – 1.81 V/Fc and $E_{p/2}$ = – 1.75 V/Fc for **2** and E_p(red.) = – 1.84 V/Fc and $E_{p/2}$ = – 1.74 V/Fc for **3**.

Table I. Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
Co(1)	0.34950 (4)	0.4078 (1)	0.10763 (7)	2.62 (2)	C(17)	0.5566 (3)	0.1756 (9)	0.2511 (5)	2.5 (2)
Co(2)	0.65202 (4)	0.1261 (1)	0.38400 (7)	3.12 (3)	C(18)	0.5424 (3)	0.0859 (8)	0.3263 (5)	2.8 (2)
Cl	0.5205 (2)	0.4545 (5)	0.4247 (3)	13.5 (2)	C(19)	0.5065 (3)	−0.0361 (9)	0.2796 (7)	4.5 (2)
C(37)	0.491 (1)	0.427 (2)	0.506 (2)	8.4 (8)	C(20)	0.4888 (3)	0.0048 (9)	0.1779 (6)	3.9 (2)
F(1)	0.4940 (2)	0.5788 (6)	0.1512 (4)	5.5 (1)	C(21)	0.5209 (3)	0.1312 (9)	0.1582 (5)	3.0 (2)
F(2)	0.4243 (2)	0.6832 (6)	0.0957 (4)	5.6 (1)	C(22)	0.4821 (3)	0.2416 (9)	0.1104 (5)	3.2 (2)
F(3)	0.4478 (2)	0.5108 (6)	0.0211 (3)	5.0 (1)	C(23)	0.4421 (3)	0.142 (1)	0.0572 (6)	4.7 (2)
F(4)	0.3637 (3)	0.7188 (6)	0.2177 (5)	9.1 (2)	C(24)	0.4358 (3)	0.0570 (9)	0.1404 (6)	3.8 (2)
F(5)	0.4399 (2)	0.6891 (6)	0.2702 (4)	7.8 (2)	C(25)	0.4238 (3)	0.1804 (8)	0.2021 (5)	2.5 (2)
F(6)	0.3913 (3)	0.6243 (7)	0.3476 (4)	8.9 (2)	C(26)	0.4552 (3)	0.3050 (8)	0.1807 (5)	2.1 (2)
F(7)	0.3045 (2)	0.4871 (7)	0.2972 (4)	6.7 (1)	C(27)	0.3036 (4)	0.334 (1)	−0.0114 (6)	5.1 (3)
F(8)	0.3645 (2)	0.3888 (7)	0.3930 (3)	6.9 (2)	C(28)	0.2762 (3)	0.392 (1)	0.0447 (6)	5.3 (3)
F(9)	0.3079 (2)	0.2621 (7)	0.3165 (4)	7.6 (2)	C(29)	0.2871 (3)	0.537 (1)	0.0573 (6)	5.8 (3)
F(10)	0.3327 (2)	0.0334 (6)	0.0992 (4)	5.5 (1)	C(30)	0.3244 (4)	0.566 (1)	0.0114 (7)	5.6 (3)
F(11)	0.2865 (2)	0.1448 (6)	0.1688 (4)	5.4 (1)	C(31)	0.3331 (3)	0.439 (1)	−0.0330 (6)	4.8 (3)
F(12)	0.3457 (2)	0.0120 (5)	0.2456 (4)	5.2 (1)	C(32)	0.7228 (4)	0.122 (1)	0.468 (1)	9.4 (4)
F(13)	0.5683 (2)	0.1181 (7)	0.5239 (3)	6.6 (2)	C(33)	0.6887 (5)	0.160 (2)	0.5170 (7)	10.2 (4)
F(14)	0.6191 (2)	−0.0611 (7)	0.5458 (3)	7.1 (2)	C(34)	0.6660 (4)	0.284 (2)	0.4814 (8)	9.8 (4)
F(15)	0.5422 (2)	−0.0939 (7)	0.4826 (4)	7.2 (2)	C(35)	0.6851 (4)	0.323 (1)	0.4123 (9)	7.0 (3)
F(16)	0.6307 (3)	−0.3052 (6)	0.3128 (5)	9.0 (2)	C(36)	0.7197 (4)	0.224 (1)	0.4028 (7)	6.4 (3)
F(17)	0.6766 (3)	−0.2285 (8)	0.4381 (6)	12.5 (3)	H(17)	0.5534	0.2766	0.2598	
F(18)	0.6040 (3)	−0.2715 (7)	0.4265 (5)	9.6 (2)	H(18)	0.5259	0.1426	0.3629	
F(19)	0.6868 (3)	0.0152 (9)	0.1754 (5)	14.7 (2)	H(191)	0.4793	−0.0415	0.3063	
F(20)	0.6406 (3)	−0.1657 (8)	0.1654 (4)	10.0 (2)	H(192)	0.5232	−0.1256	0.2852	
F(21)	0.7014 (2)	−0.1407 (9)	0.2744 (6)	11.2 (2)	H(20)	0.4909	−0.0841	0.1457	
F(22)	0.6137 (3)	0.215 (1)	0.1026 (4)	10.9 (2)	H(21)	0.5426	0.1146	0.1197	
F(23)	0.6097 (3)	0.3835 (7)	0.1950 (5)	11.2 (2)	H(22)	0.4959	0.3135	0.0795	
F(24)	0.6762 (2)	0.2757 (7)	0.2035 (4)	6.5 (2)	H(231)	0.4529	0.0834	0.0139	
C(1)	0.4234 (3)	0.4415 (9)	0.1550 (5)	2.5 (2)	H(232)	0.4131	0.1921	0.0276	
C(2)	0.3944 (3)	0.4804 (8)	0.2193 (5)	2.5 (2)	H(24)	0.4126	−0.0198	0.1343	
C(3)	0.3648 (3)	0.3612 (8)	0.2378 (5)	2.2 (2)	H(25)	0.4304	0.1472	0.2638	
C(4)	0.3700 (3)	0.2309 (8)	0.1872 (5)	2.1 (2)	H(26)	0.4799	0.3407	0.2307	
C(5)	0.4468 (3)	0.554 (1)	0.1055 (6)	4.1 (2)	H(27)	0.3022	0.2347	−0.0304	
C(6)	0.3960 (4)	0.628 (1)	0.2622 (7)	5.0 (3)	H(28)	0.2527	0.3410	0.0697	
C(7)	0.3343 (3)	0.376 (1)	0.3096 (6)	3.9 (2)	H(29)	0.2716	0.6044	0.0896	
C(8)	0.3344 (3)	0.107 (1)	0.1768 (6)	4.0 (2)	H(30)	0.3405	0.6560	0.0121	
C(9)	0.5882 (3)	0.0287 (9)	0.3915 (5)	2.8 (2)	H(31)	0.3557	0.4284	−0.0704	
C(10)	0.6201 (3)	−0.0616 (9)	0.3510 (5)	3.0 (2)	H(32)	0.7439	0.0418	0.4813	
C(11)	0.6321 (3)	0.0083 (9)	0.2735 (5)	2.7 (2)	H(33)	0.6813	0.1083	0.5663	
C(12)	0.6111 (3)	0.1507 (9)	0.2530 (5)	2.9 (2)	H(34)	0.6407	0.3362	0.5017	
C(13)	0.5807 (3)	−0.005 (1)	0.4874 (6)	4.7 (2)	H(35)	0.6767	0.4080	0.3747	
C(14)	0.6360 (4)	−0.215 (1)	0.3806 (7)	5.4 (3)	H(36)	0.7385	0.2250	0.3576	
C(15)	0.6643 (4)	−0.066 (1)	0.2170 (7)	6.3 (3)	H(371)	0.5076	0.3477	0.5428	
C(16)	0.6281 (4)	0.256 (1)	0.1895 (7)	5.5 (3)	H(372)	0.4585	0.3868	0.4736	

[a] Atoms with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as ($^4/_3$) [$a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)$].

with the CV of an authentic sample of the tris(acetonitrile) complex[13] [(η^5-C$_5$H$_5$)Co(CH$_3$CN)$_3$]$^{2+}$ (**10**), the reversible system and the irreversible reduction peak arise from the formation of **10** on oxidation of **2** and **3**.

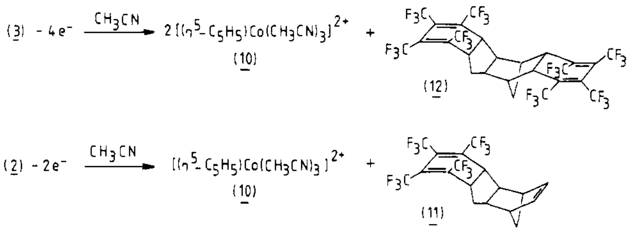
Controlled-potential electrolyses (CPE) performed at the potential of the second oxidation step of **3** proceed smoothly to a four-electron exchange (linear i_{cell} vs. Q plots; i_{cell} = cell current; Q = charge passed in coulombs). Coulometric experiments demonstrate that the number of electrons transferred in the process is always greater than 4 (4.3 on average). Cyclic voltammetry and UV–visible spectroscopy confirm that **10** has formed. Calibration of the amount of **10** using an authentic sample of the complex is in agreement with the stoichiometry in eq 1 (see Scheme V).

$$\mathbf{3} - 4\mathrm{e} \rightarrow 2\,\mathbf{10} + \mathbf{12} \qquad (1)$$

Although it is beyond the scope of this work to precisely investigate the oxidation mechanism of **3**, it appeared that the decoordination of **12** occurred in a stepwise fashion. Indeed, the CPE of **3** at a potential in between the two oxidation waves of the complex led to the formation of **10** along with another metal fragment. CV of the anolyte shows that the first oxidation wave is almost suppressed.[14] NMR analysis[15] of the solid isolated from the anolyte after separation from **10** is consistent with the decoordination of a single CpCo group, e.g., **13** (eq 2).

$$\mathbf{3} - 2\mathrm{e} \rightarrow \mathbf{10} + \mathbf{13} \qquad (2)$$

Scheme V



In a similar way, the organic molecule **11** is recovered from the electrolysis of **2** at the potential of its oxidation peak (n_{app} ca. 2 F/mol of **2**) (Scheme V). The structures

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(13) Koelle, U. *J. Organomet. Chem.* **1980**, *184*, 379.

(14) A small amount of starting material is also present since the electrolysis was interrupted after 1.9–2.0 F/mol of **3** have been transferred.

(15) **13**: ^{19}F NMR (CDCl$_3$/CCl$_3$F) 62.8 (m, 3 F), 59.9 (q, $J_{\text{F-F}}$ = 12 Hz, 3 F), 56.1 (m, 6 F), 52.1 (m, 6 F), 50.8 (m, 3 F), 50.1 ppm (m, 3 F).

Table II. Selected Distances (Å), Angles (deg), and Dihedral Angles (deg) with Estimated Standard Deviations in Parentheses

Bond Distances

Co(1)–C(1)	2.043 (7)	C(25)–C(24)	1.556 (10)	C(11)–C(12)	1.445 (10)
Co(1)–C(2)	1.956 (7)	C(24)–C(23)	1.519 (12)	C(12)–C(17)	1.536 (10)
Co(1)–C(3)	1.943 (7)	C(23)–C(22)	1.521 (11)	C(17)–C(21)	1.563 (9)
Co(1)–C(4)	2.025 (7)	C(22)–C(26)	1.551 (9)	C(17)–C(18)	1.527 (9)
C(1)–C(2)	1.447 (10)	Co(2)–C(9)	2.028 (7)	C(18)–C(9)	1.508 (10)
C(1)–C(26)	1.538 (9)	Co(2)–C(10)	1.961 (8)	C(18)–C(19)	1.559 (11)
C(2)–C(3)	1.446 (9)	Co(2)–C(11)	1.949 (7)	C(19)–C(20)	1.534 (12)
C(3)–C(4)	1.450 (9)	Co(2)–C(12)	2.035 (7)	C(20)–C(21)	1.545 (11)
C(4)–C(25)	1.541 (9)	C(9)–C(10)	1.459 (10)	C(20)–C(24)	1.531 (11)
C(25)–C(26)	1.529 (9)	C(10)–C(11)	1.438 (10)	C(21)–C(22)	1.536 (10)

Bond Angles

C(1)–Co(1)–C(3)	74.01 (0.29)	C(20)–C(24)–C(25)	110.01 (0.63)	C(11)–Co(2)–C(12)	42.40 (0.29)
C(1)–Co(1)–C(4)	78.39 (0.28)	C(23)–C(24)–C(25)	101.17 (0.61)	C(11)–Co(2)–C(17)	59.12 (0.25)
C(2)–Co(1)–C(3)	43.52 (0.28)	C(4)–C(25)–C(24)	118.65 (0.57)	C(12)–Co(2)–C(17)	28.95 (0.24)
C(2)–Co(1)–C(4)	74.93 (0.28)	C(4)–C(25)–C(26)	109.39 (0.56)	C(9)–C(10)–C(11)	111.38 (0.64)
C(3)–Co(1)–C(4)	42.82 (0.26)	C(24)–C(25)–C(26)	102.17 (0.59)	C(10)–C(11)–C(12)	114.80 (0.63)
C(2)–C(1)–C(26)	114.78 (0.60)	C(1)–C(26)–C(22)	119.06 (0.58)	C(11)–C(12)–C(17)	119.53 (0.61)
C(1)–C(2)–C(3)	112.18 (0.61)	C(1)–C(26)–C(25)	110.14 (0.54)	C(9)–C(18)–C(17)	109.80 (0.59)
C(2)–C(3)–C(4)	113.52 (0.59)	C(22)–C(26)–C(25)	104.74 (0.57)	C(9)–C(18)–C(19)	113.08 (0.60)
C(3)–C(4)–C(25)	113.14 (0.56)	C(9)–Co(2)–C(10)	42.87 (0.29)	C(17)–C(18)–C(19)	108.40 (0.62)
C(20)–C(21)–C(22)	102.35 (0.59)	C(9)–Co(2)–C(11)	73.94 (0.29)	C(18)–C(19)–C(20)	106.75 (0.62)
C(21)–C(22)–C(23)	100.97 (0.62)	C(9)–Co(2)–C(12)	78.69 (0.30)	C(19)–C(20)–C(21)	108.17 (0.63)
C(21)–C(22)–C(26)	109.80 (0.58)	C(9)–Co(2)–C(17)	56.05 (0.25)	C(19)–C(20)–C(24)	119.78 (0.75)
C(23)–C(22)–C(26)	99.75 (0.58)	C(10)–Co(2)–C(11)	43.16 (0.30)	C(21)–C(20)–C(24)	104.29 (0.65)
C(22)–C(23)–C(24)	95.61 (0.60)	C(10)–Co(2)–C(12)	74.84 (0.31)	C(17)–C(21)–C(20)	107.77 (0.63)
C(20)–C(24)–C(23)	99.92 (0.70)	C(10)–Co(2)–C(17)	71.61 (0.25)	C(17)–C(21)–C(22)	118.03 (0.59)

Least-Squares Planes[a]

plane no.	*A*	*B*	*C*	*D*	atom	*X*	*Y*	*Z*	dist, Å
1	−0.5823	0.3130	−0.7503	−7.0044	C(1)[b]	11.3063	4.0915	2.2703	−0.002
					C(2)[b]	10.2655	4.4436	3.2178	0.003
					C(3)[b]	9.3584	3.3316	3.4670	−0.003
					C(4)[b]	9.6607	2.1371	2.7270	0.002
					Co(1)[c]	9.3935	3.7714	1.5660	1.540
2	−0.6828	−0.4030	−0.6094	−13.8512	C(9)[b]	15.0634	0.2478	5.6907	−0.002
					C(10)[b]	16.0871	−0.5744	5.0784	0.004
					C(11)[b]	16.7140	0.0742	3.9588	−0.004
					C(12)[b]	16.1921	1.3812	3.6702	0.002
Dihedral Angle P1–P2 – 43.2°									
					Co(2)[c]	16.8618	1.1666	5.5917	−1.540

[a] The equation of the plane is of the form $AX + BY + CZ - D = 0$, where A, B, C, and D are constants and X, Y, and Z are orthogonalized coordinates. [b] Atoms in the plane. [c] Other atom.

of **11** and **12** are based on analytical and spectroscopic data.

Experimental Section

Preparations were carried out under nitrogen by Schlenk tube techniques. Solvents were purified by standard methods and degassed before use. $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$, $[Co(\eta^5\text{-}C_5H_4Me)(CO)_2]$, and hexafluorobut-2-yne were commercial products. Tetrabutylammonium hexafluorophosphate, used as supporting electrolyte in the electrochemical experiments, was prepared from tetrabutylammonium hydroxide and $H(PF_6)$. The salt was twice recrystallized from a water–ethanol mixture and dried at 100 °C under vacuum for 48 h. The supporting electrolyte was then stored under nitrogen.

Measurements. Infrared spectra in Nujol mull were obtained with a Pye-Unicam SP 2000 spectrophotometer. Mass spectra were recorded on a Varian Mat 311 in the "Mesures Physiques" Laboratory, University of Rennes, and NMR spectra in $CDCl_3$ or $(CD_3)_2CO$ were measured on a JEOL FX 100 spectrometer (^1H, ^{13}C, ^{19}F) and were referenced to Me_4Si (^1H, ^{13}C) or CCl_3F (^{19}F).

The electrochemical experiments were performed by using a Tacussel potentiostat ("Générateur coulométrique type GCU") and a PAR 175 waveform generator. The charge passed during the electrolyses was monitored by using a Tacussel digital integrator (Tacussel IG5 N). The current potential curves (or current–time responses for CPE) were recorded by using a Sefram TGM 164.

Chemical analyses were performed by the "Centre de Microanalyse du CNRS de Lyon".

X-ray Crystallography. Yellow crystals of **3** were obtained by recrystallization from a CH_2Cl_2–hexane mixture and examined by X-ray crystallography. $C_{36.5}H_{23}ClCo_2F_{24}$: M_r 1070.9; monoclinic; $a = 27.983$ (7) Å, $b = 9.248$ (7) Å, $c = 14.996$ (9) Å; $\beta = 103.89$ (3)°; $U = 3767$ Å^3; $Z = 4$; $D_{calcd} = 1.877$ g cm^{-3}; $F(000) = 2116$; space group P2/*n*; Mo Kα X-radiation (graphite monochromator) $\lambda = 0.7107$ Å; $\mu = 10.95$ cm^{-1}. Intensities (2763 with $I > 1\sigma(I)$) were measured on a Enraf-Nonius CAD 4F diffractometer at 293 K in the range $2 < 2\theta < 44°$ and corrected for Lorentz–polarization factors. The structure was solved by using direct methods (Multan program) and refined by full-matrix least squares and difference Fourier syntheses to R (R') = 0.046 (0.062) for 2419 intensities greater than $3\sigma(I)$. Hydrogen atoms were included.

Electrochemistry. Cyclic voltammetry (CV). All the experiments were conducted in deaerated MeCN–0.1 M $[Bu_4N][PF_6]$ solutions under nitrogen, at room temperature, in a three-electrode cell. The working electrode was a vitreous carbon disk (Metrohm rotating electrode), and the secondary electrode was made of a carbon rod. The reference electrode was either the half-cell Ag wire/Ag $[PF_6]$–MeCN–0.1 M $[Bu_4N][PF_6]$ or a silver wire pseudoreference. Ferrocene was used as an internal standard at the end of the CV experiments. All potentials are quoted against the ferrocene–ferrocenium ion couple.

Controlled-Potential Electrolyses (CPE). CPE's were carried out in a three-compartment, three-electrode cell. The working electrode was either a carbon rod or a PT gauze. The secondary electrode was separated from the working-electrode compartment by two glass frits (porosity 2).

Syntheses of Complexes $[(\eta^5\text{-}C_5H_5)Co\{\eta^4\text{-}C_4(CF_3)_4C_{10}H_{12}\}]$

(2) and $[\{(\eta^5\text{-}C_5H_5)Co\}_2\{\mu\text{-}\eta^4,\eta^4\text{-}C_4(CF_3)_4C_{10}H_{12}C_4(CF_3)_4\}]\cdot0.5CH_2Cl_2$ (3). In a typical procedure, ca. 1.5 g of $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$ (8×10^{-3} mol) was placed in a thick glass reaction vessel fitted with a Teflon stopcock. The vessel was evacuated and cooled to −178 °C, and freshly distilled solvent (toluene or cyclohexane) (~60 cm^3) and the alkyne (2.7 g, 16×10^{-3} mol) were condensed into it. The mixture was allowed to warm slowly to room temperature and then stirred at 100 °C in a thermostated oil bath for 48 h. The solvent was removed under vacuum, and the residue was extracted with CH_2Cl_2 and chromatographed on Florisil column. Elution with hexane/CH_2Cl_2 (1/1) gave a yellow band, from which a mixture of crystals **2** and **3** was isolated. Further elution with CH_2Cl_2–THF (100/5) gave the red-orange complex **4** in about 31% yield (ca. 1.2 g).

Complex **3** (ca. 0.72 g, 17%) was separated from **2** (ca. 0.16 g, 3.5%) by crystallization in cold pentane or by sublimation under vacuum (10^{-2} mb)(**2**, 120 °C; **3**, 200 °C). **2** and **3** are yellow compounds which are soluble in common organic solvents.

2. Anal. Calcd for $C_{23}H_{17}CoF_{12}$: C, 47.6; H, 2.9; Co, 10.2. Found: C, 47.8; H, 2.9; C, 10.2. The mass spectrum showed ions corresponding to $[M]^+$, *m/e* 580, $[M - CF_3]^+$, *m/e* 511, $[M - (C_5H_5CoF)]^+$, *m/e* 437, $[(C_5H_5)Co]^+$, *m/e* 124. NMR data ($CDCl_3$): ^1H, 5.55 (m, 2 H), 5.30 (s, C_5H_5), 3.10–2.0 and 1.42–1.25 ppm (m, 10 H); ^{13}C 133.2 (s, =CH), 131.3 (s, =CH), 87.2 (s, C_5H_5), 52.8, 45.5, 43.4, 42.6, 42.5, 42.3, 35.4 and 31.6 ppm ($-CH_n$, $n = 1$ or 2); ^{19}F, 52.3 (m, 6 F), 51.7 (m, 3 F), 49.2 ppm (m, 3 F).

3. Anal. Calcd for $C_{36.5}H_{23}ClCo_2F_{24}$: C, 40.9; H, 2.1; Co, 11.0; F, 42.9. Found: C, 40.8; H, 2.0; Co, 11.5; F, 42.8. The mass spectrum showed ions corresponding to $[M - 0.5CH_2Cl_2]^+$, *m/e* 1028, $[M - (0.5CH_2Cl_2) - \{(C_5H_5)CoC_4(CF_3)_4\}]^+$, *m/e* 580, $[(C_5H_5)Co]^+$, *m/e* 124. NMR data ($CDCl_3$): ^1H, 5.23 (s, C_5H_5), 5.21 (s, C_5H_5), 2.8–1.10 (m, 12 H); ^{13}C, 127.0 (q, CF_3, $^1J_{C-F} = 275$ Hz), 124.0 (q, CF_3, $^1J_{C-F} = 278$ Hz), 87.4 (s, C_5H_5), 86.6 (s, C_5H_5), 64.0 (q, $(CF_3)C$, $^2J_{C-F} = 32.7$ Hz), 63.5 (q, $(CF_3)C$, $^2J_{C-F} = 32.7$ Hz), 62.0 (q, $(CF_3)C$, $^2J_{C-F} = 32.7$ Hz), 53.4 (s), 50.5 (s), 48.5 (s), 48.2 (s), 44.4 (s), 43.7 (s), 43.1 (s), 35.5 (s), 35.0 ppm (s) ($-CH_n$, $n = 1$ or 2); ^{19}F, 56.1 (q, 3 F, $J_{F-F} = 13.4$ Hz), 54.8 (q, 3 F, $J_{F-F} = 12.2$ Hz), 52.2 (m, 12 F), 50.1 ppm (m, 6 F).

Syntheses of Complexes $[(\eta^5\text{-}C_5H_4Me)Co\{(C_4F_6)_2CO\}]$ (8) and $[(\eta^5\text{-}C_5H_4Me)Co(C_4F_6)_3]$ (9). The reaction was carried out as described above for **2** and **3** by using toluene (~110 °C). The solvent was removed in vacuo, and the residue was extracted with CH_2Cl_2 and chromatographed on Florisil column. Elution with hexane gave a red-orange band from which the product **9** was isolated in about 17% yield. Further elution with hexane/CH_2Cl_2 (1/1) gave the red-orange compound **8** (yields ca. 55%).

8. Anal. Calcd for $C_{15}H_7CoF_{12}O$: C, 36.8; H, 1.4; Co, 12.0. Found: C, 36.8; H, 1.4; Co, 11.3. Selected IR data (Nujol): $\nu(C{=}O)$ 1670 (s) cm^{-1}; $\nu(CF)$ 1220 (s), 1180 (s), 1150 (m), 1135 (sh) cm^{-1}. NMR data ($CDCl_3$): ^1H, 5.37 (m, C_5H_4Me), 2.11 ppm (s, CH_3); ^{19}F, 55.8 (m, 6 F), 51.8 ppm (m, 6 F).

9. Anal. Calcd for $C_{18}H_7CoF_{18}$: C, 34.7; H, 1.1; Co, 9.5. Found: C, 34.7; H, 1.1; Co, 9.2. The mass spectrum showed ions corresponding to $[M]^+$, *m/e* 624, $[M - F]^+$, *m/e* 605, $[C_6(CF_3)_6]^+$, *m/e* 486, $[(C_6(CF_3)_5(CF_2)]^+$, *m/e* 467, $[C_6(CF_3)_5(CF)]^+$, *m/e* 448, $[C_6(CF_3)_5C]^+$, *m/e* 429, $[C_6(CF_3)_5]^+$, *m/e* 417, $[Co(C_5H_4Me)]^+$, *m/e* 138. Selected IR data (Nujol): $\nu(C{=}C)$ 1621 (w) cm^{-1}; $\nu(CF)$ 1322 (w), 1295 (w), 1268 (m), 1220 (s), 1198 (s), 1172 (m), 1155 (m), 1138 (sh) cm^{-1}. NMR data ($CDCl_3$): ^1H, 5.92 (t, C_5H_4Me,H(2,5), $J_{H-H} = 1.7$ Hz), 4.82 (m, C_5H_4Me, H(3,4), 2.00 ppm (s, CH_3); ^{13}C, 125.2 (q, CF_3, $J_{C-F} = 276$ Hz), 123.6 (q, CF_3, $J_{C-F} = 281$ Hz), 119.2 (q, CF_3, $J_{C-F} = 279$ Hz), 107.5 (s, $C{-}CH_3$), 88.9 (s, C_4H_4CMe), 88.0 (s, C_4H_4CMe), 12.2 ppm (s, CH_3); ^{19}F, 57.4 (m, 6 F), 51.7 (m, 6 F), 50.6 ppm (m, 6 F).

Electrochemical Decoordination of the Organic Ligands. Syntheses of $C_{18}H_{12}F_{12}$ (11) and $C_{26}H_{12}F_{24}$ (12). Complex **2** or **3** (90–100 mg) was dissolved in 30 mL of a MeCN electrolyte and electrolyzed under N_2 until the cell current decayed to the background level (except for the oxidation of **3** at the potential of the first peak, see ref 15). The anolyte was syringed out of the cell and transferred to a Schlenk flask. The solvent (MeCN) was removed under vacuum, and the free ligand was separated from the supporting electrolyte $[CpCo(CH_3CN)_3][PF_6]_2$ mixture by successive additions of 30 cm^3 of degassed pentane. **11** and **12** are white solids.

11. The mass spectrum showed ions corresponding to $[M]^+$, *m/e* 456, $[M - F]^+$, *m/e* 437, $[C_6H_2(CF_3)_4]^+$, *m/e* 350, $[C_6H_6(CF_3)_3(CF_2)]^+$, *m/e* 331, $[C_8H_{10}]^+$, *m/e* 106. NMR data ($CDCl_3$): ^1H, 5.85 (m, 1 H), 5.73 (m, 1 H), 2.98 (m), 2.76 (m), 2.60 (m), 2.33 (m), 1.65 (s), 1.28 (s), 0.90 ppm (m); ^{19}F, 61.1 (q, 3 F, $J_{F-F} = 13.4$ Hz), 60.0 (q, 3 F, $J_{F-F} = 12.2$ Hz), 56.3 ppm (m, 6 F).

12. Anal. Calcd for $C_{26}H_{12}F_{24}$: C, 40.0; H, 1.5; F, 58.4. Found: C, 40.0; H, 1.5; F, 57.0. The mass spectrum showed ions corresponding to $[M - F]^+$, *m/e* 761, $[M - \{C_6H_2(CF_3)_4\}]^+$, *m/e* 430, $[C_6H_2(CF_3)_4]^+$, *m/e* 350, $[(C_5H_7)(CH_2)]^+$, *m/e* 81. NMR data: ^1H ($(CD_3)_2CO$), 3.80 (m), 3.66 (m), 3.56 (m), 3.23 (m), 3.13 (m), 2.86 (s), 2.73 (m), 2.40 ppm (m); ^{19}F ($CDCl_3$), 62.5 (m, 3 F), 61.5 (q, 3 F, $J_{F-F} = 14.6$ Hz), 60.0 (m, 6 F), 56.1 ppm (m, 12 F).

Attempted Reaction of Chemical Decoordination of the Organic Ligands. Attempts to release the free ligands from the cobalt on treatment with ceric ammonium nitrate, according a method previously described,[16] failed. No more reaction was observed when complexes **2** and **3** are treated with ceric salt in the presence of phosphine, trifluoroacetic acid, or carbon monoxide.

Acknowledgment. We are grateful to Prof. D. W. A. Sharp (University of Glasgow) for helpful discussion and to Mr. H. Le Cornec for his participation to part of this work. M.B.G.-L. is indebted to CNPq (Brasil) for a fellowship. We thank the CNRS for financial support.

Registry No. 1, 12078-25-0; **2a**, 109391-07-3; **3**, 109432-22-6; $3\cdot{}^1/_2CH_2Cl_2$, 109432-23-7; **4**, 12212-31-6; **8**, 109391-08-4; **9**, 109391-09-5; **11**, 109391-11-9; **12**, 109391-12-0; $[Co(\eta^5\text{-}C_5H_4Me)(CO)_2]$, 75297-02-8; $[CpCo(CH_3CN)_3][PF_6]_2$, 109391-10-8; $CF_3C{\equiv}CCF_3$, 692-50-2.

Supplementary Material Available: Tables of additional interatomic distances and angles and thermal parameters and a perspective view of the structure of **3** (6 pages); a listing of structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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(16) Liebeskind, L. S.; Jeweel, C. F., Jr. *J. Organomet. Chem.* **1985**, *285*, 305.