Redox disproportionation and radical coupling products of formyl(pentamethyl)cobaltocene

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Abstract

1-Formyl-1′,2′,3′,4′,5′-pentamethylcobaltocene, prepared in situ from formylcyclopentadienide, pentamethylcyclopentadienide, and Co(II) chloride, is unstable and reacts further by redox disproportionation with subsequent radical coupling, yielding decamethyl(dihydro)fulvalene, pentamethylcyclopentadienyl(pentamethylcobaltocenium)–methanol tetraphenylborate and 1,2-bis(pentamethylcobaltocenium)ethan-1,2-diol bis(tetraphenylborate). Spectroscopic and X-ray structural properties are reported. © 1998 Elsevier Science S.A. All rights reserved.

1. Introduction

In general, ferrocene compounds and the isoelectronic cobaltocenium salts are the most stable metallocenes. In comparison to the well developed ferrocene chemistry there are only very few substituted cobaltocenium compounds known because of the lack of synthetic transformations compatible with the high reactivity of the parent cobaltocene and the inertness of cobaltocenium salts towards substitution reactions. Therefore a few substituted cobaltocenes have been prepared from preformed substituted cyclopentadienides and cobalt(II) halides, in analogy to the synthesis of the parent cobaltocene [1]. In this contribution we report on our attempts to prepare 1-formyl-1′,2′,3′,4′,5′-pentamethylcobaltocene or 1-formyl-1′,2′,3′,4′,5′-pentamethylcobaltocenium salts, respectively, whose aldehyde functionality should allow, inter alia, standard Wittig olefinations directed towards the synthesis of soluble and conjugated spacered bis(cobaltocenium) salts, in continuation of our recently published results on analogous pentamethylferrocene-based molecular wires [2].

2. Results and discussion

Di(pentamethylcyclopentadienyl)dicobalt(II)dichloride [Cp*Co(II)Cl]$_2$ has been reported as a convenient reagent for the formation of unsymmetrical cobaltocenes, e.g. Cp*CoCp [3]. Accordingly, the synthesis of functionally substituted analogues Cp*CoCp–R (R = functional substituent) starting from substituted cyclopentadienes Cp–R seems possible. The use of such functionally substituted Cp–R reagents in metallocene chemistry has been developed by Rausch as early as 1980 [4,5] and has been applied in recent years by us and others for the synthesis of ferrocene compounds [6]. Formylcyclopentadiene has been chosen as the substituted Cp–R in this work because of its ready conversion to further useful derivatives, as has been shown for the corresponding pentamethylferrocenyl aldehyde [6].

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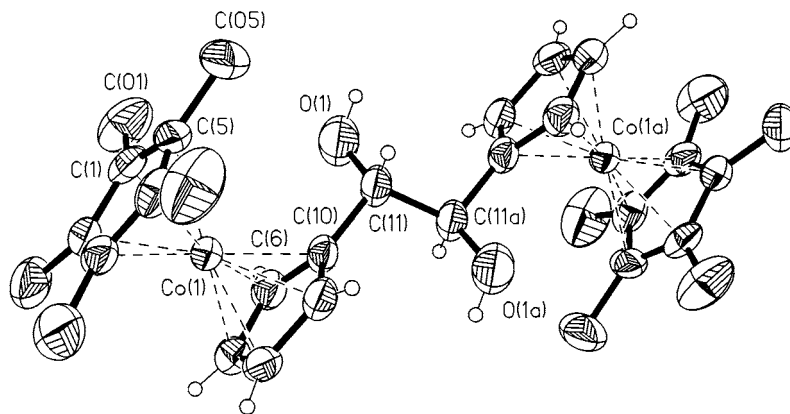
Scheme 1. Molecular structure of cation of **3**, showing the atom numbering scheme. Carbon atoms of cobaltocenium Co(1) are numbered from C(1) to C(5), C(01) to C(05), and C(6) to C(10); carbon atoms of pendant Cp* are numbered from C(12) to C(16), and C(012) to C(016), respectively. Methyl hydrogen atoms and counterion tetraphenylborate are omitted for clarity.

At this point it is interesting to note that Rausch [4] was able to synthesize 1,1′-diacetylcobaltocene and 1,1′-dicarbomethoxycobaltocene starting from Cp–C(O)CH$_3$ and Cp–C(O)OCH$_3$, respectively, but that an analogous reaction between two equivalents of formylcyclopentadienide and cobaltous chloride afforded in low yield only impure 1,1′-diformylcobaltocene [7].

The reaction of [Cp*Co(II)Cl]$_2$ with formylcyclopentadienide under appropriate experimental conditions according to work by Kölle [3] and Rausch [4] does not yield the desired formyl(pentamethyl)cobaltocene **1a** or, after the usual oxidative work-up in cobaltocene chemistry, formyl(pentamethyl)cobaltocinium salts, respectively (Scheme 1).

The main apolar product in this reaction is decamethyl(dihydro)fulvalene **2**, the dimer of the Cp* radical, which is formed most likely by oxidation and dimerization. Although **2** is an often observed byproduct in most syntheses involving pentamethylcyclopentadienide [6], the considerable amount of **2** in all our reactions under a variety of experimental conditions (stochiometry, temperature, mode of addition, reaction time, etc.) indicates that the oxidation of Cp*Li to (Cp*)$_2$ **2** is not due to accidental traces of air, but the result of an unidentified oxidant in the reaction mixture. The detailed spectral and structural properties of **2** have been recently reported by us [6].

Besides **2** as the main apolar product, five polar products are formed in this reaction, presumably cobaltocinium salts, which have been isolated from the aqueous phase of the reaction mixture by precipitation with hexafluorophosphate as counter-ion. Initially, work-up of the reaction mixture was performed according to the procedure of Kölle [3], which uses Fe(III) salts as oxidant for the conversion of Co(II) to Co(III), but this proved not necessary in later experiments. Our interpretation of this finding is that these cobaltocenium salts were formed during the course of the reac-

tion of [Cp*Co(II)Cl]$_2$ with formylcyclopentadienide by an intramolecular redox disproportionation of **1a** to **1b**, as indicated in Scheme 1. Similar chemistry has been observed for pentamethylferrocenyl(phenyl)carbenium tetrafluoroborate and other carbon-centered organometallic radicals [6]. The intermediate zwitterionic pentamethylcobaltocenium-(formylradical)anion **1b** cannot be isolated and reacts further by radical coupling, yielding pentamethylcyclopentadienyl(pentamethylcobaltocenium)methanol salt **3** (10.8%) and 1,2-bis(pentamethylcobaltocenium)glycol salt **4** (24.4%), among three other unidentified species in trace amounts (total isolated material 10 mg). The redox disproportionation of **1a** to **1b** can be rationalized by the known electron-richness of the Cp* ligand in comparison to Cp, thereby facilitating metal-centered oxidation with concomitant reduction of the aldehyde functionality. In analogy, the half-wave oxidation potential Fe(II)–Fe(III) of Cp*FeCp–R ferrocenes show a decrease of − 0.276 V in direct comparison to unmethylated CpFeCp–R ferrocenes (R = functional substituent) [6], and the half-wave reduction potential Co(III)–Co(II) of [Cp*CoCp]$^+$[PF$_6$]$^-$ has been observed at − 1.17 V in comparison to − 0.89 V for the parent cobaltocene [CpCoCp]$^+$[PF$_6$]$^-$, demonstrating an identical decrease of − 0.28 V attributable to the Cp* ligand in pentamethylated cobaltocenes [8].

The characterization of the hexafluorophosphates of **3** and **4** by NMR spectroscopy proved difficult due to low solubility, giving spectra with a poor signal-to-noise ratio, and due to unexpected complexity of the obtained spectra. Anion exchange with NaB(C$_6$H$_5$)$_4$ in methanol afforded the corresponding tetraphenylborates **3** and **4** with superior solubility, allowing the growth of X-ray quality single crystals.

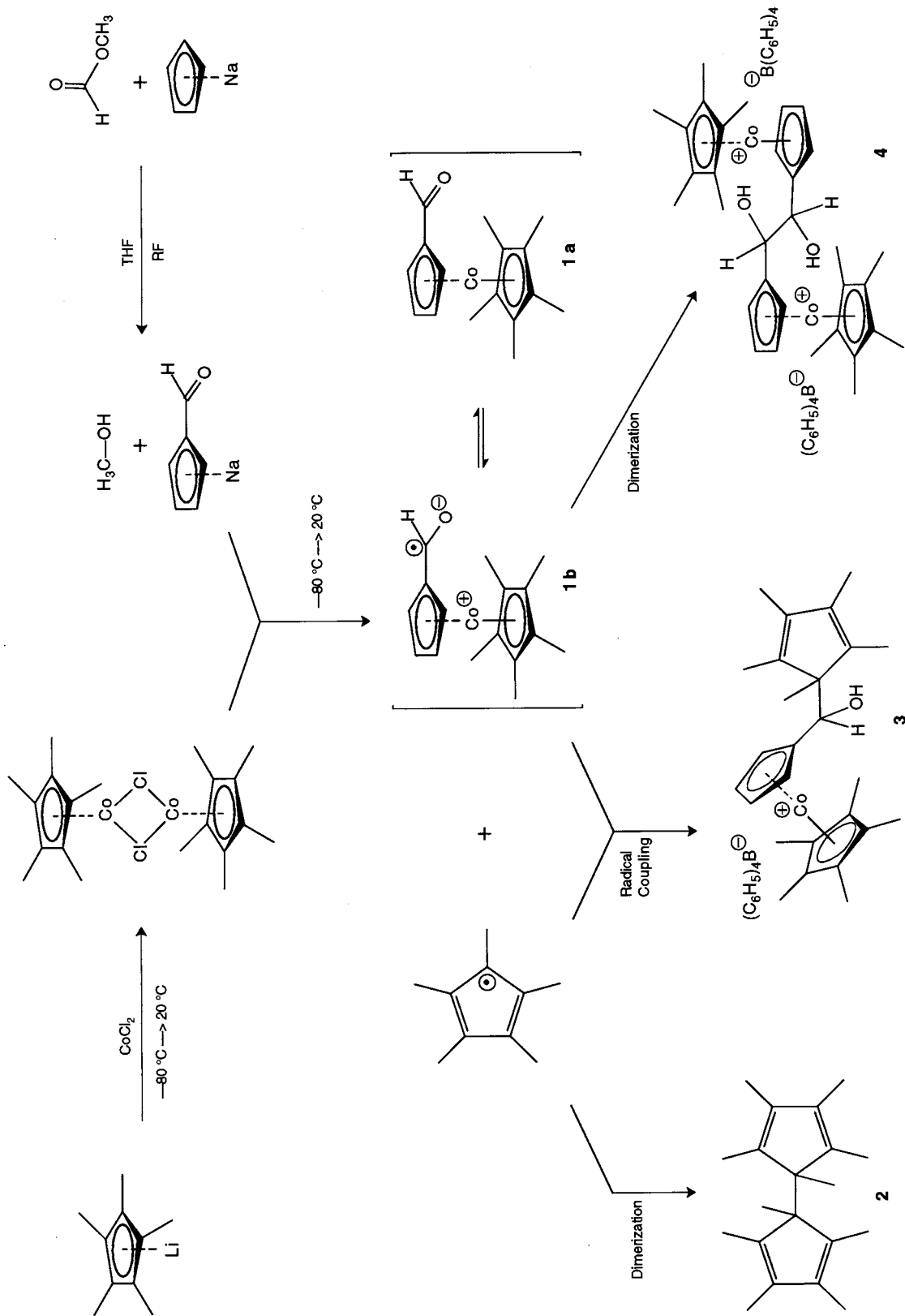Fig. 1 shows the structure of the cation of tetraphenylborate **3**, proving the connectivity of the

Fig. 1. Formation of products **2**, **3**, and **4** from formyl(pentamethyl)cobaltocene **1a/1b**.

molecule. The bond lengths and angles of the cobaltocenium moiety and of the pendant Cp* group are all in the expected range and compare well with other non-methylated cobaltocenium salts and with the structural properties of decamethyl(dihydro)fulvalene [6], respectively. Compound **3** crystallizes as a racemic mixture with regard to the chiral center C(11), in addition, the hydroxyl group and the hydrogen at this carbon are disordered with a site occupation ratio of 3:1.

Fig. 2 shows the molecular structure of the dication of **4**. Bond lengths and angles are unexceptional, similar as in structure **3**. The two halves of the dication are symmetry related by an inversion center, showing that the solid state structure corresponds to the *meso*-isomer only. In solution, both *rac* and *meso* isomers exist, according to NMR data.

Finally we also note that alternative methods to prepare the desired formyl(pentamethyl)cobaltocene **1a** failed, e.g. nucleohilic addition of 2-lithio dithiane to pentamethylcobaltocenium, subsequent oxidation (hydride abstraction), and cleavage (deprotection). In addition, attempted trapping of the intermediate formyl(pentamethyl)cobaltocene **1a** with Wittig reagents (e.g. $FcCH = P(C_6H_5)_3$) failed, no olefinic product could be detected in the reaction mixture.

3. Summary

This work was initiated with the aim of synthesizing formyl(pentamethyl)cobaltocene or formyl(pen-

tamethyl)cobaltocenium salts, respectively, as potential valuable synthons in analogy to the isoelectronic pentamethylferrocenyl aldehyde. However, the target compound(s) cannot be synthesized by extension of established synthetic transformations in metallocene chemistry. The high donor capacity of the Cp* ligand leads to intramolecular redox disproportionation of the intermediate formyl(pentamethyl)cobaltocene with subsequent radical coupling of the ylidic pentamethylcobaltocenium-(formyl)radical-anion, yielding undesired C–C coupled follow-up products, as has been shown by X-ray crystal structure analyses.

4. Experimental

General techniques and instrumentation have been published recently [9]. (Cp*CoCl)$_2$ [3], formylcyclopentadienide [4], and pentamethylcyclopentadiene [10] were synthesized according to published procedures.

4.1. Reaction of Co(II) chloride with formylcyclopentadienide and pentamethylcyclopentadienide

A 2.0 M THF solution of sodium cyclopentadienide (3.9 ml, 7.8 mmol) was added to 0.7 ml methyl formiate (11.7 mmol) dissolved in 40 ml THF and the mixture was refluxed for 2 h, resulting in a solution of sodium formylcyclopentadienide and methanol. In a separate Schlenk flask, 1.2 ml (7.8 mmol) pentamethylcyclopentadiene was dissolved in 30 ml THF, cooled to $-80°C$, and metallated with 3.9 ml (7.8 mmol) of a 2.0 M *n*-butyl lithium solution in hexane by allowing the stirred mixture slowly warm to room temperature (r.t.). After 1 h this solution of lithium pentamethylcyclopentadienide was cooled to $-30°C$ and one equivalent cobalt(II) chloride (1g, 7.8 mmol) was added in one portion under an atmosphere of argon. After stirring for 0.5 h at r.t., the resulting solution of [Cp*CoCl]$_2$ was cooled to $-30°C$ and the sodium formylcyclopentadienide solution from above was added. The dark green mixture was stirred over night at ambient temperature.

Work-up: the brown mixture was hydrolized with H_2O, the aqueous layer was extracted several times with 30 ml portions of ether, the combined ether fractions were dried with Na_2SO_4, and volatile materials were removed in vacuo, yielding 390 mg (1.44 mmol, 36.9%) decamethyldihydrofulvalene **2** with spectral properties as recently published [6]. To the aqueous phase from above was added 1.3 g (8 mmol) NH_4PF_6, the resulting precipitate of a mixture of crude cobaltocenium hexafluorophosphates was chromatographed on alumina with ether:acetonitrile (9:1) as eluent, affording five yellow fractions. Fractions 2, 3, and 4 (total amount of material: 10 mg) were not characterized further. To facilitate spectroscopic and structural characterization
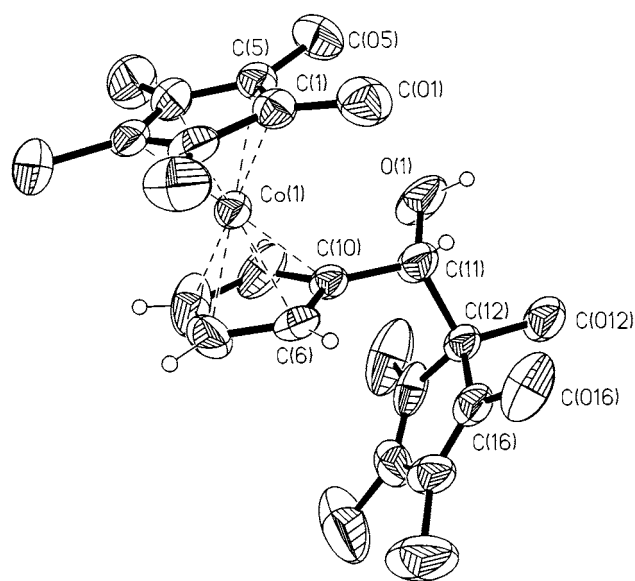
Fig. 2. Molecular structure of dication of **4**, showing the atom numbering scheme. Carbon atoms of cobaltocenium Co(1) are numbered analogously as in structure **3**. Methyl hydrogen atoms, counterions tetraphenylborates and solvent molecules are omitted for clarity.

(see below), the cobaltocenium hexafluorophosphates of fractions 1 and 5 were converted to the corresponding tetraphenylborates by first dissolving them in methanol and then precipitating the corresponding tetraphenylborates by addition of a solution of sodium tetraphenylborate. In this manner, pentamethylcyclopentadienyl(pentamethyl-cobaltocenium)methanol tetraphenylborate **3** (620 mg, 0.86 mmol, 11.0%) and 1,2-bis(pentamethylcobaltocenium)-ethan-1,2-diol bis-tetraphenylborate **4** (2.3 g, 1.9 mmol, 48.7%) were obtained in pure form. Crystallization from acetonitrile afforded X-ray quality single crystals for both compounds.

4.2. Data for pentamethylcyclopentadienyl(pentamethylcobaltocenium)methanol tetraphenylborate 3

Anal. Found: C, 80.73; H, 7.63. $C_{50}H_{56}BCoO$ Calc.: C, 80.86; H, 7.60%. M.p. 250°C, dec. MS (FAB): m/z (%) 423.4 (M^+ of cation, 100). IR data (KBr, cm^{-1}): 3546–3078s, 2997w, 2964m, 2927m, 1729s, 1663m, 1478m, 1428m, 1382m, 1262s, 1098s, 1075s, 1025s, 803s, 743m, 733s, 706s. ^1H-NMR (CDCl$_3$): δ 1.41–1.68 (15H, m, 5 CH$_3$); 1.73 (15H, s, Cp*); 4.05–4.72 (6H, m, subst. Cp and C(OH)H); 6.88–7.41 (20H, m, B(C$_6$H$_5$)$_4$). ^{13}C-NMR (CDCl$_3$): δ 9.5–10.0 [Cp* and CH$_3$(sp^3)]; 19.5 [4 CH$_3$(sp^2)]; 71.6 (C(OH)H); 82.0 (subst. Cp); 84.2 (subst. Cp); 121.7–136.3 (B(C$_6$H$_5$)$_4$).

4.3. Data for 1,2-bis(pentamethyl-cobaltocenium)ethan-1,2-diol bis-tetraphenylborate 4

Anal. Found: C, 79.16; H, 6.82. $C_{80}H_{82}B_2Co_2O_2$ Calc.: C, 79.08; H, 6.80%. M.p. 240°C. MS (FAB): m/z (%) 895.5 (M^+ of dication plus one B(C$_6$H$_5$)$_4$, 22); 576.5 (M^+ of dication, 76); 287.3 (M^+/2 of dication, 100). IR data (KBr, cm^{-1}): 3572–3116s, 3054m, 2998m, 1659w, 1580m, 1478s, 1455m, 1426s, 1385s, 1266m, 1142m, 1075m, 1027s, 745s, 735s, 614s. ^1H-NMR (CD$_3$CN): δ 2.13 (30H, s, Cp*); 4.00–5.10 (12H, m, subst.Cp and C(OH)H–C(OH)H); 6.83–7.26 (40H, m, B(C$_6$H$_5$)$_4$). ^{13}C-NMR (CD$_3$CN): δ 13.2 (Cp*); 81.5–85.5 (subst. Cp and C(OH)H–C(OH)H); 118.2–136.6 (B(C$_6$H$_5$)$_4$).

4.4. X-ray structure of 3 and 4

A Siemens P4 diffractometer with graphite-monochromatized Mo–K$_\alpha$ radiation ($\lambda = 71.073$ pm) was used for data collection. Crystal data, data collection, and refinement parameters of **3** and **4** are summarized in Table 1. The unit cells were determined by the automatic indexing of 25 centered reflections and con-

Table 1
Crystal data and structure refinement for **3** and **4**

	3	**4**
Molecular formula	$C_{50}H_{56}BCoO$	$C_{80}H_{82}B_2Co_2O_2 \cdot 3CH_3CN$
Formula weight	742.69	13338.10
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a (pm)	1422.2(2)	1125.6(2)
b (pm)	1387.8(3)	1344.5(1)
c (pm)	2081.1(2)	1375.6(2)
α (°)	90	68.49(1)
β (°)	92.69(2)	69.09(2)
γ (°)	90	79.46(1)
Volume (nm^3)	4.1030(11)	1.8060(4)
Z	4	1
Temperature (K)	213	213
$D_{calc.}$ (Mg/m^3)	1.202	1.230
Absorption coefficient (mm^{-1})	0.454	0.510
$F(000)$	1584	708
Color, habit	Yellow prism	Yellow platelet
Crystal size (mm)	0.70 × 0.25 × 0.15	0.45 × 0.35 × 0.11
θ range for data collection (°)	2.79–20.24	3.06–21.00
Index ranges	$-1 \leq h \leq 13$	$0 \leq h \leq 10$
	$-1 \leq k \leq 13$	$-13 \leq k \leq 13$
	$-21 \leq l \leq 21$	$-13 \leq l \leq 14$
Reflections collected	4075	3978
Independent reflections	3835 ($R_{int} = 0.0351$)	3727 ($R_{int} = 0.0387$)
Reflections with $I > 2\sigma(I)$	2594	2850
Absorption correction	None	ψ-scan
Max. and min. transmission	—	0.980 and 0.885
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3443/0/499	3495/0/437
Goodness-of-fit on F^2	1.053	1.033
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0464$ $wR_2 = 0.0885$	$R_1 = 0.0426$ $wR_2 = 0.0933$
R indices (all data)	$R_1 = 0.0914$ $wR_2 = 0.1061$	$R_1 = 0.0664$ $wR_2 = 0.1050$
Largest difference peak and hole (e nm^{-3})	247 and −196	584 and −196

firmed by examination of the axial photographs. Data were measured via ω-scan and corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography [11] and an empirical absorption correction [12] was made in the case of **4**. The structures were solved by direct methods, SHELXS-86 [13], and refined by a full-matrix least-squares procedure using SHELXL-93 [14]. All non-H atoms were refined with anisotropic

Table 2
Atomic coordinates (10^4) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for **3**

	x	y	z	U_{eq}
Cation				
Co(1)	4466(1)	2108(1)	2792(1)	37(1)
C(1)	5074(4)	825(4)	3021(2)	41(1)
C(2)	4174(4)	890(4)	3289(3)	48(2)
C(3)	4190(4)	1709(5)	3703(2)	49(2)
C(4)	5096(4)	2138(4)	3685(2)	52(2)
C(5)	5643(4)	1600(4)	3271(2)0	42(1)
C(6)	3850(4)	2109(4)	1888(2)	44(1)
C(7)	3290(4)	2564(6)	2322(3)	69(2)
C(8)	3794(7)	3342(5)	2575(3)	80(2)
C(9)	4686(5)	3360(4)	2315(3)	65(2)
C(10)	4717(3)	2581(4)	1876(2)	37(1)
C(12)	5239(3)	2766(4)	748(2)	42(1)
C(13)	4852(5)	3784(4)	769(2)	53(2)
C(14)	3949(5)	3760(6)	533(2)	66(2)
C(15)	3702(4)	2781(6)	340(2)	57(2)
C(16)	4425(4)	2211(5)	452(2)	47(2)
C(01)	5359(4)	53(4)	2562(3)	62(2)
C(02)	3374(4)	199(4)	3180(3)	74(2)
C(03)	3396(4)	2065(5)	4103(2)	80(2)
C(04)	5425(4)	3028(5)	4050(3)	79(2)
C(05)	6657(3)	1746(4)	3140(3)	63(2)
C(012)	6117(4)	2703(4)	336(2)	61(2)
C(013)	5425(6)	4631(5)	1003(3)	105(3)
C(014)	3305(6)	4619(6)	479(4)	152(4)
C(015)	2739(4)	2536(6)	60(3)	115(3)
C(016)	4474(5)	1151(4)	314(3)	81(2)
C(11)	5495(4)	2365(5)	1437(2)	57(2)
O(1)	6345(3)	2676(6)	1700(2)	93(2)
C(11A)	5495(4)	2365(5)	1437(2)	57(2)
O(1A)	5872(13)	1609(14)	1520(8)	71(6)
Anion				
B(1)	5363(4)	−3263(4)	3305(3)	35(2)
C(17)	5093(3)	−2870(4)	2578(2)	32(1)
C(18)	5656(3)	−2916(4)	2053(3)	49(1)
C(19)	5407(5)	−2500(4)	1460(3)	61(2)
C(20)	4564(5)	−2019(4)	1377(2)	63(2)
C(21)	3995(4)	−1943(4)	1876(3)	50(2)
C(22)	4254(4)	−2349(4)	2468(2)	44(1)
C(23)	6258(3)	−4011(4)	3344(2)	35(1)
C(24)	6376(4)	−4741(4)	2892(3)	48(2)
C(25)	7080(5)	−5420(4)	2945(3)	59(2)
C(26)	7699(4)	−5415(4)	3468(4)	59(2)
C(27)	7615(4)	−4724(4)	3935(3)	55(2)
C(28)	6910(4)	−4036(4)	3872(2)	46(1)
C(29)	4489(3)	−3871(3)	3607(2)	33(1)
C(30)	3700(4)	−4215(4)	3259(2)	38(1)
C(31)	2997(3)	−4739(4)	3542(3)	45(1)
C(32)	3057(4)	−4939(4)	4191(3)	51(2)
C(33)	3830(5)	−4627(4)	4549(3)	57(2)
C(34)	4521(4)	−4108(4)	4263(3)	47(2)
C(35)	5608(3)	−2286(3)	3711(2)	34(1)
C(36)	6439(4)	−1772(4)	3612(2)	47(2)
C(37)	6659(4)	−907(5)	3901(3)	64(2)
C(38)	6044(6)	−486(4)	4302(3)	73(2)
C(39)	5204(5)	−947(5)	4407(3)	75(2)
C(40)	5011(4)	−1827(4)	4124(3)	55(2)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.
Disordering: the hydroxyl group at C(11) [= C(11A)] is disordered at two positions with a ratio 3:1 for O(1) and O(1A).

Table 3
Atomic coordinates (10^4) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for **4**

	x	y	z	U_{eq}
Dication				
Co(1)	1581(1)	2428(1)	6558(1)	37(1)
O(1)	−160(3)	3843(3)	4660(3)	76(1)
C(1)	1076(5)	1123(3)	6404(4)	47(1)
C(2)	2166(4)	868(3)	6757(4)	50(1)
C(3)	1833(5)	1061(3)	7761(4)	51(1)
C(4)	554(5)	1450(3)	8037(4)	53(1)
C(5)	75(4)	1491(3)	7192(4)	52(1)
C(6)	2253(4)	3533(3)	5034(3)	46(1)
C(7)	3146(4)	3276(3)	5603(4)	50(1)
C(8)	2575(5)	3529(3)	6578(4)	51(1)
C(9)	1313(4)	3948(3)	6616(4)	46(1)
C(10)	1112(4)	3951(3)	5658(3)	38(1)
C(11)	−64(4)	4395(3)	5326(4)	45(1)
C(01)	960(6)	980(4)	5419(4)	88(2)
C(02)	3436(5)	429(4)	6184(5)	85(2)
C(03)	2718(6)	852(4)	8434(5)	97(2)
C(04)	−198(6)	1752(4)	9050(4)	102(2)
C(05)	−1266(4)	1802(4)	7168(5)	93(2)
Anion				
B(1)	2687(5)	−3224(4)	7344(4)	42(1)
C(12)	1247(4)	−2622(3)	7586(3)	41(1)
C(13)	325(5)	−2932(4)	7298(4)	60(1)
C(14)	−867(5)	−2422(5)	7395(4)	70(2)
C(15)	−1215(5)	−1578(5)	7798(4)	69(2)
C(16)	−355(5)	−1266(3)	8108(4)	60(1)
C(17)	855(4)	−1777(3)	7995(3)	47(1)
C(18)	3612(4)	−2713(3)	7707(3)	39(1)
C(19)	3292(4)	−2744(3)	8793(4)	49(1)
C(20)	4024(5)	−2350(4)	9174(4)	63(1)
C(21)	5151(5)	−1903(4)	8459(5)	64(1)
C(22)	5526(4)	−1874(4)	7387(5)	62(1)
C(23)	4779(4)	−2268(3)	7020(3)	49(1)
C(24)	2690(4)	−4498(3)	8062(3)	43(1)
C(25)	1620(5)	−5060(4)	8803(4)	56(1)
C(26)	1710(6)	−6137(4)	9426(4)	70(2)
C(27)	2863(7)	−6701(4)	9326(4)	71(2)
C(28)	3944(5)	−6186(4)	8604(4)	62(1)
C(29)	3855(4)	−5117(4)	7987(3)	52(1)
C(30)	3182(4)	−3025(3)	6009(3)	38(1)
C(31)	3489(4)	−3843(3)	5547(4)	45(1)
C(32)	3829(4)	−3648(4)	4430(4)	54(1)
C(33)	3889(4)	−2624(5)	3714(4)	58(1)
C(34)	3586(4)	−1789(4)	4129(4)	57(1)
C(35)	3244(4)	−1993(3)	5250(4)	51(1)
Solvent molecules				
N(1)	2262(10)	−4235(7)	12096(7)	240(5)
C(36)	2707(7)	−4788(6)	11634(6)	107(2)
C(37)	3341(8)	−5399(5)	10993(6)	129(3)
N(2)	5875(14)	548(12)	9142(9)	255(7)
C(38)	5000	0	10000	186(8)
C(39)	5875(14)	548(12)	9142(9)	255(7)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.
Symmetry transformations to generate equivalent atoms: no. 1: $-x$; $-y+1$; $-z+1$; no. 2: $-x+1$, $-y$, $-z+2$.
Disordering: an acetonitrile molecule lies in an inversion center, therefore N(2) = C(39) with a ratio of 1:1.

displacement parameters (Tables 2 and 3). Hydrogen atoms were placed in calculated positions. Disordering: in structure **3**, the hydroxyl group at C(11) [= C(11A)] is disordered at two positions with the ratio 3:1 for O(1) and O(1A); and in structure **4**, an acetonitrile molecule lies in an inversion center, therefore N(2) = C(39) with a ratio of 1:1.

5. Supplementary material available

The authors have deposited atomic coordinates for structures **3** and **4** at the Cambridge Crystallographic Data Centre. The coordinates may be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK, on quoting the full journal citation.

Acknowledgements

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