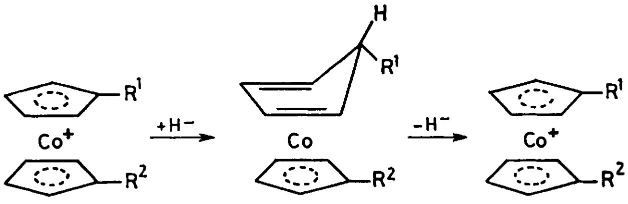
Electrochemical Behaviour and *X*-Ray Structure of (η-Cyclopentadienyl)-(4—5-η-2-methoxycarbonylcyclopent-4-en-1,3-ylene)cobalt

By **Nabil El Murr,*** Laboratoire de Polarographie Organique associé au CNRS (LA 33), Faculté des Sciences Gabriel, 6 boulevard Gabriel, 21100 Dijon, France
Yves Dusausoy, Laboratoire de Minéralogie et Cristallographie, Faculté des Sciences, 54037 Nancy Cédex, France
John E. Sheats and **Marc Agnew,** Chemistry Department, Rider College, Lawrenceville, N.J. 08648, U.S.A.

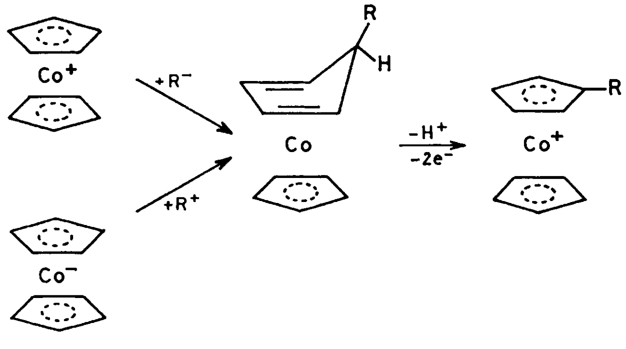
A study has been made of the electrochemical properties in non-aqueous media, crystal structure, and ^1H and ^{13}C n.m.r. spectra of the title complex $[Co(C_5H_5)(C_5H_5CO_2Me)]$. The structural studies indicate that, in the cyclopentadiene ring, the CO_2Me group occupies the *exo* position with respect to the metal. The unusual oxidation of the complex into the substituted cobalticinium salt is not due to its geometry, but probably to the influence of the CO_2Me group on the formation of the radical cation obtained by one-electron oxidation. Evidence for the existence of the radical cation of (1a) is provided by cyclic voltammetry.

FERROCENE, $[Fe(\eta\text{-}C_5H_5)_2]$, undergoes electrophilic substitution extremely readily, so that many substituted derivatives can be prepared. Attempts to carry out electrophilic substitution on cobaltocene have invariably led to oxidation yielding unsubstituted cobalticinium cation. Milder electrophiles such as alkyl halides result in nucleophilic addition and lead to the *exo*-substituted cyclopentadiene(cyclopentadienyl)cobalt derivatives.[1-4] These complexes can also be obtained by addition of nucleophiles to the cobalticinium cation [5-7] or of electrophiles to the cobaltocene anion.[4,8]



SCHEME 1

The derivatives of the cyclopentadiene(cyclopentadienyl)cobalt can be divided into two classes: complexes in which the *exo* position on the *sp*³ carbon is occupied by a hydrogen atom, and those in which this *exo* position is occupied by an organic group. After their oxidation, the first class of complexes readily yields the cobalticinium cations [5,9] (Scheme 1). The *exo*-substituted complexes are more interesting because their oxidation, if it is possible, offers a route to the substitution of cobaltocene or colbalticinium salts (Scheme 2). Many fruitless attempts were made in this field [2,6,9,10] and only one successful example was reported by us [11] concerning (5-methoxycarbonylcyclopenta-1,3-diene)(cyclopentadienyl)cobalt, (1a). We have assigned the *exo* position for the CO_2Me group only on the basis of the existence of an absorption at 2 760 cm⁻¹ in the i.r. spectrum.[4,12]



SCHEME 2

The unusual behaviour of complex (1a) towards oxidation can be attributed either to an *endo* geometry of the CO_2Me group (and thus our previous assignment would be incorrect) or to the specific redox properties of the *exo* complex. In order to answer this question and to propose a coherent mechanism for the oxidation of (1a), we have determined its crystal structure and studied the ^1H and ^{13}C n.m.r. spectra and also reinvestigated the electrochemical behaviour in non-aqueous media.

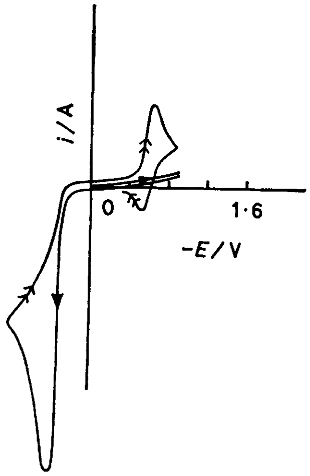


FIGURE 1 Cyclic voltammogram of (1a), in CH_2Cl_2 with 0.2 mol dm⁻³ $[NBu_4][PF_6]$, at a scan rate of 0.1 V s⁻¹

RESULTS AND DISCUSSION

Electrochemistry.—We recently [11] pointed out that the electrochemical oxidation of (1a) in aqueous alcoholic medium leads to the formation of a substituted cobalticinium salt in only 10% yield while the chemical oxidation occurs in quantitative yield. Thus we re-examined the electro-oxidation of (1a) in non-aqueous media such as CH_2Cl_2. The voltammogram obtained from a CH_2Cl_2 solution of (1a) containing 0.1 mol dm^{-3} $[NBu_4][PF_6]$ as the supporting electrolyte (Figure 1) shows that, for slow scanning rates (0.1 V s^{-1}), the oxidation is irreversible and leads to a new reducible species. This species can be easily identified as the (methoxycarbonyl)cobalticinium cation. Exhaustive electrolysis on this solution, using a carbon gauze as working electrode, confirmed this result and gave a quantitative yield of the substituted cobalticinium hexafluorophosphate.

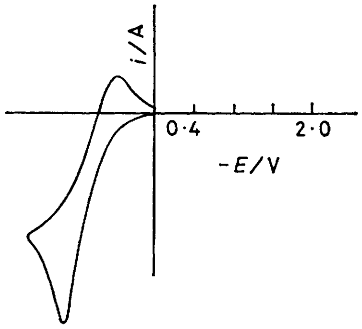
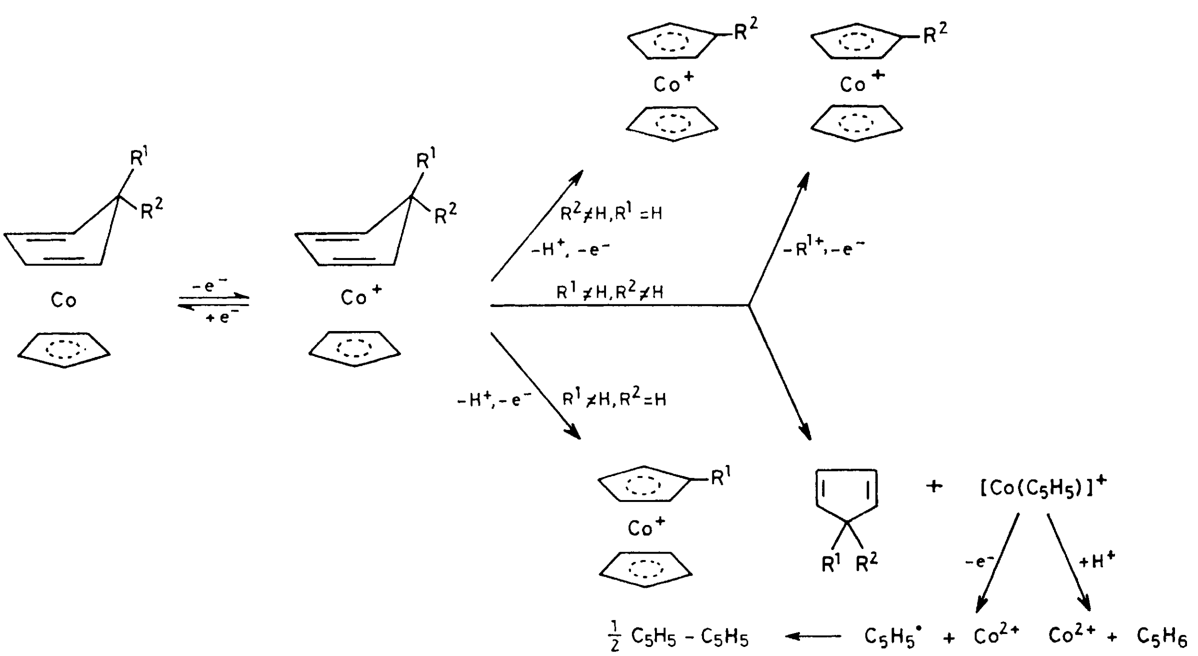


FIGURE 2 Cyclic voltammogram of (1a), in CH_2Cl_2 with 0.2 mol dm^{-3} $[NBu_4][PF_6]$, at a scan rate of 20 V s^{-1}



SCHEME 3

A qualitative study of the solution of (1a) in CH_2Cl_2 by cyclic voltammetry shows that the oxidation peak at 0.46 V [*versus* the standard calomel electrode (s.c.e.)] becomes partially reversible for scanning rates faster than 20 V s^{-1} (Figure 2). This finding, together with our preliminary results on the oxidation of cyclopentadiene(cyclopentadienyl)cobalt derivatives,[9,11] allows us to propose the following mechanism in which the first stage is the formation of an unstable radical cation (Scheme 3). The stability of the radical cation and its ability to remove a proton from the oxidative medium are the main factors which influence the yield of the substituted cobalticinium salts. The existence of a proton in the *exo* position facilitates this path, when this *exo* position is occupied by an organic group, and it is this group which can greatly influence the formation of the radical cation.

Crystal Structure.—The crystal was found to be orthorhombic with space group $P2_12_12_1$. Cell parameters were determined by least-squares calculations on 50 values of θ measured on a three-circles CAD3 Nonius diffractometer.

Crystal data. $C_{12}H_{13}CoO_2$, $a = 22.15(2)$, $b = 8.96(1)$, $c = 5.99(1)$ Å, $Z = 4$, $D_c = 1.377$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 14.9$ cm^{-1}; crystal dimensions $0.11 \times 0.010 \times 0.07$ mm.

Intensities for $\theta < 35°$ were measured on the same instrument using Mo-K_α radiation, the θ—2θ scanning mode, and periodically measured reference reflections. 880 Independent intensities which satisfied the statistical criterion $I_0(hkl) > 3\sigma(I_0)(hkl)$ were used in subsequent refinement. Lorentz and polarisation factors were applied, but not absorption corrections.

The structure was determined by direct methods using Multan.[13] The individual atomic parameters were refined anisotropically by a local diagonal least-squares program. Neutral atom scattering factors were taken from ref. 14. The agreement index R was 0.067 with unweighted data. Final atomic parameters are listed in the Tables 1—3. The structure-factor Tables and

TABLE 1

Atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	*X*	*Y*	*Z*
Co	3 979(1)	3 499(2)	4 530(3)
O(1)	3 465(8)	8 040(15)	8 024(19)
O(2)	2 919(7)	8 096(12)	4 815(19)
C(1)	3 787(6)	6 247(13)	5 295(19)
C(2)	3 791(8)	5 003(16)	7 060(25)
C(3)	3 212(9)	4 068(24)	6 551(35)
C(4)	3 083(8)	4 313(23)	4 264(43)
C(5)	3 522(12)	5 446(23)	3 370(33)
C(6)	3 343(8)	7 563(13)	5 963(24)
C(7)	3 058(9)	9 289(23)	8 884(25)
C(8)	4 114(9)	1 242(19)	3 815(26)
C(9)	4 544(11)	1 657(26)	5 451(33)
C(10)	4 959(10)	2 919(23)	4 555(42)
C(11)	4 770(15)	3 140(28)	2 349(34)
C(12)	4 240(13)	2 153(22)	1 878(32)

TABLE 2

Interatomic distances (Å) with estimated standard deviations in parentheses

Co–C(1)	2.534(11)	C(3)–C(4)	1.412(33)
Co–C(2)	2.064(14)	C(4)–C(5)	1.453(29)
Co–C(3)	2.028(20)	C(5)–C(1)	1.457(23)
Co–C(4)	1.954(16)	C(1)–C(6)	1.533(17)
Co–C(5)	2.089(22)	C(6)–O(2)	1.196(19)
Co–C(8)	2.086(17)	C(6)–O(1)	1.330(18)
Co–C(9)	2.080(23)	O(1)–C(7)	1.480(24)
Co–C(10)	2.043(21)	C(8)–C(9)	1.361(27)
Co–C(11)	2.087(26)	C(9)–C(10)	1.505(31)
Co–C(12)	2.063(19)	C(10)–C(11)	1.389(33)
C(1)–C(2)	1.537(18)	C(11)–C(12)	1.415(36)
C(2)–C(3)	1.468(26)	C(12)–C(8)	1.441(25)

TABLE 3

Bond angles (°) with estimated standard deviations in parentheses

C(1)–C(2)–C(3)	105.5(1.3)	C(11)–C(12)–C(8)	109.1(1.9)
C(2)–C(3)–C(4)	105.0(1.6)	C(12)–C(8)–C(9)	108.1(1.7)
C(3)–C(4)–C(5)	110.7(1.8)	C(1)–Co–C(2)	37.3(0.5)
C(4)–C(5)–C(1)	105.9(1.6)	C(2)–Co–C(3)	42.0(0.7)
C(5)–C(1)–C(6)	111.9(1.2)	C(3)–Co–C(4)	41.5(0.8)
C(2)–C(1)–C(6)	112.4(1.1)	C(4)–Co–C(5)	41.9(0.8)
C(1)–C(6)–O(2)	125.0(1.3)	C(5)–Co–C(1)	35.1(0.6)
C(1)–C(6)–O(1)	112.5(1.2)	C(8)–Co–C(9)	38.1(0.7)
O(2)–C(6)–O(1)	122.5(1.4)	C(9)–Co–C(10)	42.8(0.8)
C(6)–O(1)–C(7)	117.6(1.3)	C(10)–Co–C(11)	39.3(0.9)
C(8)–C(9)–C(10)	107.6(1.8)	C(11)–Co–C(12)	39.8(0.9)
C(9)–C(10)–C(11)	107.1(1.9)	C(12)–Co–C(8)	40.6(0.8)
C(10)–C(11)–C(12)	107.8(2.0)		

thermal parameters are available as Supplementary Publication No. SUP 22466 (27 pp.).*

A projection of the molecule on (001) is shown in Figure 3; the CO_2Me group occupies the *exo* position relative to the cobalt atom. It was not possible to find the hydrogen on C(1) from the difference-Fourier map. Supposing that the C(1)–H bond length was 1.08 Å and that the hybridisation of C(1) was sp^3, the *endo* hydrogen atom would be 2.90 Å away from the metal. This distance is shorter than that found by Churchill and Mason[15] in the case of the cyclopentadienyl(phenylcyclopentadiene)cobalt (3.0 Å). The methoxycarbonyl- and phenyl-cyclopentadiene molecules exhibit similar conformations. The substituted cyclopentadiene ring is non-planar with C(1) bent away from the cobalt atom. The angle between the C(2), C(3), C(4), C(5) and C(5), C(1), C(2) planes is 32°, the distance between the metal and C(1) is 2.53(1) Å, the average Co–C distance for the carbons C(2)—C(5) is 2.03(2) Å, and is 2.07(2) Å for the five carbons of the cyclopentadienyl ring. The angle between the plane of the cyclopentadienyl ring and the plane of the carbons C(2)—C(5) is 4.5°. These results indicate that the bonding of the ' cyclopentadiene ' to the metal is stronger than that for the cyclopentadienyl group [the distance between Co and the C(3)–C(4) bond is 1.99(2) Å] (Figure 4). The short bond length of 1.41 Å between C(3) and C(4) shows that the complex, in the solid state, is nearer to structure (1) than to structure (2).

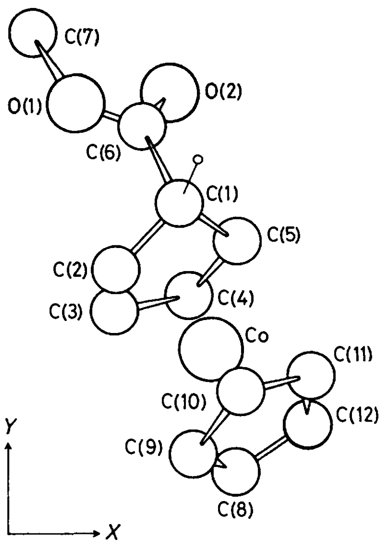


FIGURE 3 View of molecule (1a) with the atom numbering system

Proton and ^{13}C *N.M.R. Spectra.*—The proton and ^{13}C n.m.r. spectra of (1a) are given in Table 4. The peaks

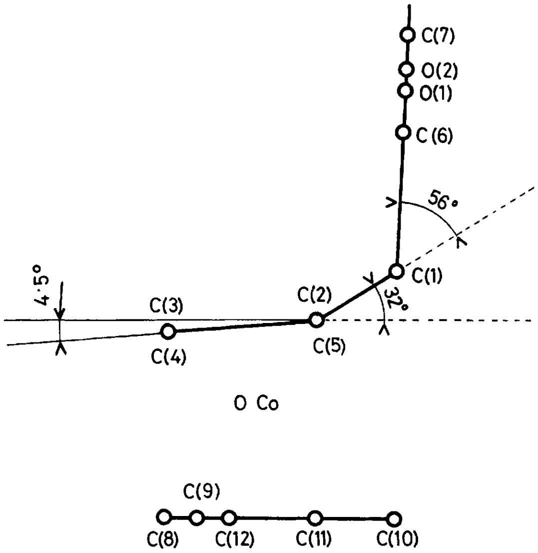


FIGURE 4 Angles between planes in molecule (1a)

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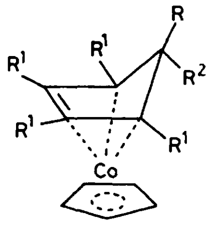
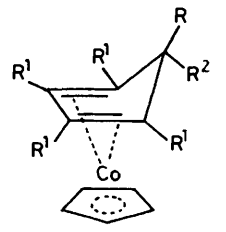
* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

were assigned by selective heteronuclear decoupling of specific protons, which caused collapse to a singlet of the carbon bearing the decoupled protons. Coupling constants were measured from the completely coupled ^{13}C spectrum. The relative intensities of the peaks in the ^{13}C n.m.r. spectra were determined from an Overhauser-suppressed pulse-delayed spectrum which gave accurate integrated values.



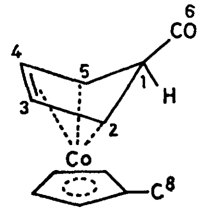
(1a) R = CO$_2$Me, R^1 = R^2 = H
(1b) R = Ph, R^1 = R^2 = H
(1c) RR^2 = O, R^1 = CF$_3$



(2a) R = CO$_2$Me, R^1 = R^2 = H
(2b) R = COPh, R^1 = R^2 = H
(2c) RR^2 = O, R^1 = Me

TABLE 4

Proton and carbon-13 n.m.r. spectra of (1a)



Position	^{1}H, δ/p.p.m.	^{13}C, δ/p.p.m.	^1J(C–H) Hz	^2J(C–H) Hz
1	3.46	53.807	142.8	5.0
2,5	2.79	38.173	173.5	5.8
3,4	5.35	75.295	176.8	5.8
6		169.047		4.2
7	3.46	51.110	146.5	0
8	4.83	79.330	175.2	6.6

The chemical shifts of the hydrogens at C(1) (3.46), C(2,5) (2.79), C(3,4) (5.35), and C(8) (4.83 p.p.m.) are in agreement with those for [Co(C$_5$H$_5$)(C$_5$H$_6$)] reported by Green *et al.*[5] [C(1) 2.68, C(2,5) 2.45, C(3,4) 5.25, and C(8) 4.59 p.p.m.] if one considers the downfield shifts of 0.2—1.0 p.p.m. normally produced by a methoxycarbonyl group.

The chemical shift of the carbons C(8), of the unsubstituted cyclopentadienyl ring, lies between that of ferrocene (67.9 p.p.m.) and cobalticinium ion (85.89 p.p.m.) and is slightly upfield from the values (84—85 p.p.m.) observed for the unsubstitutied cyclopentadienyl ring of cyclopentadienone(cyclopentadienyl)cobalt complexes.[16] A marked difference, however, is observed between the shifts for C(2,5) and C(3,4). The shifts for C(2),C(5) (89.61 p.p.m.) and C(3),C(4) (79.86 p.p.m.) of [Co(C$_5$H$_5$)(C$_5$Me$_4$O)] (2c) are typical of values expected for an η-butadienyl system, whereas both ^{1}H and ^{13}C n.m.r. data for complex (1a) are consistent with sp^3 hybridisation of C(2,5) and sp^2 hybridisation for C(3),C(4). Thus structure (1a), with one π and two σ bonds is preferable to (2a) which contains an η-butadienyl system. These observations are consistent with the bond lengths for C(2),C(3) and C(3),C(4) observed by *X*-ray crystallography.

Thus complex (1a) more closely resembles the phenyl analogue (1b),[15,17] which possesses shorter bonds for C(3),C(4) than for C(2),C(3) and C(4),C(5). Similarly [Co(C$_5$H$_5$){C$_5$(CF$_3$)$_4$O}] possesses structure (1c), while [Co(C$_5$H$_5$)(C$_5$H$_5$COPh)] and [Co(C$_5$H$_5$)(C$_5$Me$_4$O)] possess structures (2b) [18] and (2c).[19] Several workers [20-22] have attempted to explain the differing degrees of puckering and the differing bond orders at C(2),C(3) and C(3),C(4) in terms of differing contributions of electron density from the orbitals on the metal atom to the various available molecular orbitals of the cyclopentadiene or cyclopentadienone rings. Apparently structures (1) and (2) represent limiting forms and slight variations in the steric and electronic effects of the substituents are sufficient to change the degree to which the metal orbitals overlap with the molecular orbitals of the rings, so that the complex adopts either structure (1) or (2). If sufficient data were available for different substituents a smooth transition would probably be observed between structures (1) and (2).[22]

The crystal structure and the analysis of the ^{1}H and ^{13}C n.m.r. spectra of the [Co(C$_5$H$_5$)(C$_5$H$_5$CO$_2$Me)] (1a) confirm our preliminary speculations on the *exo* position of the methoxycarbonyl group towards the metal. The transformation of this complex into the substituted cobalticinium salt, by chemical or electrochemical methods, remains the sole example in the series of the *exo*-substituted cyclopentadiene(cyclopentadienyl)cobalt derivatives. On the whole, the chemical reaction with trityl tetrafluoroborate occurs [as in the case of cyclohexadienyl(cyclopentadienyl)iron [23]], through an *endo*-hydride abstraction. Electrochemically, this oxidation leads first to the corresponding radical cation, which is then transformed, by an *endo*-proton elimination, into the methoxycarbonylcobaltocene. This *endo* elimination is probably facilitated by the electron-withdrawing effect of the *exo*-methoxycarbonyl group.

EXPERIMENTAL

Complex (1a) was prepared by reaction of the cobaltocene anion with CO$_2$ followed by addition of MeI.[8] Single crystals were obtained by crystallisation from a mixture of hexane and diethyl ether. The electrochemical experiments were performed in a Metrohm electrochemical cell, with a saturated calomel electrode as reference and a platinum wire as auxiliary electrode; these two electrodes were separated from the solution by a fritted glass disc. The working electrode was a dropping mercury electrode for the polarographic experiments, a glassy carbon electrode for the voltammetry studies, and a carbon gauze for the controlled-potential electrolysis.

The ^{1}H n.m.r. spectrum of complex (1a) was recorded on a JEOL C60-HL 60-MHz spectrometer in CDCl$_3$ at room temperature. The ^{13}C n.m.r. spectra were obtained on a JEOL FX-60 pulsed Fourier-transform spectrometer at

15.03 MHz with proton-noise decoupling bandwidth of 1 kHz. Peak positions were assigned by selective heteronuclear decoupling of specific protons, causing collapse to a singlet of the carbon bearing the decoupled protons. The nuclear Overhauser effect was suppressed on a completely decoupled spectrum in order to obtain an accurate integration of peak intensities.

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