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Synthesis, reactivity and X-ray molecular structure of the activated ester complex $[(\eta^5\text{-}C_5H_4COONS)Co(CO)_2]$ (NS = N-succinimidyl)

H. El Amouri [a,*], Y. Besace [a], J. Vaissermann [b], G. Jaouen [a]

[a] *Ecole Nationale Supérieure de Chimie de Paris, URA CNRS 403, 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France*
[b] *Université Pierre et Marie Curie, Place Jussieu, 75231 Paris Cedex 05, France*

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Abstract

The title compound $[(\eta^5\text{-}C_5H_4COONS)Co(CO)_2]$ (**2**) was prepared in high yield (91%) by treatment of the organometallic carboxylic acid $[(\eta^5\text{-}C_5H_4COOH)Co(CO)_2]$ (**1**) with N-hydroxysuccinimide in the presence of dicyclohexylcarbodiimide. The activated ester complex **2** was identified by spectroscopic methods, in addition its X-ray structure was determined. Compound **2** crystallizes in the triclinic space group $P\bar{1}$ with $a = 6.1880(8)$, $b = 9.722(1)$, $c = 10.869(1)$ Å, $\alpha = 83.37(1)$, $\beta = 83.91(1)$ and $\gamma = 86.30(1)°$, $V = 645(1)$ Å^3 and $Z = 2$. The stability of the above species **2** and its reactivity as labelling agent for amines and amino-esters are investigated and discussed.

Keywords: Co; Ester complex; Synthesis; X-ray structure; Aminoesters; Organometallic carboxylic acid

1. Introduction

Interest in labelling specific sites of peptides and proteins by organometallic entities has been growing during this last decade [1]. Several papers on η^5-Cp–metallocarbonyl labelling agents (M = Mo, W, Re, Fe) have been reported, where the π-bonded η^5-Cp ring is attached to an alkyl chain terminated by a succinimidyl ester unit [2]. The use of these metallocarbonyl labelling agents has been shown to be a valuable method to assay the number of such exposed amino acids in certain proteins, by monitoring the metal–carbonyl bands using FT-IR techniques [2b], however, lack of X-ray structure analysis hampered the identification of the labelled sites in these proteins. Furthermore, any chemical transformation that takes place during the labelling process, and not amenable to show M–CO absorption, could not be detected.

In this paper we report on the synthesis of $[(\eta^5\text{-}C_5H_4COONS)Co(CO)_2]$ (**2**) in high yield (91%) as well as its X-ray molecular structure. Complex **2** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$. The activated ester compound **2** reacts with benzyl amine and β-alanine ethyl ester to give the expected conjugate compounds $[(\eta^5\text{-}C_5H_4CONH\text{–}CH_2Ph)Co(CO)_2]$ (**3**) and $[(\eta^5\text{-}C_5H_4CONH\text{–}(CH_2)_2\text{–}COOEt)Co(CO)_2]$ (**4**) in 61% and 44% yields respectively. The potential use and stability of **2** as a labelling agent for amino-esters and amines are presented and discussed.

2. Results and discussion

Treatment of the organometallic carboxylic acid complex $[(\eta^5\text{-}C_5H_4COOH)Co(CO)_2]$ (**1**) [3] with one equivalent of N-hydroxysuccinimide (NHS) in the presence of dicyclohexylcarbodiimide (DCC) in THF afforded the activated ester complex $[(\eta^5\text{-}C_5H_4COONS)Co(CO)_2]$ (**2**) as an orange microcrystalline solid (Scheme 1). This compound was identified by spectroscopic methods and its structure was confirmed by X-ray analysis.

The ^{1}H NMR spectrum of **2** shows the usual pair of multiplets in the area (5.6–5.9 ppm) characteristic of the functionalized π-bonded Cp ring and a singlet appearing at 2.91 ppm, attributed to the succinimidyl unit. The ^{13}C NMR spectrum recorded at room temperature did not show signals of the metal–carbonyls, however,

* Corresponding author.

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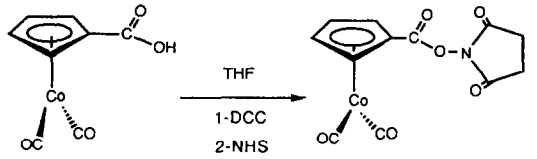


Scheme 1.

they become visible at low temperature; this trend was found for all the cobalt carbonyl derivatives. Thus, the ^{13}C spectrum of **2** recorded at 233 K showed the presence of one signal for the two metal bound carbonyls centered at 201.48 ppm, while the organic carbonyls appear as singlets at 169.74 and 159.69 ppm, we also note the presence of three signals for the π-bonded Cp ring at 106.50, 90.49 and 85.18 ppm. At higher field there is a singlet centered at 24.91 ppm attributed to the N-succinimidyl unit. The IR spectrum recorded in KBr disc shows two strong absorptions at 2038 and 1973 cm^{-1}, corresponding to the metal–carbonyl ligands. We also note the presence of three vibrations in the area 1720–1780 cm^{-1}, attributed to the organic carbonyls. To ascertain the structure of **2** without ambiguity an X-ray analysis was performed.

2.1. X-ray molecular structure of $[(\eta^5\text{-}C_5H_4COONS)Co(CO)_2]$ (2)

Crystals of the activated ester compound **2** suitable for X-ray study were obtained by recrystallization from ether/hexane mixture. Complex **2** crystallizes in the $P\bar{1}$ space group. A view of the molecule is shown in Fig. 1. Crystal data, selected bond distances and angles and atomic coordinates are given in Tables 1 to 3. The structure shows that the $-Co(CO)_2$ unit is bonded symmetrically to the functionalized cyclopentadienyl ligand with $Co-Cp_{centroid}$ distance of 1.70 Å, which is shorter than those reported for the analogous activated ester complex of molybdenum $[(\eta^5\text{-}C_5H_4COONS)MoMe-$

Table 1
Crystallographic data for $[(\eta^5\text{-}C_5H_4COONS)Co(CO)_2]$ (2)

Chemical formula	$C_{12}H_8O_6NCo$
FW	321.1
Crystal system	triclinic
Space group	$P\bar{1}$
Z	2
a (Å)	6.1880(8)
b (Å)	9.722(1)
c (Å)	10.869(1)
α (°)	83.37(1)
β (°)	83.91(1)
γ (°)	86.30(1)
V (Å^3)	645(1)
$F(000)$	162
ρ_{calc} (g cm^{-3})	0.83
μ (Mo k α) (cm^{-1})	6.74
Diffractometer	CAD4
Monochromator	graphite
Radiation	Mo K α (0.71070)
Temperature (°C)	20
Scan type	$\omega/2\theta$
Scan range θ (°)	$0.8+0.34\tan\theta$
2θ range (°)	3–50
No. of reflection collected	2272
No. of reflection used (criteria)	1349 ($I > 3\ \alpha\ (I)$)
R	0.037
R_w *	0.039
Absorption correction * *	min. 0.82; max. 1.19
Secondary ext.	no
Weighting scheme	unit weights
RMS (shift/esd)	0.10
LS parameters	207

* $R_w = [\Sigma_i w_i (F_o - F_c)^2 / \Sigma_i w_i F_o^2]^{1/2}$.
* * DIFABS, Ref. [7].

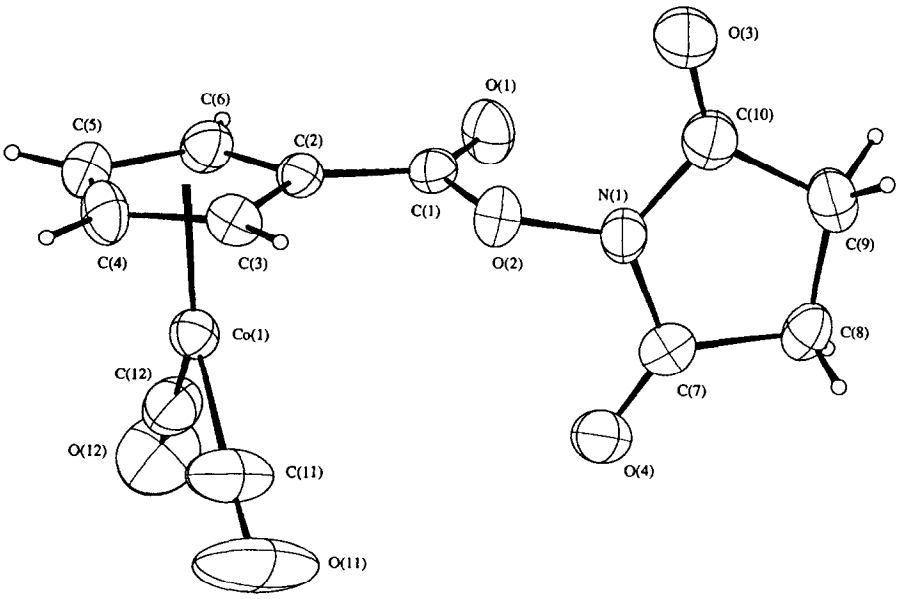


Fig. 1. The molecular structure and atom labelling for $[(\eta^5\text{-}C_5H_4COONS)Co(CO)_2]$ (1).

Table 2
Selected bond lengths (Å) and angles (°) for [(η^5-C_5H_4COONS)-$Co(CO)_2$] (**2**)

Co(1)–C(11)	1.727(7)	O(11)–C(11)	1.125(7)
Co(1)–C(12)	1.729(7)	O(12)–C(12)	1.138(7)
Co(1)–C(2)	2.082(5)	Co(1)–C(3)	2.046(5)
Co(1)–C(4)	2.106(6)	Co(1)–C(5)	2.098(6)
Co(1)–C(6)	2.068(6)	O(1)–C(1)	1.199(6)
O(2)–N(1)	1.383(5)	O(2)–C(1)	1.398(6)
O(3)–C(10)	1.180(7)	O(4)–C(7)	1.195(6)
N(1)–C(7)	1.385(7)	N(1)–C(10)	1.373(7)
C(1)–C(2)	1.438(7)	C(2)–C(3)	1.435(7)
C(2)–C(6)	1.413(7)	C(3)–C(4)	1.395(8)
C(4)–C(5)	1.384(8)	C(5)–C(6)	1.423(8)
C(7)–C(8)	1.501(8)	C(8)–C(9)	1.484(9)
C(9)–C(10)	1.510(9)		
C(2)–Co(1)–C(3)	40.7(2)	C(2)–Co(1)–C(4)	66.8(2)
C(3)–Co(1)–C(4)	39.2(2)	C(2)–Co(1)–C(5)	66.7(2)
C(3)–Co(1)–C(5)	65.8(2)	C(4)–Co(1)–C(5)	38.4(2)
C(2)–Co(1)–C(6)	39.8(2)	C(3)–Co(1)–C(6)	67.0(2)
C(4)–Co(1)–C(6)	66.2(2)	C(5)–Co(1)–C(6)	39.9(2)
C(11)–Co(1)–C(12)	91.5(3)		
Co(1)–C(11)–C(11)	177.7(8)	Co(1)–C(12)–O(12)	179.5(6)
C(2)–Co(1)–C(11)	120.4(3)	C(3)–Co(1)–C(11)	97.7(3)
C(4)–Co(1)–C(11)	110.6(3)	C(5)–Co(1)–C(11)	146.5(3)
C(6)–Co(1)–C(11)	160.2(3)	C(2)–C0(1)–C(12)	128.6(3)
C(3)–Co(1)–C(12)	168.8(3)	C(4)–Co(1)–C(12)	141.5(3)
C(5)–Co(1)–C(12)	109.1(3)	C(6)–Co(1)–C(12)	102.5(3)
N(1)–O(2)–C(1)	112.3(4)	O(2)–N(1)–C(7)	121.0(4)
O(2)–N(1)–C(10)	121.5(5)	C(7)–N(1)–C(10)	117.5(5)
O(1)–C(1)–O(2)	122.0(5)	O(1)–C(1)–C(2)	128.3(5)
O(2)–C(1)–C(2)	109.7(5)	Co(1)–C(2)–C(1)	121.7(3)
Co(1)–C(2)–C(3)	68.3(3)	C(1)–C(2)–C(3)	128.6(5)
Co(1)–C(2)–C(6)	69.6(3)	C(1)–C(2)–C(6)	125.2(5)
C(3)–C(2)–C(6)	105.8(5)	Co(1)–C(3)–C(2)	71.0(3)
Co(1)–C(3)–C(4)	72.7(3)	C(2)–C(3)–C(4)	109.2(5)
Co(1)–C(4)–C(3)	68.1(3)	Co(1)–C(4)–C(5)	70.5(4)
C(3)–C(4)–C(5)	108.1(5)	Co(1)–C(5)–C(4)	71.1(4)
Co(1)–C(5)–C(6)	68.9(3)	C(4)–C(5)–C(6)	108.6(5)
Co(1)–C(6)–C(2)	70.6(3)	Co(1)–C(6)–C(5)	71.2(3)
C(2)–C(6)–C(5)	108.2(5)	O(4)–C(7)–N(1)	123.5(5)
O(4)–C(7)–C(8)	131.8(5)	N(1)–C(7)–C(8)	104.7(5)
C(7)–C(8)–C(9)	106.4(5)	C(8)–C(9)–C(10)	107.4(5)
O(3)–C(10)–N(1)	125.0(6)	O(3)–C(10)–C(9)	131.0(6)
N(1)–C(10)–C(9)	104.0(5)		

$(CO)_3$] with Mo–$Cp_{centroid}$ bond distances of 2.01 Å (a) and 2.02 Å (b) [2a], and for that of [(η^5-C_5H_4COMe)$MoMe(CO)_3$] with Mo–$Cp_{centroid}$ bond distance of 2.01 Å [4]. We also note the presence of the ester unit grafted to the Cp ring, whereby the plane containing the N-succinimidyl fragment is almost orthogonal to that of the η-cyclopentadienyl with $\theta = 93°$. This geometry was also observed for the analogous molybdenum derivative [(η^5-C_5H_4COONS)$Mo(CO)_3$-Me] with $\theta = 82°$ (a) and 85° (b), and presumably may influence the reactivity of these activated esters with amino-acids in view of forming a peptide linkage.

2.2. Reactivity of 2 with benzylamine and β-alanine ethylester

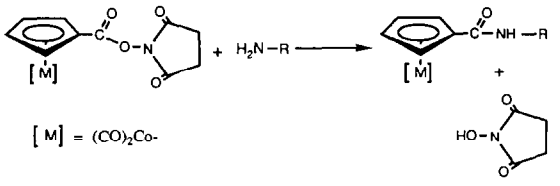
When **2** was treated with a fivefold excess of benzylamine in THF at room temperature, a precipitate was formed after 5 min. The reaction mixture was stirred for a total of 12 h, the supernatant phase was separated and afforded the major compound identified spectroscopically as the expected conjugate adduct [(η^5-C_5H_4CO-NH–CH_2Ph)$Co(CO)_2$] (**3**) (Scheme 2).

The light pink precipitate was separated and found to be insoluble in most organic solvents and sparingly soluble in CH_3CN. The ^1H NMR spectrum recorded in CD_3CN shows the presence of a broad signal at 7.9 ppm attributed to (–N–H) groups, and a set of multiplets in the aromatic region (7.2–7.5 ppm). We also note the presence of a large signal centered at 2.9 ppm, the IR spectrum in KBr disc indicates the absence of M–CO absorptions, and the presence of two strong bands at 1674 and 1647 cm^{-1}. We also note the presence of a large band at 3200 cm^{-1}, which indicates the presence of hydrogen bonding related to the amine function (–NH–). The elemental analysis suggests the presence of a cobalt element. Attempts to obtain suitable crystals for X-ray analysis to identify this compound have so far been unsuccessful.

In a similar fashion, treatment of **2** with β-alanine ethylester in THF afforded the conjugate adduct [(η^5-C_5H_4CONH–$(CH_2)_2$–COOEt)$Co(CO)_2$] (**4**) as the major species, isolated from the aqueous phase (Scheme 2) with the formation of a light pink precipitate which gave similar spectroscopic data to that obtained previously.

Table 3
Fractional parameters for [(η^5-C_5H_4COONS)$Co(CO)_2$] (**2**)

Atom	x	y	z	U_{iso}
Co(1)	0.1839(1)	−0.30152(8)	0.86733(7)	0.0451
O(1)	0.1393(6)	0.0713(4)	0.7006(4)	0.0559
O(2)	0.4423(6)	0.0351(4)	0.8039(3)	0.0507
O(3)	0.4377(9)	0.3230(5)	0.7652(5)	0.0877
O(4)	0.6817(7)	−0.0734(4)	0.6049(4)	0.0640
O(11)	0.6131(9)	−0.4265(7)	0.8362(9)	0.1222
O(12)	0.0395(9)	−0.4549(6)	0.6842(5)	0.0955
N(1)	0.5467(7)	0.1127(5)	0.7029(4)	0.0503
C(1)	0.2282(8)	0.0113(5)	0.7856(5)	0.0429
C(2)	0.1417(8)	−0.0897(5)	0.8824(4)	0.0403
C(3)	0.247(1)	−0.1619(6)	0.9844(5)	0.0488
C(4)	0.105(1)	−0.2556(6)	1.0520(6)	0.0561
C(5)	−0.083(1)	−0.2498(6)	0.9926(6)	0.0567
C(6)	−0.0621(9)	−0.1489(6)	0.8869(5)	0.0504
C(7)	0.6661(9)	0.0493(6)	0.6080(5)	0.0475
C(8)	0.754(1)	0.1667(7)	0.5188(6)	0.0529
C(9)	0.669(1)	0.2963(7)	0.5711(7)	0.0744
C(10)	0.533(1)	0.2551(7)	0.6918(6)	0.0650
C(11)	0.442(1)	−0.3797(8)	0.8491(8)	0.0796
C(12)	0.096(1)	−0.3942(7)	0.7573(6)	0.0659



Scheme 2.

We digress to point out that previously Vollhardt [5] has shown one of the most elegant synthetic procedures for the preparation of polycyclic arenes by use of the organometallic reagent $CpCo(CO)_2$; during the reaction course three substituted alkynes are combined by the well-known mechanism of [2 + 2 + 2]. The mechanism was extensively investigated and involves the loss of the two carbonyl ligands as the first step to yield the active species "CpCo", which would combine three alkyne ligands in a selective cyclotrimerization process. We feel that the activated ester complex $[(\eta^5\text{-}C_5H_4CO\text{-}ONS)Co(CO)_2]$ (**2**) also contains labile carbonyl ligands, as the parent molecule $CpCo(CO)_2$, which could decoordinate during the reaction course with amines and/or amino-esters. This may explain the formation of the minor side products which do not contain any M–CO absorptions.

3. Conclusions

In this paper we have prepared the novel activated succinimidyl ester complex $[(\eta^5\text{-}C_5H_4COONS)Co(CO)_2]$ (**2**), and its reactivity as a potential conjugate with amino-esters has been demonstrated. It is worth mentioning that the M–CO bond energy [6] in these activated ester compounds remains essential in designing a stable "organometallic labelling synthon" in order to avoid any side reactions. In this respect we recently prepared a stable mono-cationic Ru-species bearing a succinimidyl leaving group but containing $[Cp^*Ru][CF_3SO_3]$ moiety rather than a metallocarbonyl fragment. These studies, as well as the identification of the pink complexes, will be the subject of future reports.

4. Experimental section

4.1. General procedures

All manipulations were carried out under argon atmosphere using Shlenk techniques. Solvents were purified and dried prior to use by conventional distillation techniques. All reagents obtained from commercial sources were used without further purification. ^1H and ^{13}C NMR spectra were recorded on a Bruker AM 250 MHz instrument. ^1H NMR chemical shifts are reported in parts per million referenced to residual solvent proton resonance. IR spectra were obtained on a Bruker spectrometer IR45 from samples prepared either on KBr discs or in CH_2Cl_2 solutions. All absorptions are expressed in wave numbers (cm^{-1}). Elemental analyses were performed by the Microanalytical Laboratory of the University of Paris VI. The organometallic carboxylic acid complex $[(\eta^5\text{-}C_5H_4COOH)Co(CO)_2]$ (**1**) was prepared following the synthetic procedure reported by Rausch and coworkers [3].

4.2. Synthesis of $[(\eta^5\text{-}C_5H_4COONS)Co(CO)_2]$ (2)

A solution of NHS (100 mg, 0.84 mmol.) in 10 cm^3 THF was added to an orange solution of $[(\eta^5\text{-}C_5H_4COOH)Co(CO)_2]$ (**1**) (171 mg, 0.76 mmol) in 20 cm^3 THF in the presence of DCC (167 mg, 0.84 mmol) and the reaction mixture was stirred over night. The aqueous phase was filtered then chromatographed on silica gel using CH_2Cl_2 as eluent to yield an orange band. The solvent was removed under vacuum to afford orange fluffy crystals. Yield 222 mg, 91%. Spectroscopic data for **2**. ^1H NMR ($(CD_3)_2CO$): δ 5.78 (t, $J_{H-H} = 2.5$ Hz, 2H, $-C_5H_4$), 5.69 (t, $J_{H-H} = 2.5$ Hz, 2H, $-C_5H_4$), 2.91 (s, 4H, $-CH_2-CH_2-$, –NS). ^{13}C NMR ($(CD_3)_2CO$) $T = 233$ K: δ 201.48 (M–CO), 169.74, 159.69 (CO), 106.50, 90.49, 85.18 ($-C_5H_4$), 24.91 ($-CH_2-CH_2-$, –NS). IR/KBr disc (ν cm^{-1}): (M–CO) 2038 (s), 1973 (s), (CO) 1773, 1735, 1725. Anal. Found: C, 44.92; H, 2.68; N, 4.39. $C_{12}H_8NO_6Co$ calc.: C, 44.86; H, 2.49; N, 4.36%.

4.3. Synthesis of $[(\eta^5\text{-}C_5H_4CONH\text{–}CH_2Ph)Co(CO)_2]$ (3)

100 μl, 1.55 mmol of benzylamine was added dropwise to an orange solution of $[(\eta^5\text{-}C_5H_4COONS)Co(CO)_2]$ (**2**) (100 mg, 0.31 mmol) in 20 cm^3 THF, and the mixture was stirred under argon. After 5 min a light pink precipitate was formed, the reaction was stirred for a total of 12 h, then the precipitate was filtered and washed with THF several times. This pink compound was collected and separated (15 mg). The filtrate was chromatographed on silica gel using CH_2Cl_2 as eluent, the orange band was collected and afforded red–orange crystals identified as $[(\eta^5\text{-}C_5H_4CONH\text{–}CH_2Ph)Co(CO)_2]$ (**3**). Yield 60 mg, 61%. Spectroscopic data for **3**. ^1H NMR ($(CD_3)_2CO$): δ 7.90 (b, 1H, –CONH–), 7.28 (m, 5H, C–H phenyl), 5.72 (t, 2H, $-C_5H_4$), 5.37 (t, 2H, $-C_5H_4$), 5.37 (t, 2H, $-C_5H_4$), 4.49 (d, 2H, $-CH_2-$). ^{13}C NMR ($(CD_3)_2CO$) $T = 233$ K: δ 202.30 (M–CO), 162.61 (CO), 137.51, 127.81, 126.69 (C-phenyl), 95.23, 86.11, 82.48 ($-C_5H_4$), 42.33 ($-CH_2-$). IR/KBr disc (ν cm^{-1}): (M–CO) 2026 (s), 1963 (s), (CON) 1634, 1554. Anal. Found: C, 59.15; H, 4.25; N, 4.77. $C_{15}H_{12}NOCo$ calc. C, 57.50; H, 3.83; N, 4.47%.

4.4. Synthesis of $[(\eta^5\text{-}C_5H_4CONH\text{-}(CH_2)_2\text{-}COOEt)\text{-}Co(CO)_2]$ (4)

The preparation of these compounds was performed in a similar way to that reported in the previous section. A solution of β-alanine ethylester chlorohydrate (58 mg, 0.37 mmol) was deprotonated by NEt_3. After removal of the white precipitate ($NEt_3 \cdot HCl$), the filtrate was added to an orange solution of $[(\eta^5\text{-}C_5H_4COONS)\text{-}CO(CO)_2]$ (2) (136 mg, 0.42 mmol) in 10 cm^3 THF. The reaction mixture was stirred for 12 h, during the course of the reaction a light pink precipitate was formed, which was separated (yield 10 mg). The filtrate was chromatographed on silica gel to afford an orange microcrystalline solid 4. Yield 60 mg, 44%. Spectroscopic data for 4. ^1H NMR ($CDCl_3$): δ 6.50 (b, 1H, –CONH–), 5.39 (t, 2H, $-C_5H_4$), 5.18 (t, 2H, –C5H4), 4.18 (q, 2H, $-COOCH_2-$), 3.63 (m, 2H, $-CON-CH_2-$), 2.60 (t, 2H, $-CONC-CH_2-$), 1.28 (t, 3H, $-COOC-CH_3$). ^{13}C NMR ($(CD_3)_2CO$) $T = 233$ K: δ 202.32 (M–CO), 172.00, 162.45 (CO), 95.42, 85.47, 82.47 ($-C_5H_4$), 60.10 ($-COOCH_2-$), 33.98, 32.71 ($-CH_2-CH_2-$), 13.17 (–CH3). IR/KBr disc (ν cm^{-1}): (M–CO) 2035 (s), 1962 (s), (CO-ester) 1728 (s), –CON 1628, 1560. Anal. Found: C, 48.88; H, 4.44; N, 4.40. $C_{13}H_{14}NO_5Co$ calc.: C, 48.29; H, 4.33; N, 4.33%.

4.5. X-ray crystallography

Suitable crystals of $[(\eta^5\text{-}C_5H_4COONS)Co(CO)_2]$ (2) were obtained by recrystallization from ether/hexane solution. Crystallographic data are collected in Table 1. Accurate cell dimensions and orientation matrices were obtained by least-squares refinement of 25 accurately centered reflections on a Nonius CAD4 diffractometer equipped with graphite-monochromated Mo K α radiation. No significant variations were observed in the two check reflections during data collection. The data were corrected for Lorentz and polarization effects; an empirical absorption correction (DIFABS) [7] was applied. Computations were performed using the CRYSTALS program [8], modified locally for a Microvax II computer. Scattering factors and corrections for anomalous absorption were taken from Ref. [9]. The structure was solved by direct methods (SHELXS) [10], and refined by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were then located on a difference Fourier map and their coordinates refined with an isotropic thermal parameter. The structure was refined to $R = 0.037$ and $R_w = 0.039$ with use of 1349 reflections for 207 least-squares parameters.

5. Supplementary material available

Anisotropic displacement parameters (Table S1), fractional parameters for H atoms (Table S2), observed and calculated structure factors (Table S3, 9 pages) are available. Ordering information is given on any current masthead page.

Acknowledgment

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