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Cyclopentadienylcobalt complexes of some azepines ☆

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Abstract

The complexes $[(C_5R_5)Co(2\text{-}5\text{-}\eta\text{-}C_6H_6NR')]$ (R′ = C(O)OEt; R = H (**6a**) or Me (**9a**)) are prepared from *N*-ethoxycarbonyl azepine and $[(C_5R_5)Co(C_2H_4)_2]$ (R = H (**5**) or Me (**8**)). On treatment with methoxide ion, **6a** is partially converted into the *N*-methoxycarbonyl derivative **6b**. Complex **9a** can be reduced with $LiAlH_4$ to give the *N*-methyl derivative **9b**. Complexes **6a**, **9a** and **9b** were shown to be fluxional in solution. The complexes undergo a degenerate valence tautomerization, which is much more facile in **9b** than in **6a** and **9a**. Restricted rotation around the N–C(O) bond was found in **6a**, leading to the presence of two diastereomers at low temperatures. No dinuclear azepine-bridged complexes were obtained from **6a**, **9a** and **9b** after treatment with **5** or **8**.

Keywords: Cobalt; Cyclopentadienyl; Azepine complexes; Fluxionality

1. Introduction

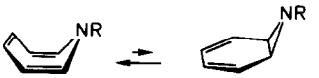
Compared with the myriad of transition metal complexes with cyclic polyenes the number of known complexes with *N*-heterocycles as π ligands is comparatively small. For example, in contrast with cyclopentadiene, which is frequently found in the η^4 coordination mode, complexes with η^4-pyrrole are very rare [1]. Although, as with pyridine, participation of all ring atoms and all the six π electrons in the bonding to the metal (i.e. η^5-pyrrole and η^6-pyridine respectively) is found more often, still only a limited number of such complexes has been reported [2].

In contrast with cycloheptatriene, the complex chemistry of its heterocyclic analog azepine has received rather limited attention. Free azepines **1** are in equilibrium with their valence tautomers, the benzene imides **2**. Generally, the azepine **1** is thermodynamically much favoured [3]. Unlike the aromatic pyrrole and pyridine, the polyene **1** is expected to behave much more like its all-carbon homocyclic analogue with respect to metal coordination, and the tendency to form a π complex involving the nitrogen atom should be low.

In 1965, Fischer and Rühle [4] reported the formation of iron tricarbonyl complexes of several azepines, including that of the parent system 1H-azepine **1a**. The latter ligand is very unstable and was generated in the complexed state from the *N*-ethoxycarbonyl derivative **3b**. A 2-5-η^4 coordination of the heterocycles to the metal was postulated from spectroscopic data [4]. This was confirmed by X-ray structure determinations of several derivatives [5].

Tricarbonyl chromium, molybdenum und tungsten complexes **4** of azepine-1-carboxylates have also been reported. In these complexes, the heterocycles adopt a 2-7-η^6 coordination mode to the metal [6].

Here we report the synthesis, structure and dynamic behaviour of some cyclopentadienyl and pentamethylcyclopentadienyl cobalt complexes of *N*-substituted azepines. We were especially interested in the possibility of trapping the benzene imine structure **2** in a $(C_5R_5)Co$ complex, and, in view of our studies of dinuclear cycloheptatriene complexes [7], in the potential of the azepines to function as bridging ligands.



1a, R = H
1b, R = C(O)OEt

2

Form 1.

☆ Dedicated to Professor Herbert Schumann on occasion of his 60th birthday.

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2. Results and discussion

2.1. Cyclopentadienylcobalt complexes of N-ethoxycarbonyl azepine and N-methoxycarbonyl azepine

Treatment of a solution of *N*-ethoxycarbonylazepine (**1b**) with one molar equivalent of the Jonas reagent $[CpCo(C_2H_4)_2]$ (**5**) at 20–50°C gave the complex **6a**, which was isolated as a red air-sensitive solid after column chromatography with about 60% yield.

The NMR spectra of **6a** are consistent with the asymmetric 2-5-η^4-coordination of the azepine seven-membered ring to the CpCo moiety. The ^1H NMR spectral data are summarized in Table 1. In the room-temperature ^1H and ^{13}C NMR spectra, the six azepine ring CH groups appear as six distinct resonances. A series of $^1H^1H$ decoupling experiments was carried out to assign the proton spectrum. From the decoupling pattern two chains of three vicinal protons each were established (Scheme 1). However, when the resonances a, d and f (Table 1) were irradiated, the intensity of the resonances c, b and e dropped to nearly zero, in addition to the decoupling effects elsewhere in the spectrum. The same effect was notable with resonances a, d and f when c, b and e respectively were decoupled. This behaviour is indicative of a transfer of spin saturation between the two respective sites [8], caused by chemical exchange. The exchange network established by these experiments is also indicated in Scheme 1.

The two low field ^1H resonances (e and f in Table 1) were considerably broadened at room temperature and coalesced on heating of the sample to 330 K. At this temperature, only the signals due to the Cp and ethyl protons remained sharp; all the others were broadened to various degrees. When the temperature was lowered to 220 K, only sharp ^1H resonances were observed (Table 1). However, the signals of the ethyl group are now split into two sets of triplets and quartets, with an approximate intensity ratio of 1:2. Likewise, resonances a and b of the azepine ring protons are also split into two overlapping sets of pseudo-doublets.

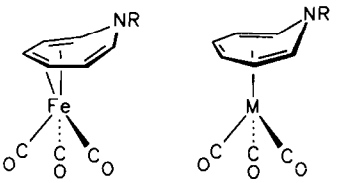
Table 1
^1H NMR data for **6a** (R = H; R′ = C(O)OEt), **6b** (R = H; R′ = C(O)OMe) and **9a** (R = Me; R′ = C(O)OEt)

	δ (ppm) (multiplicity)			
	6a [a]		**6b**, ambient [a]	**9a**, ambient [a]
	Ambient [a]	220 K [b]		
C_5R_5	4.56 (s)	4.86 (s)	4.54 (s)	1.70 (s)
NR′	4.01 (q), 0.92 (t)	4.07 (q) [c], 1.19 (t) [c], 4.14 (q) [d], 1.30 (t) [d]	3.38 (s)	4.07 (q), 0.96 (t)
CH a	3.47 (“t”)	3.66 (m)	3.44	2.71 (“t”)
CH b	3.68 (“t”)	3.91 (m)	3.66	3.24 (“t”)
CH c	4.36 (“t”)	4.66 (m)	4.34	4.02 (m)
CH d	4.90 (“t”)	4.79 (“t”)	4.88	4.95 (“t”)
CH e	6.55 (br)	6.08 (“d”) [c], 5.97 (“d”) [d]	6.52	5.75 (br)
CH f	6.74 (br)	6.32 (“d”) [c], 6.39 (“d”) [d]	6.72	6.79 (br)

[a] In C_6D_6.
[b] In CD_2Cl_2.
[c] Major isomer.
[d] Minor isomer.

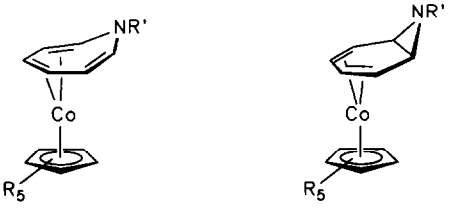
Obviously, two independent dynamic processes are operative in **6a**. A high energy process, which is relatively slow on the T_2 NMR time scale at room temperature, interconverts the two sets of vicinal CH protons (a–d–f and c–b–e). The residence time for the protons in the individual sites is comparable with their spin–lattice nuclear relaxation times T_1, and therefore spin saturation transfer is observed.

The spectral changes at high temperatures and the spin saturation transfer can be explained by a degenerate valence tautomerization **6** ⇌ **6′** (Scheme 2). The formation of more symmetric structures at high temperature, e.g. the η^4-benzene imine complex **7** can be ruled out since this should be accompanied by a shift of the resonances of the ethoxycarbonyl group. However, **7**



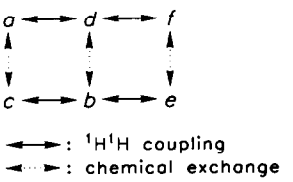
3a, R = H
3b, R = C(O)OEt

4, M = Cr, Mo, W

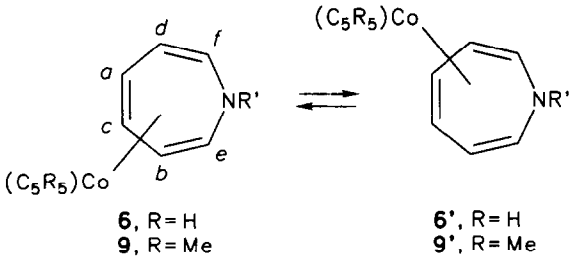


6a, R = H, R′ = C(O)OEt
6b, R = H, R′ = C(O)OMe
9a, R = Me, R′ = C(O)OEt
9b, R = Me, R′ = Me

7



Scheme 1.



6, R = H
9, R = Me

6', R = H
9', R = Me

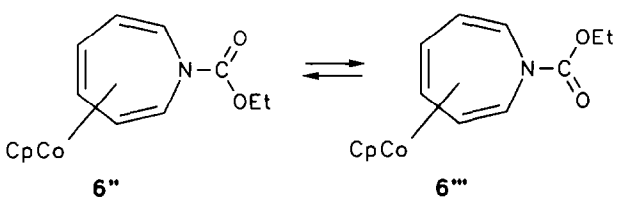
Scheme 2.

could well be a transition state or short-lived intermediate of the valence tautomerization.

The splitting of the resonances at low temperatures is conveniently explained by the hindered rotation of the ethoxycarbonyl group around the N–C(O) bond. The two conformations **6″** and **6‴** (Scheme 3) have different energies and are therefore not equally populated. From the equilibrium constant at 220 K, obtained by integration of the methyl and low field CH proton resonances, we calculate a difference in free enthalpy ΔG^0(220 K) of about 1.3 kJ mol^{-1}. Similar dynamic effects have been observed in **3**; ΔG^0 for the two rotamers was found to be about 1.7 kJ mol^{-1} at 215 K [9]. Restricted rotation about the N–C(O) bond was also observed in the metaltricarbonyl complexes **4** [6].

The proton resonances of the ring CH groups adjacent to the nitrogen atom (i.e. positions 2 and 7) should be affected most by the rotation of the carboxylate group. Therefore the resonances e and f (Table 1) can be assigned to these sites. By means of simple chemical shift considerations (the resonances of protons on carbon–carbon double bonds are shifted to a higher field on complexation; the "inner" protons of a η^4-diene ligand resonate at lower field than do the "outer" protons), and by application of the coupling and exchange networks in Scheme 1, the ^{1}H NMR spectrum of **6a** could be completely assigned. The assignment so obtained is indicated in Scheme 2.

When **6a** was heated with excess NaOMe in methanol for a few hours, about 50% conversion of **6a** into the *N*-methoxycarbonyl derivative **6b** was observed. Complexes **6a** and **6b** could not be separated from each other by column chromatography. In the ^{1}H NMR spectrum of the mixture a sharp singlet was observed for the methoxy group of **6b** at $\delta = 3.38$ ppm, in addition to a second Cp peak at $\delta = 4.54$ ppm. The



6″ **6‴**

Scheme 3.

azepine ring proton resonances of **6a** and **6b** are superimposed.

The reaction of **6a** with methoxide ion is markedly different from that of **3b**. In the latter case, decarboxylation to give the 1H-azepine complex **3a** took place under very similar reaction conditions [4].

2.2. Pentamethylcyclopentadienylcobalt complexes of N-ethoxycarbonyl azepine and N-methyl azepine

When **1b** was refluxed with [Cp*Co(C$_2$H$_4$)$_2$] (**8**) in toluene for several hours, the red complex **9a** was obtained with a good yield after chromatography.

The azepine part of the ^{1}H NMR spectrum of **9a** (Table 1) was very similar in general appearance to that of **6a**. It also showed an analogous broadening of the resonances at high temperature. An array of spin–spin couplings and saturation transfer identical with that of **6a** (Scheme 1) was observed at room temperature; the assignment of the proton spectrum is the same as for **6a**. Further proof for our assignment comes from a comparison of the proton chemical shifts of **6a** and **9a**. As expected, only the chemical shifts of the diene CH groups bonded to the cobalt atom are affected by the substitution of Cp* for Cp.

In the ^{13}C NMR spectrum of **9a** all the resonances expected for a static structure (on the T_2 NMR time scale) with an η^4-coordinated azepine were found. No attempts were made to assign this spectrum completely.

The carboxyl group in **9a** could be reduced with LiAlH$_4$ in ether to give the *N*-methyl derivative **9b**, which was isolated after chromatography with an 80% yield. The brownish-red solid is more air sensitive than its precursor **9a** but, unlike the free ligand *N*-methylazepine [3a], it is thermally stable.

At room temperature, only three broad resonances were observed in the ^{1}H and ^{13}C NMR spectra for the six CH groups of the azepine ring. On cooling to 200 K, the ^{1}H signals split into the six CH resonances expected for a static structure (Table 2). The frequency differences between the exchanging resonances in **6b** are

Table 2
Variable-temperature ^{1}H NMR data for **9b**

	δ (ppm) (multiplicity, relative intensity)	
	Room temperature [a]	220 K [b]
C_5Me_5	1.84 (s, 15)	1.83 (s, 15)
NMe	2.62 (s, 3)	2.85 (s, 3)
CH a	3.41 (m, 2)	2.57 (br, 1)
CH b	3.71 (br, 2)	3.06 (br t, 1)
CH c	3.41 (m, 2)	3.48 (br, 1)
CH d	3.71 (br, 2)	4.45 (br m, 2)
CH e	4.87 (br d, 2)	4.45 (br m, 2)
CH f	4.87 (br d, 2)	5.3 (br m, 1)

[a] In C_6D_6.
[b] In CD_2Cl_2.

comparable with those in **6a**. Hence, it can be safely assumed that the activation barrier which separates the valence tautomers **6** and **6′** from each other is considerably smaller in **6b** than in **6a**. Based on the present work and on data from the literature [9,10], we can conclude for the ease of the valence tautomerization that

$$[CpCo(\eta^4\text{-}C_7H_8)]\,(\mathbf{10a}) < \mathbf{6a}, \mathbf{9a}, \mathbf{3} < \mathbf{9b}$$

2.3. Attempted preparation of dinuclear complexes with azepines as bridging ligands

The mononuclear cycloheptatriene complexes $[(C_5R_5)M(1\text{-}4\text{-}\eta^4\text{-cycloheptatriene})]$ (M = Co; R = H, (**10a**) or Me (**10b**) (M = Rh; R = H (**11**)) are known to add another $(C_5R_5)Co$ fragment to give dinuclear cycloheptatriene bridged complexes [7,11]. Depending on R, two quite different types of product were obtained. For R = H the two metals adopt a *syn* position with respect to the bridging cycloheptatriene, whilst they are in an *anti* position for R = Me. In both types of complex, only the triene part of the cycloheptatriene is involved in the metal coordination.

This prompted us to test for an analogous reaction behaviour of the azepine complexes **6** and **9**. However, neither of these showed a tendency to take up another $(C_5R_5)Co$ fragment. When **6a** was treated with one equivalent of **5** and heated to 50°C, most of **5** was converted into its thermal decomposition product $[H(CpCo)_4CMe]$ [12], and 80% of **6a** could be recovered after chromatography. Likewise, 96% of **9a** and 75% of **9b** were recovered after **9a** and **9b** respectively had been heated with **8** at 100°C for several hours.

3. Experimental section

3.1. General procedures

All operations were carried out under an atmosphere of purified nitrogen (BASF R3-11 catalyst) using Schlenk techniques. Solvents were dried by conventional methods. Petroleum ether refers to the fraction with a boiling point of 40–60°C. The compounds $[(\eta\text{-}C_5R_5)Co(C_2H_4)_2]$ (R = H (**5**) [13] or Me (**8**) [14]) and *N*-ethoxycarbonyl azepine (**1b**) [15] were prepared as described in the literature. NMR spectra were obtained on a Bruker AC 200 instrument (200.1 MHz for ^1H; 50.3 MHz for ^{13}C). $^{13}C\{^1H\}$ spectra were measured using the *J*-modulated spin echo (JMOD) technique; multiplicities determined by this method are indicated as odd (u) or even (g). Mass spectra were measured in the electron impact ionization mode at 70 eV on a Finnigan MAT 8230 spectrometer.

3.2. Cyclopentadienylcobalt[2-5-η-N-ethoxycarbonyl)-azepine] (6a)

A solution of 320 mg (1.9 mmol) of (*N*-ethoxycarbonyl)azepine (**1b**) and 685 mg (3.8 mmol) of **5** in 100 ml of petroleum ether is heated at 50°C for 3 h. The dark-brown mixture is cooled to room temperature. ^1H NMR analysis shows the presence of **6a** and $[H(CpCo)_4(CMe)]$. Most of the solvent is removed in vacuo, the mixture deposited on a column of deactivated alumina (5% H_2O) and eluted with petroleum ether–toluene. The main red fraction is collected and again chromatographed on Al_2O_3–5% H_2O. Removal of solvent from the red fraction affords 270 mg (84%) of dark-red **6a**. $^{13}C\{^1H\}$ NMR (JMOD, in CD_2Cl_2): δ 14.64 (g, Me), 48.48 (g, br, CH), 62.02 (g, br, CH), 62.88 (u, CH_2), 65.95 (g, CH), 81.02 (g, Cp), 86.95 (g, CH), 107.91 (g, CH), 120.12 (g, CH) ppm; quarternary carbon atom not observed. Mass spectroscopy (MS); *m/z* 289 (34%, M^+), 243 (11, $[CpCo(C_6H_6NCOH)]^+$), 124 (100, $[CpCo]^+$), 65 (9, Cp^+), 59 (26, Co^+). Anal. Found: C, 58.68; H, 5.67; N, 4.91. $C_{14}H_{16}CoNO_2$ (289.219) Calc.: C, 58.14; H, 5.58; N, 4.84%.

3.3. Reaction of 6a with methoxide ion

60 mg (0.21 mmol) of **6a** is added to a solution of NaOMe in methanol (prepared from 16 mg (0.7 mmol) of Na and 2 ml of methanol). The mixture is heated to 50°C for 5 h. After cooling to room temperature the solution is directly chromatographed on alumina. A red fraction is obtained (51 mg after removal of solvent), which is identified by ^1H NMR analysis as an approximately 1:1 mixture of **6a** and [CpCo{(N-methoxycarbonyl)azepine}] (**6b**).

3.4. Pentamethylcyclopentadienylcobalt[2-5-η-(N-ethoxycarbonyl)azepine] (9a)

A solution of 407 mg (2.5 mmol) of **1b** and 1.25 g (5.0 mmol) of **8** in 100 ml of toluene is refluxed for 2 h. The dark-brown mixture is cooled to room temperature and filtered. The volume of the filtrate is reduced in vacuo and the solution chromatographed on Al_2O_3–5% H_2O using toluene as eluant. Removal of solvent from the red band affords 376 mg (92%) of dark-red **9a**. $^{13}C\{^1H\}$ NMR (JMOD, in C_6D_6): δ 10.00 (g, $C_5\mathit{Me}_5$), 14.48 (g, Me), 53.00 (g, CH), 62.10 (u, CH_2), 67.40 (g, br, CH), 68.99 (g, CH), 89.48 (g, CH), 90.50 (u, C_5Me_5), 107.50 (g, CH), 119.95 (g, br, CH), 153.91 (u, $\mathit{C}(O)O$) ppm. MS: *m/z* 359 (53%, M^+), 286 (16, $[Cp^*Co(C_6H_6N)]^+$), 209 (51), 194 (10, $[Cp^*Co]^+$), 192 (70), 133 (42), 59 (9, Co^+).

3.5. Pentamethylcyclopentadienylcobalt[2-5-η-(N-methyl)azepine] (9b)

80 mg (2 mmol) of $LiAlH_4$ are added in small portions to a solution of 360 mg (1 mmol) of **9a** in 50 ml of ether. The mixture is refluxed for 3 h and cooled to room temperature; then the solvent is removed in vacuo. The residue is extracted with petroleum ether. The extract is chromatographed on Al_2O_3–5% H_2O with toluene–tetrahydrofuran as eluant. The orange–red fraction affords 246 mg (82%) of **9b** after removal of the solvent. $^{13}C\{^1H\}$ NMR (JMOD, in CD_2Cl_2): δ 10.54 (g, C_5Me_5), 45.67 (g, NMe), 70.9 (g, br, 2CH), 80.7 (g, br, 2CH), 89.2 (u, C_5Me_5), 105.9 (g, br, 2CH) ppm. MS: m/z 301 (62%, M^+), 221 (41), 194 (100, $[Cp^*Co]^+$), 192 (24), 133 (24).

Acknowledgments

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