η^4-Complexes of 4,7-Dihydroacepentalene: Facile Degenerate Haptotropic Rearrangement of (η^5-Cyclopentadienyl)(η^4-4,7-dihydroacepentalene)cobalt(I) in Contrast to its Tricarbonyliron Counterpart

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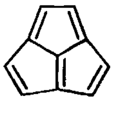
The (cyclopentadienyl)cobalt(I) complex **4** of the 4,7-dihydroacepentalene[++)] derivative **2b** has been prepared by the reaction of the ligand with (cyclopentadienyl)bis(ethene)cobalt(I). NOE experiments indicate a complexation at the convex face of the polyolefinic ligand. ^{1}H-NMR spectra establish a degenerate haptotropic rearrangement with CpCo migration from one diene unit to the adjacent one. The activation energy of this process is estimated to be 15 kcal/mol. An X-ray crystal structure determination of (η^4-4,7-dihydroacepentalene)tricarbonyliron derivative **3a** shows a distorted coordination of $Fe(CO)_3$ at the convex face of the ligand, too.

Haptotropic rearrangements of cyclic as well as linear polyolefin metal complexes have been investigated for some time[1)]. Recently, Vollhardt et al.[2)] have reported on the degenerate haptotropic rearrangement of the (η^5-cyclopentadienyl)cobalt(I) (CpCo) complex of an η^4-coordinated linear 1,3,5-hexatriene. The activation energy of 25.6 ± 1.2 kcal/mol has been found to be 5–8 kcal/mol smaller than for the corresponding tricarbonyliron [$Fe(CO)_3$] complex. For the CpCo complex of acepentalene (**1**) Hofmann et al.[3)] have calculated a degenerate haptotropic rearrangement of the CpCo fragment from one ring to another to occur with an activation energy of about 25 kcal/mol. As a model for the cross-conjugated polyolefinic system present in acepentalene (**1**) and its complexes, 4,7-dihydroacepentalenes **2**[4)] have been prepared with the intention to observe a degenerate haptotropic rearrangement on the cross-conjugated triene unit. However, the $Fe(CO)_3$ complex **3a** does not show a fluxionality up to 150°C[5)].

As the propensity to migration appeared to be higher for CpCo complexes than for their $Fe(CO)_3$ analogues[2)], it seemed reasonable to use the CpCo complex of a tetraene **2**. In this paper we report on the first degenerate haptotropic rearrangement on a coordinated cross-conjugated triene unit and on the first crystal structure determination of a dihydroacepentalene complex.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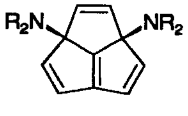

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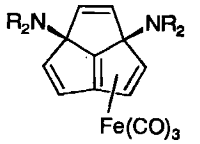

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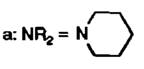
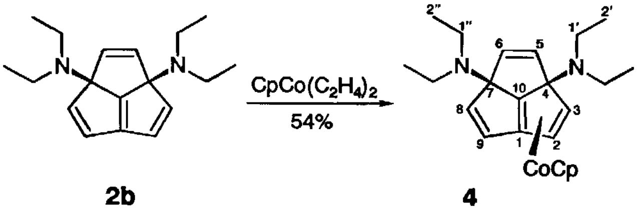


b: $NR_2 = NEt_2$

The CpCo complex of the bis(diethylamino)tetraene **2b** is obtained by reaction of **2b** with $CpCo(C_2H_4)_2$[6)] as a dark brown oil in 54% yield. **4** has been identified on the basis of its spectroscopic data, and the molecular formula has been established by high-resolution mass spectrometry. A difference NOE experiment shows an interaction between the Cp and the methyl protons, indicating the CpCo fragment to be attached to the *exo* face of the convex triene ligand as the diethylamino groups.



2b **4**

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[++)] The numbering of the ring system corresponds to the tricyclodecatetraene nomenclature used in the Exp. Part. Thus, 4,7-substitution would be 2a,4a-substitution in acepentalene numbering.

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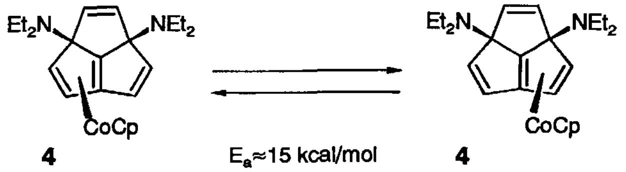
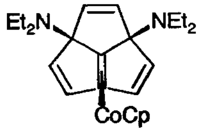
The ^{1}H-NMR spectrum of CpCo complex **4** is temperature-dependent. At 253 K the spectrum (80 MHz, [D$_8$]-toluene) is rather similar to that of the corresponding Fe(CO)$_3$ complex **3b**[5]. With increasing temperature an exchange phenomenon is observed. The chemical shift difference of 5-H and 6-H (AB line system) becomes smaller, and the signals finally coalesce. Similarly, the signals assigned to the methyl protons are clearly resolved triplets at 253 K and coalesce with rising temperature. At 333 K a rather simple spectrum is observed, which does not yet show the signals of 2(9)-H and 3(8)-H. At 373 K signals assignable to the latter protons appear; however, the quality of the spectrum suffers from the beginning thermal decomposition of the complex. Cooling below the coalescence temperature reconstitutes the original spectrum.

These observations indicate a degenerate haptotropic rearrangement of complex **4**, in which the CpCo fragment changes its place from one diene unit to the adjacent one. From the coalescence temperature of the signals assigned to the methyl protons (298 K) and the chemical shift difference the activation energy of the process has been estimated to be 15 kcal/mol[7]. The coalescence temperature of 5-H and 6-H (298 K) leads to a similar value for the activation energy; however, the chemical shift difference for 5-H and 6-H below the coalescence temperature ($\Delta\delta = 0.12$) is within the range of the normal temperature dependence of the chemical shift. Therefore, the value calculated from the methyl resonance signals ($\Delta\delta = 0.32$) appears to be more reliable. The same results are obtained by measurements of the ^{1}H-NMR spectrum in [D$_8$]tetrahydrofuran instead of [D$_8$]toluene.



Haptotropic rearrangements, in which a metal atom migrates from one ring to an adjacent one, have been used to explain the course of some reactions[8] and have been the subject of theoretical studies[3]. So far, only a few systems are known, for which such a rearrangement has been proved by experiment[9,10]. (Naphthalene)tricarbonylchromium and some of its derivatives are so far the only systems, for which a *degenerate* rearrangement of this kind has been detected[10]. However, in these cases it has been necessary to break the molecular symmetry by substitution with deuterium or other groups for the detection of the rearrangement. In contrast, **4** is the first system, which allows direct monitoring of a degenerate haptotropic rearrangement by NMR spectroscopy.

For degenerate haptotropic rearrangements in (naphthalene)tricarbonylchromium systems activation energies of about 30 kcal/mol have been predicted by calculations[3b] and determined experimentally[10]; this value is considerably higher than that for **4**. According to calculations of Albright et al.[3b], the Cr(CO)$_3$ fragment in (naphthalene)tricarbonylchromium(0) does not migrate directly from one ring to the other, but takes a more complicated route which involves almost complete dissociation from the ligand. In contrast to naphthalene, the ligand of **4** contains a *cross-conjugated* system of two anellated cyclopentadiene rings[11], the central double bond of which suffers from a symmetric out-of-plane bending (oop bending)[12].



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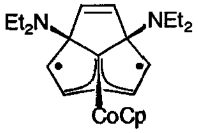

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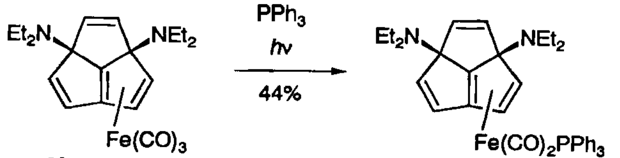
If one assumes an intramolecular rearrangement, the mechanism of the degenerate haptotropic rearrangement of **4** might involve a 16-e species like **5** or a diradical 18-e species like **6** as an intermediate or a transition state. While **6** would be a coordinatively saturated trimethylenemethane complex, the 16-e compound **5** might be stabilized to some extent by interaction with the lone pairs of the amino groups. However, a differentiation between **5** and **6** would refer to the position of the CpCo fragment relative to the bond C(1)–C(10), and there is no obvious criterion to decide which description of the intermediate or transition state is more correct.

At a first glance, a complete decomplexation of the ligand from CpCo followed by recomplexation of either one of the two diene units may appear as a possible alternative. However, such a decomplexation should take place stepwise. The less strained double bond C(2)–C(3) should be decomplexed first[13], and this would lead to the proposed intermediate **5**. As this process should be reversible, the complete decomplexation of the polyolefinic ligand does not seem very likely. If a complete decomplexation occured, **5** should be an intermediate in the subsequent recomplexation, too. The complete decomplexation would therefore be a detour without any obvious reason. In addition, formation of CpCo clusters was not observed, although these should be formed from intervening of decomplexed CpCo fragments. Finally, Bönnemann[14] showed that a decomplexation of diolefinic ligands of CpCo complexes usually occurs at significantly higher temperatures than that of the process observed here. With regard to the suggestion of Vollhardt[2] we note that a "walk" mechanism is impossible in cross-conjugated systems like **4**.

There are at least two reasons, why the activation energy for the degenerate haptotropic rearrangement in **4** should be so much smaller than for (naphthalene)tricarbonylchromium (30 kcal/mol) and for the CpCo complex of a linear 1,3,5-hexatriene (25.6 kcal/mol). On the one hand, due to the symmetric oop bending, **4** is a strained species of rather high energy[12], and on the other hand, an intermediate or transition state like **5** or **6** should clearly be less strained, thus lower in energy. Both effects would lead to a decrease in activation energy.

A confirmation of the hypothesis that a 1,10-η^2-coordinated 4,7-dihydroacepentalene should be favoured over a 2,3-η^2-coordinated one, has been found earlier, when complexes **3** were reduced with sodium metal to the corresponding (1,10-η^2-4,7-dihydroacepentalene)ferrates(−II)[5]. To test, whether the corresponding CpCo complex reacts in an analogous manner, **4** has been treated with sodium metal in [D$_8$]tetrahydrofuran under ESR and NMR control. After 6 d and 19 h an ESR spectrum is obtained, which shows a signal at g = 2.1444 ($\Delta\nu_{1/2}$ = 150 G) indicating the formation of a radical anion $\mathbf{5}^{\bullet -}$ with considerable electron density on the metal atom. Further exposure to sodium results in NMR spectra of poor quality, finally resulting in a broad singlet at δ = 5.7.



3b **7**

Due to the lack of proton-bearing ligands at the iron atom, it has previously been impossible to assign the position of the Fe(CO)$_3$ group in complexes **3** in a similar manner as for the CpCo analogue **4**. To facilitate an NOE ^{1}H-NMR experiment, a triphenylphosphane ligand has been introduced into complex **3b** by a photochemically induced ligand exchange reaction. The (triphenylphosphane)dicarbonyliron complex **7** is obtained in 44% yield and was subjected to NOE measurements. In contrast to what has been expected for an arrangement with the Ph$_3$P(CO)$_2$Fe group on the same convex side as the Et$_2$N groups, no NOE is observed between the *ortho* protons of the PPh$_3$ ligand and those of the diethylamino groups. This leaves open the possibility of the Ph$_3$P(CO)$_2$Fe and Fe(CO)$_3$ group in **7** and **3**, respectively, being attached on the concave side of the tricyclic ligand, i.e. opposite to the diethylamino groups. Such negative evidence like a non-observable NOE, however, has to be interpreted with great care.

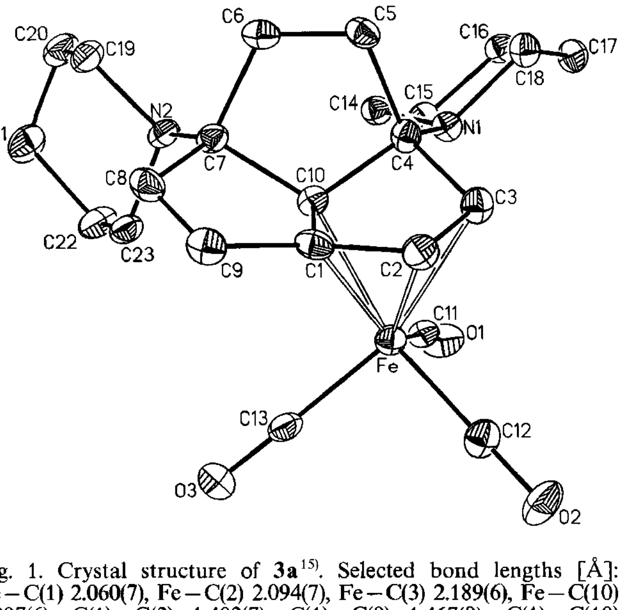


Fig. 1. Crystal structure of **3a**[15]. Selected bond lengths [Å]: Fe−C(1) 2.060(7), Fe−C(2) 2.094(7), Fe−C(3) 2.189(6), Fe−C(10) 2.097(6), C(1)−C(2) 1.402(7), C(1)−C(9) 1.467(8), C(1)−C(10) 1.450(6), C(2)−C(3) 1.424(7), C(3)−C(4) 1.537(6), C(4)−C(5) 1.542(10), C(4)−C(10) 1.498(6), C(4)−N(1) 1.476(7), C(5)−C(6) 1.322(7), C(6)−C(7) 1.545(8), C(7)−C(8) 1.551(7), C(7)−C(10) 1.556(8), C(7)−N(2) 1.462(6), C(8)−C(9) 1.332(7). Selected bond angles [°]: C(1)−C(2)−C(3) 105.7(4), C(1)−C(10)−C(4) 107.2(4), C(1)−C(10)−C(7) 103.5(4), C(2)−C(1)−C(9) 139.8(5), C(2)−C(1)−C(10) 108.2(4), C(2)−C(3)−C(4) 109.7(4), C(3)−C(4)−C(10) 95.2(4), C(4)−C(10)−C(7) 113.7(5), C(9)−C(1)−C(10) 110.3(4), C(8)−C(7)−C(10) 102.1(4)

Table 1. Atomic coordinates [Å × 10^4] and equivalent isotropic displacement factors [Å^2 × 10^3] for **3a**. * Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U_{eq}
Fe	1129(1)	9178(1)	2758(1)	24(1)*
O(1)	4766(5)	8925(4)	2635(3)	39(2)*
O(2)	-331(5)	12448(4)	2641(3)	47(2)*
O(3)	265(5)	8266(4)	4939(3)	44(2)*
N(1)	4187(5)	7572(4)	1033(3)	23(2)*
N(2)	3418(5)	4272(4)	3186(3)	26(2)*
C(1)	-167(6)	7973(6)	2558(4)	27(2)*
C(2)	-548(7)	9364(6)	1836(4)	30(2)*
C(3)	1079(6)	9297(6)	1214(4)	28(2)*
C(4)	2362(6)	7625(5)	1329(4)	24(2)*
C(5)	2046(6)	6498(6)	943(4)	26(2)*
C(6)	1879(6)	5336(6)	1677(4)	27(2)*
C(7)	1869(6)	5427(5)	2733(4)	25(2)*
C(8)	51(7)	5546(7)	3366(4)	30(3)*
C(9)	-1066(7)	6993(6)	3256(4)	32(3)*
C(10)	1717(6)	7118(5)	2408(3)	22(2)*
C(11)	3380(7)	8977(5)	2634(4)	27(2)*
C(12)	207(6)	11176(6)	2687(4)	32(3)*
C(13)	605(7)	8639(6)	4089(4)	30(2)*
C(14)	5523(6)	6179(5)	1519(4)	25(2)*
C(15)	7288(6)	6355(6)	1281(4)	29(2)*
C(16)	7867(6)	6715(6)	164(4)	29(2)*
C(17)	6424(6)	8076(6)	-364(4)	30(2)*
C(18)	4663(6)	7873(6)	-63(4)	27(2)*
C(19)	3717(7)	2692(6)	3233(4)	33(2)*
C(20)	5507(7)	1643(6)	3537(4)	37(3)*
C(21)	5659(8)	1751(6)	4542(4)	41(3)*
C(22)	5225(7)	3403(6)	4523(5)	39(3)*
C(23)	3438(7)	4437(6)	4162(4)	29(2)*

A single crystal X-ray analysis of **3a** has established the structure as presented in Figure 1 with the tricarbonyliron fragment on the convex face of the tricyclic ligand. It shows the same orientation in iron complexes of type **3** and the cobalt complex **4**. Atomic coordinates are given in Table 1.

The structure shows a distorted coordination of the olefinic ligand to the tricarbonyliron unit. This is documented by significant deviations from the usual structural characteristics of (diene)tricarbonyliron complexes[16].

Usually, the Fe−C$_{\text{diene}}$ bond lengths in these complexes are 2.03−2.08 Å for the inner and 2.10−2.16 Å for the outer carbon atoms[16]. In **3a** the bond Fe−C(10) is rather short [2.097(6) Å], Fe−C(3) is rather long [2.189(6) Å], and Fe−C(2) also is rather long [2.094(7) Å]. This indicates the tricarbonyliron unit to be located much closer to the bond C(1)–C(10) than to the bond C(2)–C(3). In accord with this, the bond C(1)–C(10) [1.450(6) Å] is longer than the bond C(2)–C(3) [1.424(7) Å] with a standard range of 1.394–1.434 Å[16]. The coordination of the double bond C(1)–C(10) seems to be stronger than that of C(2)–C(3), giving C(1)–C(10) more single bond character than C(2)–C(3). The weaker coordination of the double bond C(2)–C(3) is in accord with the experimental finding, that upon reduction with sodium the double bond C(2)–C(3) is selectively decomplexed with formation of a η^2 coordination at the double bond C(1)–C(10)[5].

Another remarkable feature is that the single bond C(7)–C(10) is much longer [1.556(8) Å] than the bond C(4)–C(10) [1.498(6) Å]. The bond length C(4)–C(10) in **3a** compares well with the corresponding value in **8**, the only uncomplexed 4,7-dihydroacepentalene derivative with known molecular structure[17]. In contrast, the bond length C(7)–C(10) in **3a** is remarkably similar to the corresponding bond length in triquinacene (1.558 Å)[18].

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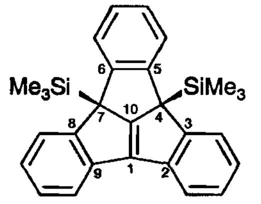

The convex shape of the system makes it likely that a partial planarisation of the carbon skeleton occurs upon coordination of the diene unit to a metal. This would bend the π-orbital lobes on the convex side of the ligand closer together, which is necessary for an effective coordination. In addition, the symmetric oop bending in the ligand[12] would be reduced to some extent. One possible measure of the degree of oop bending are the interplanar angles α = C(1)–C(4)–C(10)/C(1)–C(7)–C(10) and β = C(2)–C(1)–C(10)/C(9)–C(1)–C(10). In the uncomplexed derivative **8** these are α = 136.9° and β = 147.6°[17]. Surprisingly, a planarisation in **3a** relative to the structure of **8** is observed only at C(1): The interplanar angle in **3a** is β = 168.2°. In contrast, in **3a** for C(10) an enhanced pyramidisation is found, the interplanar angle being α = 120.4°.

The deformation of the ligand in **3a** becomes also clear by inspection of the dihedral angles along the central double bond. While the dihedral angle C(9)–C(1)–C(10)–C(4) is 141.6° for **3a** and 141.9° for **8**, the dihedral angle C(2)–C(1)–C(10)–C(7) is 147.6° for **3a** and 142.6° for **8**. Apparently, the bond C(7)–C(10) is not only unexpectedly long (vide supra), but also contributes more to the oop bending in **3a** than the bond C(4)–C(10).

Any structural comparison between compounds **3a** and **8** has to take into account, that the peripheral double bonds in **8**, but not in **3a**, are incorporated in aromatic delocalized π systems. This presumably lengthens these bonds as compared to those in **3a**, thus reducing the molecular strain.

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Experimental

All operations were performed under argon in flame dried reaction vessels. Solvents were dried and deoxygenated by stirring over NaAl(C_2H_5)$_4$ and subsequent distillation. – ^{1}H NMR: Bruker AM 200 (200.1 MHz), WP 80 (80 MHz). – ^{13}C NMR: Bruker WM 300 (75.46 MHz). Chemical shifts refer to δ_{TMS} = 0.00 according to the chemical shift of residual solvent signals. – ESR: Varian E-9 (X-Band). – IR: Nicolet 7199 FT-IR. – MS: Varian 311 A. – HRMS: Finnigan MAT 8230.

Crystallisation of **3a**: In a Schlenk tube 43 mg (0.1 mmol) of **3a**, which had been purified by column chromatography (15 g silica gel, column 25 × 2 cm, diethyl ether), was heated at 0.0005 mbar to 45°C for 2 h and then to 120°C. Sublimed **3a** (30 mg, 70%) was transferred to a slim Schlenk tube and sublimed again at 90°C/0.0005 mbar. Yellow crystals deposited on the inner wall of the tube, predominantly as single crystals (13 mg, 30%).

Crystal Structure Determination of **3a**: Crystal dimensions $0.09 \times 0.05 \times 0.03$ mm^3, measured on a Nicolet R3m/V diffractometer with Mo-K_α radiation at 133 K. Cell dimensions, refined from the diffractometer angles of 29 centered reflections ($3° \leq 2\Theta \leq 15°$), a = 8.471(5), b = 9.985(7), c = 14.347(10) Å, α = 71.16(5), β = 75.09(5), γ = 64.77(4)°, V = 1028.7(5) Å^3; Z = 2, $d_{cal.}$ = 1.402 gcm^{-3}, μ = 0.76 mm^{-1}, triclinic, space group $P\bar{1}$, data collection of 2687 unique intensities ($2\Theta_{max}$ = 45°), 2093 observed [$F_o > 4\sigma(F)$], structure solution with direct methods and refinement with full matrix least squares (SHELXTL-PLUS, release 3.43), 288 parameters, rigid groups for hydrogen atoms at the piperidine ring with common isotropic U values, the other hydrogen atomic positions were taken from a Fourier map and refined without constraints. Anisotropic U values were refined for all other atoms. R = 0.047, R_w = 0.048, $w^{-1} = (\sigma^2(F_o) + 9.55 \cdot 10^{-4} \cdot F_o^2)$. Maximal residual electron density 0.435 eÅ^{-3}.

{1,2,3,10-η^4-4,7-Bis(diethylamino)tricyclo[5.2.1.0^{4,10}]deca-1(10),2,5,8-tetraene}(η^5-cyclopentadienyl)cobalt(I) (**4**): In a flame-dried reaction flask equipped with an argon inlet and a magnetic stirring bar, 200 mg (0.74 mmol) of 4,7-bis(diethylamino)-4,7-dihydroacepentalene (**2b**)[4] and 250 mg (1.38 mmol) of (cyclopentadienyl)bis(ethene)cobalt(I)[6] were stirred in 10 ml of pentane at –78°C and are then allowed to warm to 25°C for 5 h. After 4 h of stirring at 25°C, the reaction mixture was chromatographed on silica gel (Kieselgel 60, 40–63 μm, 230–400 mesh ASTM, Merck, column 40 cm × 2 cm), which had been deactivated with a 1% solution of dimethylamine in diethyl ether followed by flushing with pentane. Elution with pentane yielded first some unreacted **2b**, then with pentane/diethyl ether (10:1) **4** was eluted. The solvent was evaporated into a cold trap at 150 mbar, and the residual dark brown oil was dried at 0.001 mbar. Yield 160 mg (54%) of **4**. – IR (film): $\tilde{\nu}$ = 3096 cm^{-1} (s, Cp), 3045 (m, =CH), 2963 (s), 2929 (m), 2866 (m), 2812 (m), 1564 (s), 1452 (s), 1370 (m, Et–N), 1206 (s, Et–N), 1109 (m, Co–Cp), 1065 (s, Et–N), 1010 (m, Co–Cp), 799 (s, Co–Cp). – ^{1}H NMR (200 MHz, [D$_8$]toluene, 223 K): δ = 1.04 (t, 6H, 2′-H), 1.36 (t, 6H, 2″-H), 2.20–3.25 (m, 8H, 1′-, 1″-H), 3.32 (bs, 1H, 3-H), 4.83 (bs, 1H, 2-H), 4.87 (s, 5H, Cp-H), 5.53 (d, 1H, 6-H, $^3J_{5,6}$ = 5.9 Hz), 5.65 (d, 1H, 5-H), 6.34 (d, 1H, 8-H, $^3J_{8,9}$ =

5.3 Hz), 6.64 (d, 1H, 9-H). – ^{1}H NMR (80 MHz, 223 K, [D$_8$]toluene): as at 200 MHz, but $^3J_{2,3}$ = 2.6 Hz. – ^{13}C NMR (75.46 MHz, [D$_8$]tetrahydrofuran, 223 K): δ = 16.1 (q, C-2′ or C-2″, $^1J_{C,H}$ = 125 Hz), 17.8 (q, C-2′ or C-2″, $^1J_{C,H}$ = 125 Hz), 45.5 (t, C-1′ or C-1″, $^1J_{C,H}$ = 131 Hz), 48.3 (t, C-1′ or C-1″, $^1J_{C,H}$ = 131 Hz, 53.5 (s, C-10), 67.8 (d, C-8 or C-9, $^1J_{C,H}$ = 168 Hz), 68.8 (d, C-8 or C-9, $^1J_{C,H}$ = 172 Hz), 80.0 (d, Cp, $^1J_{C,H}$ = 175 Hz), 84.3 (s, C-4 or C-7), 87.5 (s, C-4 or C-7), 108.5 (s, C-1), 129.1 (d, C-5 or C-6, $^1J_{C,H}$ = 164 Hz), 136.1 (d, C-5 or C-6, $^1J_{C,H}$ = 164 Hz), 140.6 (d, C-2 or C-3, $^1J_{C,H}$ = 160 Hz), 145.1 (d, C-2 or C-3, $^1J_{C,H}$ = 163 Hz). – MS (70 eV): *m/z* (%) = 394 (31) [M$^+$], 368 (15) [M – C_2H_2], 365 (33) [M – C_2H_5], 339 (65) [M – C_2H_5 – C_2H_2], 323 (26) [M – $N(C_2H_5)_2$ + H], 294 (100) [M – C_2H_5 – $N(C_2H_5)_2$ + H], 128 (22), 124 (21) [CoCp].

$C_{23}H_{31}CoN_2$ Calcd. 394.18193
Found 394.18209 ± 0.0006 (HRMS)

Reduction of **4** *with Sodium Metal:* A solution of 20 mg (0.05 mmol) of **4** in 1 ml of [D$_8$]tetrahydrofuran was transferred to the lower part of a constricted NMR tube, and 4 cm of thin sodium wire were introduced into the upper part of the tube to reside above the constriction. The tube was sealed under vacuum, and the sodium wire was activated by partial melting. A control ^{1}H-NMR spectrum was taken before the reaction was started, then the solution was brought into contact with the sodium wire at –78 °C. Frequent checks by ^{1}H-NMR measurements showed a decrease in the resolution. After 6 d and 19 h an ESR spectrum was obtained. ESR (X Band): g = 2.1444 ($\Delta\nu_{1/2}$ = 150 G). Then the reaction proceeded rather slowly, and the tube was allowed to warm to room temp. After 4 months, the ^{1}H-NMR spectrum showed a singlet at δ = 5.7 besides some signals assignable to ethyl groups.

{1,2,3,10-η^4-4,7-Bis(diethylamino)tricyclo[5.2.1.$0^{4,10}$]deca-1(10),2,5,8-tetraene}dicarbonyl(triphenylphosphane)iron(0) (**7**): A solution of 100 mg (0.25 mmol) of **3b**[5] and 78 mg (0.3 mmol) of triphenylphosphane in 1 ml of THF was irradiated at 25 °C for 5 h (Duran, 150 W Hg medium-pressure lamp). The solvent was evaporated into a cold trap, and the residue was dissolved in pentane and subjected to column chromatography (silica gel, deactivated with a dilute solution of diethylamine in diethyl ether, then flushed with pentane, column 20 cm × 1 cm). Excess triphenylphosphane was first eluted with pentane, then **7** is eluted with pentane/diethyl ether (10:1). 68.3 mg (44%) of **7**, yellow solid, m.p. 224 °C. – IR (film): $\tilde{\nu}$ = 1980 cm^{-1} (s, CO), 1917 (s, CO). – ^{1}H NMR (200 MHz, CDCl$_3$): δ = 1.01 (m, 12H, 2′-, 2″-H), 2.00 (m, 2H, 1′-H), 2.32 (q, 2H, 1′-H, $^3J_{1',2'}$ = 6.9 Hz), 2.37 (dd, 1H, 3-H, $^3J_{2,3}$ = 3.1, $J_{3,P}$ = 1.7 Hz), 2.67 (q, 4H, 1″-H, $^3J_{1'',2''}$ = 6.9 Hz), 4.45 (dd, 1H, 2-H, $J_{2,P}$ = 1.7 Hz), 5.62 (d, 1H, 6-H, $^3J_{5,6}$ = 6.0 Hz), 5.88 (d, 1H, 5-H), 6.52 (d, 1H, 8-H, $^3J_{8,9}$ = 5.4 Hz), 7.3–7.6 (m, 15H, Ph). – ^{31}P NMR (81.0 MHz, CDCl$_3$): δ = 76.8. – MS (70 eV): *m/z* (%) = 616 (3) [M$^+$ – CO], 588 (15) [M$^+$ – 2 CO], 354 (86) [M$^+$ – CO – PPh$_3$], 326 (50) [M$^+$ – 2 CO – PPh$_3$], 255 (100) [M$^+$ – Fe(CO)$_2$PPh$_3$ – CH$_3$].

$C_{36}H_{41}FeN_2P$ [M – 2 CO] Calcd. 588.2357
Found 588.2441 ± 0.008 (HRMS)

CAS-Registry-Nummern

2b: 135638-93-6 / **3a**: 135684-41-2 / **3b**: 135684-42-3 / **4**: 135645-41-9 / **5** (radical anion): 135645-42-0 / **7**: 135645-43-1 / CpCo(C_2H_4)$_2$: 69393-67-5

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