the mixture which was stirred at room temperature for 3 h. The resulting white precipitate of potassium 3-dithiocarboxy-3-aza-5-aminopentanoate dihydrate was filtered, washed with acetone and air dried [yield: 3.50 g (65.3%)]. The precipitate was recrystallized twice from hot water and single crystals suitable for X-ray analysis were obtained after cooling in a refrigerator overnight.

Crystal data

$K^+.C_5H_9N_2O_2S_2^-.2H_2O$
$M_r = 268.39$
Monoclinic
$P2_1/c$
$a = 13.8156\,(12)$ Å
$b = 6.947\,(2)$ Å
$c = 12.4225\,(14)$ Å
$\beta = 111.66\,(1)^\circ$
$V = 1108.0\,(4)$ Å^3
$Z = 4$
$D_x = 1.609$ Mg m^{-3}
$D_m = 1.606$ Mg m^{-3}
D_m measured by flotation in a $CHBr_3/n\text{-}C_4H_{10}$ mixture
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9.76\text{–}15.96^\circ$
$\mu = 0.848$ mm^{-1}
$T = 293\,(2)$ K
Prismatic
0.4 × 0.3 × 0.2 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scan
Absorption correction: none
2729 measured reflections
2493 independent reflections
2031 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.0228$
$\theta_{\rm max} = 27^\circ$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 8$
$l = -17 \rightarrow 17$
3 standard reflections frequency: 120 min intensity decay: 0.6%

Refinement

Refinement on F
$R = 0.039$
$wR = 0.041$
$S = 0.957$
2031 reflections
144 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o)]$
$(\Delta/\sigma)_{\rm max} = 0.03$
$\Delta\rho_{\rm max} = 0.608$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.390$ e Å^{-3}
Extinction correction: *SDP* (Frenz, 1982)
Extinction coefficient: $1.32\,(2) \times 10^{-6}$
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

S1—C1	1.717 (3)	N1—C1	1.351 (4)
S2—C1	1.708 (3)	N1—C2	1.477 (4)
O1—C5	1.257 (3)	C4—C5	1.516 (3)
C2—C3	1.523 (4)	N1—C4	1.459 (4)
O2—C5	1.259 (4)	N2—C3	1.478 (4)
C1—N1—C2	121.5 (2)	S2—C1—N1	119.6 (2)
C1—N1—C4	121.1 (2)	N1—C2—C3	113.6 (2)
C2—N1—C4	117.3 (2)	N2—C3—C2	111.5 (2)
S1—C1—S2	120.9 (2)	O1—C5—O2	124.2 (2)
N1—C4—C5	115.5 (2)	O1—C5—C4	119.4 (3)
S1—C1—N1	119.6 (2)	O2—C5—C4	116.4 (3)

The title structure was solved by direct and difference Fourier methods, and refined by full-matrix least-squares techniques. Almost all H atoms were found in a difference Fourier map; the exception being H(S). However, H atoms attached to C and N atoms were placed at calculated positions (C—H and N—H = 0.95 Å) and were allowed to ride on the adjacent atom, with $U(H) = 1.2U$(carrier atom). Water H atoms were refined isotropically. All calculations were performed on a PDP 11/73 computer using the *SDP* (Frenz, 1982) program.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SDP*. Program(s) used to refine structure: *SDP*. Molecular graphics: *ORTEX* (McArdle, 1994). Software used to prepare material for publication: *SDP*.

This work was financially supported by the Ministry for Science and Technology of the Republic of Serbia. The financial support of Mr Dunjić Dušan is also greatly appreciated.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: KA1221). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-(Ferrocenylmethyl)-6-methoxy-3-methylbenzonitrile and 10-(Ferrocenylmethyl)phenanthrene-9-carbonitrile

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Abstract

The structures of the title compounds, 2-(ferrocenylmethyl)-6-methoxy-3-methylbenzonitrile, $[Fe(C_5H_5)(C_{15}H_{14}NO)]$, (1), and 10-(ferrocenylmethyl)phenanthrene-9-carbonitrile, $[Fe(C_5H_5)(C_{21}H_{14}N)]$, (2), revealed that the cyano groups of the arylacetonitrile migrated to the aromatic systems during aryne reactions. The ori-

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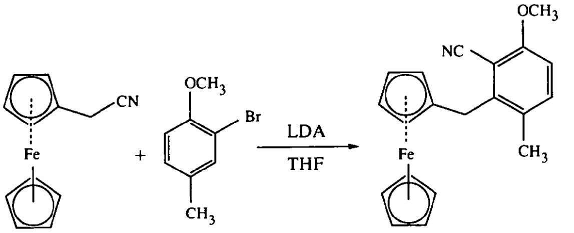
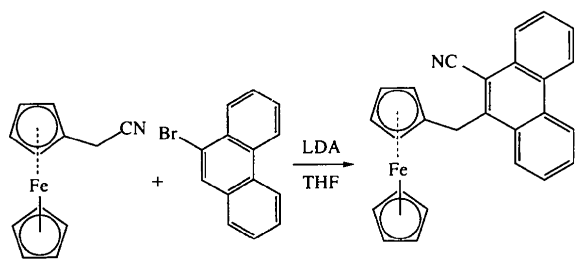
entation of the two cyclopentadienyl rings of the ferrocenyl moiety of (1) is close to a staggered conformation, while that of (2) is nearly eclipsed.

Comment

Haloarenes react with arylacetonitriles and lithium diisopropylamide (LDA) to give aryne α-arylated nitriles and rearranged 2-arylmethylbenzonitriles by the aryne arylation (Roberts, Vaughan, Carlsmith & Semonev, 1956) and tandem addition–rearrangement aryne mechanisms (Pansegrau, Rieker & Meyers, 1988), respectively. The latter pathway is particularly important in that a cyano and an arylmethyl group can be simultaneously delivered to adjacent positions on an aromatic ring allowing the synthesis of multisubstituted aromatic compounds with specific substitution patterns. Previous studies (Biehl & Khanapure, 1989) have shown that electron-releasing groups on the haloarene favor the rearrangement pathway. To see if similar groups on the nitrile also favor the rearrangement pathway, ferrocenylacetonitrile was chosen for study since it is a superb carbocation stabilizer (Feinberg & Rosenblum, 1969) and thus should also be a strong electron-releasing group. As shown below, ferrocenylacetonitrile was found to react with 2-bromo-4-methylanisole and 9-bromophenanthrene to give the rearranged nitriles 2-ferrocenylmethyl-6-methoxy-3-methylbenzonitrile, (1), and 10-ferrocenylmethylphenanthrene-9-carbonitrile, (2) (Lu, 1996).



(1)



(2)

The crystal structure of compound (1) revealed that the nitrile group of ferrocenylacetonitrile migrated to the anisole *ortho* to the methoxyl group, while the methylene C atom became attached to the C atom of the phenyl group to which the Br atom was originally bonded (Fig. 1). The phenyl and ferrocenyl groups were linked *via* the methylene C21 atom, with a C1—C21—C31 angle of 113.1 (2)° (Table 1). The slightly enlarged angle would reduce interactions between these two bulky groups. The phenyl ring plane is rotated relative to the cyclopentadienyl (Cp) planes of the ferrocenyl moiety, with a dihedral angle between the phenyl ring and Cp(1) (C31–C35) of 67.3 (1)°. In structure (2), the methylene C atom replaces the bromine substituent, while the nitrile group has migrated to the phenanthrene *ortho* to the methylene group (Fig. 2). The 14-atom phenanthrene skeleton is not quite planar, with an r.m.s. deviation of

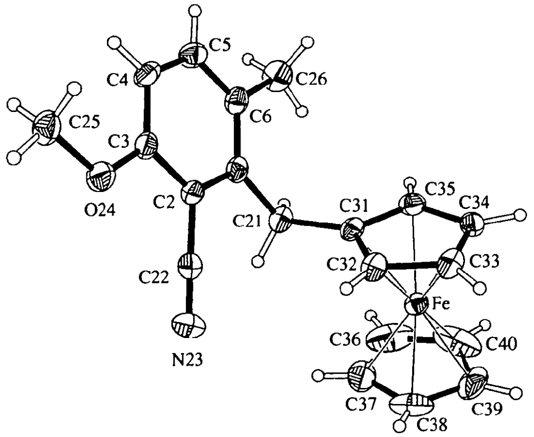


Fig. 1. The structure of compound (1) showing 40% probability displacement ellipsoids. H atoms are drawn as small circles of arbitrary radii.

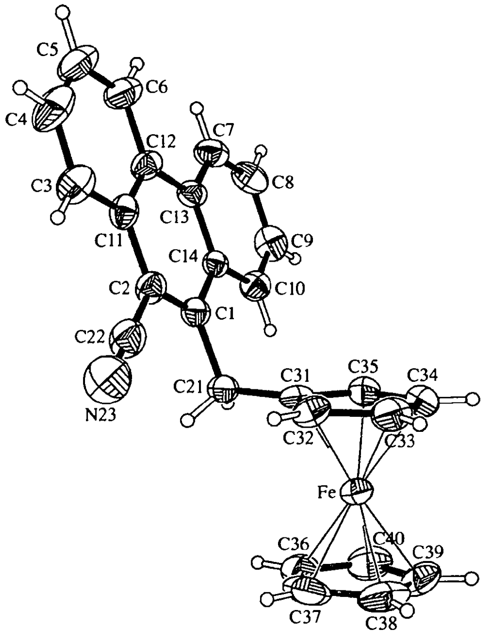


Fig. 2. The structure of compound (2) showing 40% probability displacement ellipsoids. H atoms are drawn as small circles of arbitrary radii.

0.019 Å for the C atoms. As indicated in the structural studies of phenanthrene molecules, atoms C6 and C7 (present numbering), along with their attached H atoms, are overcrowded (Kay, Okaya & Cox, 1971) and deviate from the plane defined by the 14 C atoms by −0.022 (4) and 0.025 (4) Å, respectively. This is similar to structure (1) in that the phenanthrene plane is twisted relative to the Cp planes of the ferrocenyl group, with a dihedral angle between the phenanthrene and Cp(1) planes of 72.5 (1)°. In both structures, the cyano group atoms are tilted out from the planes of the aromatic rings with deviations of 0.021 (4) and 0.028 (5) Å for compound (1), and of 0.016 (6) and 0.038 (6) Å for compound (2) for the C22 and N23 atoms, respectively. The C22—N23 distances [1.141 (4) for (1) and 1.138 (5) Å for (2)] are very close to those of our previous work (Zhang, Refat & Biehl, 1995).

The orientations of the two cyclopentadienyl rings of the ferrocenyl groups of compounds (1) and (2) are neither staggered nor eclipsed, but that of (1) is close to a staggered conformation, with the torsion angle C31—*Cnt*1—*Cnt*2—C36 42.4 (3)° (*Cnt*1 and *Cnt*2 are the centroids of the C31–C35 and C36–C40 rings, respectively), while that of compound (2) is nearly eclipsed, with a torsion angle of 5.3 (4)°. The two Cp planes are almost parallel to one another, with a dihedral angle of 1.3 (2) for (1) and 0.5 (3)° for (2). The distances between the Fe atom and the centroids of the Cp rings are 1.644 (1) and 1.652 (2) Å for (1), and 1.645 (2) and 1.649 (2) Å for (2). In compound (2), the distance between atoms Fe and C31, to which the methylene C atom is attached, is significantly longer [2.056 (3) Å] than other Fe—C distances of (1) and (2). The average Fe—C distances [2.034 (3) for (1) and 2.034 (4) Å for (2) (exclusive of Fe—C31)] are very close to the value of 2.033 Å found in the molecular structure of ferrocene studied at 173 K (Seiler & Dunitz, 1979).

Experimental

Both compounds were recrystallized from hexane–methylene chloride solution.

Compound (1)

Crystal data

[Fe(C$_5$H$_5$)(C$_{15}$H$_{14}$NO)]
M_r = 345.21
Monoclinic
$P2_1/c$
a = 19.244 (3) Å
b = 8.882 (1) Å
c = 9.736 (2) Å
β = 103.99 (1)°
V = 1614.8 (5) Å^3
Z = 4
D_x = 1.420 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 10–15°
μ = 0.937 mm^{-1}
T = 220 (2) K
Plate
0.35 × 0.25 × 0.10 mm
Orange

Data collection

$R3m/V$ diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (Sheldrick, 1990*b*)
$T_{\min}$ = 0.622, $T_{\max}$ = 0.911
3016 measured reflections
2828 independent reflections
2223 reflections with $F > 4\sigma(F)$

$R_{\rm int}$ = 0.0194
$\theta_{\max}$ = 25°
$h = -22 \rightarrow 22$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 11$
3 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.0367
$wR(F^2)$ = 0.1068
S = 1.063
2645 reflections
208 parameters
H atoms riding (C—H 0.96 Å)

$w = 1/[\sigma^2(F_o^2) + (0.0531P)^2 + 0.8321P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.453 e Å^{-3}
$\Delta\rho_{\min}$ = −0.340 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for (1)*

Fe—C36	2.026 (3)	C1—C2	1.406 (4)
Fe—C40	2.027 (3)	C1—C21	1.522 (4)
Fe—C38	2.028 (3)	C2—C3	1.406 (4)
Fe—C39	2.030 (3)	C2—C22	1.439 (4)
Fe—C37	2.033 (3)	C3—O24	1.359 (3)
Fe—C35	2.035 (3)	C3—C4	1.380 (4)
Fe—C32	2.039 (3)	C4—C5	1.385 (4)
Fe—C33	2.040 (3)	C5—C6	1.383 (4)
Fe—C34	2.041 (3)	C6—C26	1.507 (4)
Fe—C31	2.042 (2)	C21—C31	1.510 (3)
C1—C6	1.402 (4)	C22—N23	1.141 (4)
C6—C1—C2	118.3 (2)	C3—C4—C5	119.1 (3)
C6—C1—C21	122.3 (2)	C6—C5—C4	123.2 (3)
C2—C1—C21	119.4 (2)	C5—C6—C1	118.6 (3)
C3—C2—C1	122.0 (2)	C5—C6—C26	119.3 (3)
C3—C2—C22	117.6 (2)	C1—C6—C26	122.1 (3)
C1—C2—C22	120.5 (2)	C31—C21—C1	113.1 (2)
O24—C3—C4	125.9 (3)	N23—C22—C2	179.4 (3)
O24—C3—C2	115.3 (2)	C3—O24—C25	117.9 (2)
C4—C3—C2	118.8 (3)		

Compound (2)

Crystal data

[Fe(C$_5$H$_5$)(C$_{21}$H$_{14}$N)]
M_r = 401.27
Monoclinic
$P2_1/c$
a = 12.328 (3) Å
b = 19.923 (5) Å
c = 7.710 (2) Å
β = 96.63 (2)°
V = 1881.0 (8) Å^3
Z = 4
D_x = 1.417 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 10–15°
μ = 0.812 mm^{-1}
T = 220 (2) K
Plate
0.30 × 0.20 × 0.10 mm
Orange

Data collection

$R3m/V$ diffractometer
$\omega/2\theta$ scans

$R_{\rm int}$ = 0.0258
$\theta_{\max}$ = 25°

Absorption correction:
ψ scans (Sheldrick, 1990*b*)
$T_{\min} = 0.824$, $T_{\max} = 0.922$
3577 measured reflections
3311 independent reflections
2077 reflections with $F > 4\sigma(F)$
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 23$
$l = 0 \rightarrow 8$
3 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0501$
$wR(F^2) = 0.1294$
$S = 1.027$
2867 reflections
253 parameters
H atoms riding (C—H 0.96 Å)
$w = 1/[\sigma^2(F_o^2) + (0.0515P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.336$ e Å^{-3}
$\Delta\rho_{\min} = -0.283$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. *Selected geometric parameters (Å, °) for (2)*

Fe—C37	2.029 (5)	C3—C4	1.368 (6)
Fe—C33	2.030 (4)	C3—C11	1.405 (6)
Fe—C39	2.031 (4)	C4—C5	1.381 (7)
Fe—C34	2.033 (4)	C5—C6	1.371 (6)
Fe—C40	2.034 (4)	C6—C12	1.400 (5)
Fe—C32	2.034 (4)	C7—C8	1.360 (6)
Fe—C36	2.035 (4)	C7—C13	1.407 (5)
Fe—C35	2.038 (4)	C8—C9	1.398 (6)
Fe—C38	2.038 (4)	C9—C10	1.367 (5)
Fe—C31	2.056 (3)	C10—C14	1.415 (5)
C1—C2	1.370 (5)	C11—C12	1.401 (5)
C1—C14	1.444 (5)	C12—C13	1.470 (5)
C1—C21	1.527 (5)	C13—C14	1.416 (5)
C2—C22	1.450 (6)	C21—C31	1.513 (5)
C2—C11	1.453 (5)	C22—N23	1.138 (5)
C2—C1—C14	119.0 (3)	C12—C11—C3	119.8 (4)
C2—C1—C21	119.6 (3)	C12—C11—C2	118.6 (4)
C14—C1—C21	121.4 (3)	C3—C11—C2	121.6 (4)
C1—C2—C22	119.9 (4)	C6—C12—C11	118.0 (4)
C1—C2—C11	123.1 (4)	C6—C12—C13	122.8 (4)
C22—C2—C11	117.0 (4)	C11—C12—C13	119.2 (3)
C4—C3—C11	120.5 (5)	C7—C13—C14	118.3 (4)
C3—C4—C5	120.1 (4)	C7—C13—C12	121.6 (3)
C6—C5—C4	120.2 (4)	C14—C13—C12	120.1 (3)
C5—C6—C12	121.4 (5)	C10—C14—C13	118.4 (3)
C8—C7—C13	121.9 (4)	C10—C14—C1	121.7 (3)
C7—C8—C9	120.3 (4)	C13—C14—C1	119.9 (3)
C10—C9—C8	119.4 (4)	C31—C21—C1	111.4 (3)
C9—C10—C14	121.7 (4)	N23—C22—C2	178.3 (5)

Data were corrected for both structures for Lorentz, polarization and absorption effects. Both structures were solved by direct methods (Sheldrick, 1990*a*). Refinement on F^2 for all reflections. Weighted *R*, *wR*, and goodnesses of fit (*S*) were based on F^2. Full-matrix least-squares refinement was performed for both structures. All non-H atoms were refined anisotropically, while all H atoms were refined using a riding model.

For both compounds, data collection: *R3m/V* diffractometer control program; cell refinement: *R3m/V* diffractometer control program; data reduction: *R3m/V* diffractometer control program; program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990*b*); software used to prepare material for publication: *SHELXL93*.

This work was supported by grants from the Robert A. Welch Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BS1011). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 723–725

Dichlorobis(1,10-phenanthroline-*N*,*N*′)-cobalt(II)–Acetonitrile (1/1.5)

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Abstract

The title complex, $[CoCl_2(C_{12}H_8N_2)_2].1.5CH_3CN$, is a monomer, with the Co atom in an octahedral environment provided by two Cl^- ions and four N atoms from the two bidentate 1,10-phenanthroline molecules.

Comment

The reaction of cobalt(II) halides with neutral bidentate ligands in alcohol or acetone has been previously reported (Su & Huang, 1984). Using spectroscopic methods only, they had assigned *trans*-octahedral geometry to