ELSEVIER

Journal of Organometallic Chemistry 490 (1995) 243–247

Journal of Organometallic Chemistry

Crystal structures of anil of benzoylferrocene and its derivative of mercury: specific arrangement of the ferrocenyl and phenyl groups around the C=N bond

Shou Quan Huo [a], Ying Zhu [b], Yang Jie Wu [a,*]

[a] *Department of Chemistry, Zhengzhou University, Zhengzhou 450052, People's Republic of China*
[b] *National Laboratory of Applied Organic Chemistry at Lanzhou University, Lanzhou 730000, People's Republic of China*

Received 1 September 1994

Abstract

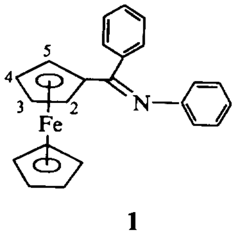
The crystal structures of [(phenylimino) phenylmethyl]ferrocene (1) and 2-chloromercurio-1-[(phenylimino)phenylmethyl]ferrocene (2) have been determined by X-ray diffraction methods to obtain structural information on the anils of benzoylferrocene and their mercurated derivatives. The most striking feature is the specific arrangements of the phenyl and cyclopentadienyl rings around the C=N bond. It has been found that the *N*-phenyl ring adopts a *trans* conformation with the ferrocenyl moiety, and the twist angles of both the *N*-phenyl and *C*-phenyl rings out of the plane of C=N bond are much larger than that of the substituted ferrocenyl ring out of this plane. A comparison between the structures of 1 and 2 is presented. The intramolecular coordination between the Hg and N in compound 2 is confirmed, showing an N–Hg distance of 2.870 Å, shorter than the sum of van der Waals radii of N and Hg (3.05–3.15 Å).

Keywords: Ferrocene; Iron; Mercury; Crystal structure

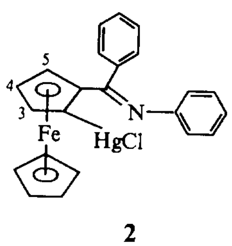
---

1. Introduction

In a previous paper we have reported the synthesis and characterization of anils of benzoylferrocene and their *ortho*-mercurated derivatives [1]. The conformations of these compounds were discussed on the basis of the NMR data. It was found that the anils exist as a mixture of *trans* and *cis* isomers in solution in which the *trans* isomer predominates. The intramolecular coordination N → Hg in the mercurated anils was inferred by the chromatographic behaviour and spectral feature of the compounds. In order to obtain more structural information on the anils and the mercurated derivatives, a single-crystal structure determination is undoubtly necessary. We report here the single-crystal X-ray diffraction studies on [(phenylimino)phenylmethyl]ferrocene (1) and 2-chloromercurio-1-[(phenylimino)phenylmethyl]ferrocene (2). The compounds are of interest also in that there are three aromatic systems of different types (one is ferrocene and the others are benzenes) attached to the C=N bond, which can therefore offer a possibility to compare the behaviours of these systems in these compounds.



1



2

2. Results and discussion

2.1. Molecular structure of compound 1

The structure of 1 is depicted in Fig. 1, with the bond distances and the selected angles in Tables 1 and 2 respectively. The molecule displays a *trans* conformation with the ferrocenyl moiety and the *N*-phenyl ring

---

[*] Corresponding author.

SSDI 0022-328X(94)05201-8

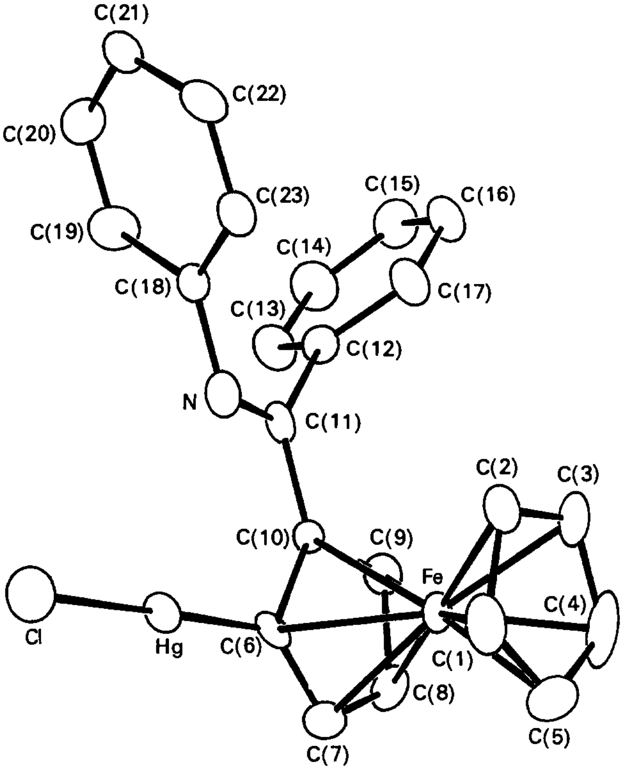


Fig. 1. Structure of 1.

lying on the different sides of C=N bond. This is in accord with the NMR studies, where this conformer is a much more populous species when compared with the *cis* conformer [1]. The structure of [1-(4-chlorophenylimino)ethyl]ferrocene determined recently also exhibits the *trans* conformation [2], while the structure of *O*-(2-cyanoethyl)-benzoyl ferrocene oxime, with a similar structure of ferrocenylimines, was reported to adopt a *cis* conformation with the ferrocenyl moiety and $-OC_2H_4CN$ group on the same side of C=N bond [3].

Table 1
Bond distances (Å) for 1

Fe–C(1)	2.067(4)	C(6)–C(10)	1.447(6)
Fe–C(2)	2.056(4)	C(7)–C(8)	1.429(7)
Fe–C(3)	2.042(4)	C(8)–C(9)	1.412(6)
Fe–C(4)	2.049(5)	C(9)–C(10)	1.424(6)
Fe–C(5)	2.060(5)	C(10)–C(11)	1.491(6)
Fe–C(6)	2.058(4)	C(11)–C(12)	1.492(6)
Fe–C(7)	2.059(4)	C(12)–C(13)	1.391(6)
Fe–C(8)	2.057(4)	C(12)–C(17)	1.384(6)
Fe–C(9)	2.049(4)	C(13)–C(14)	1.391(7)
Fe–C(10)	2.047(4)	C(14)–C(15)	1.389(7)
N–C(11)	1.282(6)	C(15)–C(16)	1.387(7)
N–C(18)	1.412(5)	C(16)–C(17)	1.419(6)
C(1)–C(2)	1.410(7)	C(18)–C(19)	1.386(7)
C(1)–C(5)	1.429(6)	C(18)–C(23)	1.401(6)
C(2)–C(3)	1.446(7)	C(19)–C(20)	1.399(7)
C(3)–C(4)	1.412(6)	C(20)–C(21)	1.392(8)
C(4)–C(5)	1.415(6)	C(21)–C(22)	1.381(7)
C(6)–C(7)	1.426(6)	C(22)–C(23)	1.369(6)

Table 2
Selected bond angles (°) for 1

C(2)–C(1)–C(5)	106.9(4)	C(10)–C(11)–C(12)	118.5(3)
C(1)–C(2)–C(3)	108.8(4)	C(11)–C(12)–C(13)	120.0(4)
C(2)–C(3)–C(4)	107.0(5)	C(11)–C(12)–C(17)	121.1(4)
C(3)–C(4)–C(5)	108.4(4)	C(13)–C(12)–C(17)	118.9(4)
C(1)–C(5)–C(4)	108.9(5)	C(12)–C(13)–C(14)	120.2(4)
C(7)–C(6)–C(10)	107.0(4)	C(13)–C(14)–C(15)	121.1(4)
C(6)–C(7)–C(8)	108.2(4)	C(14)–C(15)–C(16)	119.6(4)
C(7)–C(8)–C(9)	108.5(4)	C(15)–C(16)–C(17)	119.1(4)
C(8)–C(9)–C(10)	108.2(4)	C(12)–C(17)–C(16)	121.2(4)
C(6)–C(10)–C(9)	108.0(4)	C(19)–C(18)–C(23)	119.3(4)
C(6)–C(10)–C(11)	123.4(4)	C(18)–C(19)–C(20)	120.7(4)
C(9)–C(10)–C(11)	128.6(4)	C(19)–C(20)–C(21)	118.6(5)
N–C(11)–C(10)	116.4(4)	C(20)–C(21)–C(22)	120.8(4)
N–C(11)–C(12)	125.2(4)	C(21)–C(22)–C(23)	120.4(4)
N–C(18)–C(19)	118.5(4)	C(18)–C(23)–C(22)	120.3(4)
N–C(18)–C(23)	122.0(4)	C(11)–N–C(18)	122.0(4)

The C–C distances in the ferrocenyl moiety vary from 1.410(7) to 1.447(6) Å whilst the C–C–C angles range between 106.9(4) and 108.9(5)°; the Fe–C distances lie between 2.042(4) and 2.067(4) Å. The distances from iron to the substituted and unsubstituted rings are 1.656 and 1.661 Å respectively. The C=N bond distance is 1.282(4) Å, longer than that in [1-(4-chlorophenylimino) ethyl]ferrocene [2]. C(18), N, C(11), C(12) and C(10) are essentially coplanar with largest deviation of 0.066 Å for N from the least-squares plane, and thus C(11) has a non-equivalent sp^2 hybridization state with the following bond angles: N–C(11)–C(12), 125.2(4)°; N–C(11)–C(10), 116.4(4)°; C(10)–C(11)–C(12), 118.5(3)°. As predicted previously [1], the N–C(11)–C(10) angle is smaller than 120° and thus favours directing mercury into the *ortho* position of the substituted Cp ring by N coordination in the mercuration reaction; furthermore, the angle C(6)–C(10)–C(11) is also smaller than the C(9)–C(10)–C(11) angle by 5.2° owing to the steric hindrance between the substituted Cp ring and the *C*-phenyl ring. It can be noted from the large N–C(11)–C(12) angle that the steric repulsion between the *C*-phenyl and *N*-phenyl rings is quite remarkable; thus the C(18)–N–C(11) angle of 122.0(4)° is also larger than the ideal value of 120°.

The most striking and interesting feature of the molecule is the specific arrangements of the phenyl rings and the Cp rings around the plane of C=N bond. The substituted Cp ring is approximately coplanar with the plane by a twist angle of only 8.16° whereas the *C*-phenyl forms a much larger angle with the plane (50.68°), indicating the better conjugation between the Cp ring and the C=N bond, but the related bond distances C(11)–C(10) and C(11)–C(12) are almost the same. The dihedral angle between the N-phenyl ring

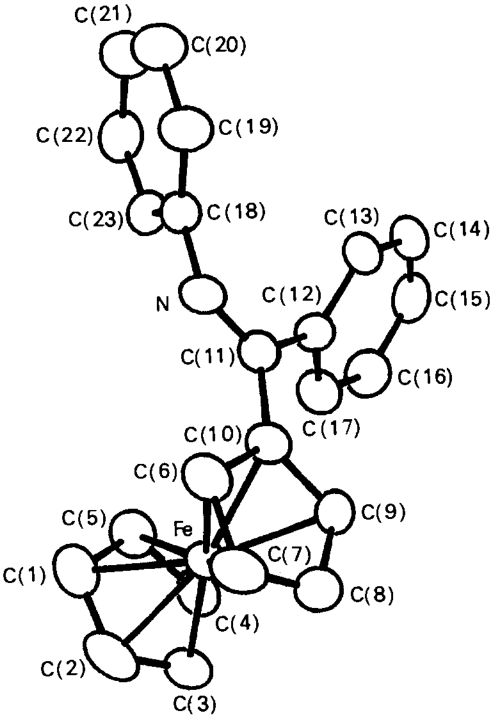


Fig. 2. Structure of **2**.

and the plane is 61.38°. The Cp rings are nearly parallel to each other, with an interangle of 2.34°.

2.2. *Molecular structure of 2*

The structure of **2** is shown in Fig. 2, indicating a structure of 1,2-disubstituted ferrocene which has been proposed for the mercurated anils of benzoylferrocene [1]. The bond distances and selected bond angles are listed in Table 3 and 4 respectively. The N–Hg distance is 2.870 Å, shorter than the sum of van der Waals radii of Hg, 1.5–1.6 Å [4–7], and N, 1.55 Å [8], which indicates the presence of an intramolecular coordination in the compound. Comparison with other *ortho*-mercurated ferrocenylimines reveals some differences; compare the N–Hg distances of 2.897 Å for 2-chloromercurio-1-[(4-methoxyphenyl) iminomethyl]ferrocene [9] and 2.766 Å for 2-chloromercurio-1-[1 [(4-chlorophenyl) imino]ethyl]ferrocene [10].

Table 3
Bond distances (Å) for **2**

Hg–Cl	2.306(3)	C(6)–C(7)	1.39(1)
Hg–C(6)	2.03(1)	C(6)–C(10)	1.45(2)
Fe–C(1)	2.027(9)	C(7)–C(8)	1.39(1)
Fe–C(2)	2.05(1)	C(8)–C(9)	1.45(1)
Fe–C(3)	2.03(2)	C(9)–C(10)	1.44(1)
Fe–C(4)	2.03(1)	C(10)–C(11)	1.48(1)
Fe–C(5)	2.039(9)	C(11)–C(12)	1.51(1)
Fe–C(6)	2.016(8)	C(12)–C(13)	1.41(1)
Fe–C(7)	2.027(9)	C(12)–C(17)	1.37(1)
Fe–C(8)	2.07(1)	C(13)–C(14)	1.41(1)
Fe–C(9)	2.47(8)	C(14)–C(15)	1.38(2)
Fe–C(10)	2.029(6)	C(15)–C(16)	1.37(2)
N–C(11)	1.27(2)	C(16)–C(17)	1.41(1)
N–C(18)	1.39(2)	C(18)–C(19)	1.41(1)
C(1)–C(2)	1.41(1)	C(18)–C(23)	1.41(1)
C(1)–C(5)	1.42(2)	C(19)–C(20)	1.34(1)
C(2)–C(3)	1.37(1)	C(20)–C(21)	1.36(1)
C(3)–C(4)	1.37(2)	C(21)–C(22)	1.38(1)
C(4)–C(5)	1.39(1)	C(22)–C(23)	1.32(1)

Table 4
Selected bond angles (°) for **2**

C(2)–C(1)–C(5)	108(1)	C(10)–C(11)–C(12)	117.0(7)
C(1)–C(2)–C(3)	106(1)	C(11)–C(12)–C(13)	117.2(8)
C(2)–C(3)–C(4)	112(2)	C(11)–C(12)–C(17)	122.5(8)
C(3)–C(4)–C(5)	108(2)	C(13)–C(12)–C(17)	119.9(8)
C(1)–C(5)–C(4)	108(2)	C(12)–C(13)–C(14)	118.1(9)
C(7)–C(6)–C(10)	106.7(8)	C(13)–C(14)–C(15)	121(1)
C(6)–C(7)–C(8)	111.2(8)	C(14)–C(15)–C(16)	121.3(9)
C(7)–C(8)–C(9)	107.4(8)	C(15)–C(16)–C(17)	118.4(9)
C(8)–C(9)–C(10)	106.6(7)	C(12)–C(17)–C(16)	122(1)
C(6)–C(10)–C(9)	108.0(8)	C(19)–C(18)–C(23)	114.2(8)
C(6)–C(10)–C(11)	125.0(7)	C(18)–C(19)–C(20)	120.6(9)
C(9)–C(10)–C(11)	126.7(7)	C(19)–C(20)–C(21)	124.0(9)
N–C(11)–C(10)	120.2(7)	C(20)–C(21)–C(22)	116.8(9)
N–C(11)–C(12)	122.7(8)	C(21)–C(22)–C(23)	120.5(8)
N–C(18)–C(19)	122.7(8)	C(18)–C(23)–C(22)	124.0(8)
N–C(18)–C(23)	123.0(7)	Cl–Hg–C(6)	177.3(2)
C(11)–N–C(18)	123.8(7)		

All the bond distances and angles except those in the coordination sphere are similar to those for **1**. The distances from iron to the substituted and unsubstituted rings are 1.639 and 1.655 Å respectively. In the coordination sphere, some changes in bond angles can be noted when compared with the unmercurated compound **1**. The C(10)–C(6)–Hg angle decreases by 4.5° compared with the C(10)–C(6)–Hg(6) angle in **1** (125.1°), while the C(6)–C(10)–C(11) and C(10)–C(11)–N angles increase by 1.6 and 3.8° respectively, in comparison with the corresponding angles in **1**. The former can be attributed to the intramolecular coordination, but the cause of the latter is not very clear. Probably, the orientations of the interacting orbitals of the mercury and nitrogen atoms which guarantee the largest overlap of the orbitals play an important role; on the contrary, the steric repulsion between the mercury and the nitrogen should not be neglected. A molecular orbital consideration involving theoretical calculations is currently being performed to gain further insight into the nature of intramolecular coordination in the *ortho*-mercurated ferrocenylimines.

The arrangements of the *C*-phenyl and *N*-phenyl rings as well as the Cp rings are overall similar to those in **1**, but significant differences exist in the magnitude of the related dihedral angles. Both the *C*-phenyl and the *N*-phenyl rings form considerably large dihedral angles of 75.48 and 72.28° respectively with the plane of the C=N bond, while the angle between the substituted Cp ring and the plane is only 7.93°. The *C*-phenyl ring and the substituted Cp ring are nearly perpendicular to each other, with an interangle of 81.98°. All these features are completely consistent with those deduced from the NMR behaviours of the compound [1]. The bond distance of C(11)–C(10) is shorter than that of C(11)–C(12), suggesting better conjugation between the substituted Cp ring and the C=N bond as expected. The previous NMR study showed that, in **2**, proton 5 is highly shielded by the *C*-phenyl ring and appears at a higher field when compared with protons 3 and 4 but, in **1**, proton 5 (2) appears at lower field than proton 3 (4) [1]. This can be interpreted in terms of the interplanar angle θ between the *C*-phenyl and substituted Cp rings, since the anisotropy of the phenyl ring varies as a $\cos^2\theta$ function of the interplanar angle (the larger θ, the lower the deshielding [11]), and the interplanar angle in **2** is much larger than that in **1** (54.25°).

3. Experimental details

3.1. Compound preparation

The synthesis and characterization of **1** and **2** have been described previously [1].

3.2. Single-crystal X-ray diffraction study of 1

Crystals (red–brown in colour) were prepared by slow evaporation of a methylene chloride–petroleum ether solution. The crystal data are presented in Table 5. The diffraction intensities were collected by the ω–2θ method on an Enraf–Nonius CAD 4 diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). The structure was solved by Patterson methods, using the Enraf–Nonius SDP program package [12] on a PDD 11/44 computer. Data were corrected for the Lorentz and polarization effects, and also for absorption by an empirical method on the basis of ψ scans. All non-hy-

Table 5
Crystal and intensity collection parameters for **1**

Formula	$C_{23}H_{19}FeN$
Crystal dimensions (mm)	0.15 × 0.12 × 0.09
Crystal system	Monoclinic
Space group	$P2_1/c$
M_r	353.25
a (Å)	13.356(1)
b (Å)	11.059(1)
c (Å)	11.565(1)
β (°)	89.53(1)
V (Å^3)	1708.1
Z	4
D_c (g cm^{-3})	1.374
μ cm^{-1}	70.861
$F(000)$	736
Data collection range (°)	$1 \leqslant \theta \leqslant 60$
Number of unique data	2806
Number of observed data ($I > 3\sigma(I)$)	1934
R	0.076
R_w	0.079
$(\Delta/\sigma)_{max}$	0.05

Table 6
Final positional parameters for **1**

Atom	x	y	z	B (Å^2)
Fe	0.37157(6)	0.09382(8)	0.32040(7)	2.42(2)
N	0.3206(4)	0.4325(4)	0.4003(4)	2.9(1)
C(1)	0.3465(5)	0.4757(6)	0.9840(5)	3.7(1)
C(2)	0.6050(5)	0.4381(6)	0.0866(6)	4.1(1)
C(3)	0.6662(5)	0.4150(5)	0.1868(6)	3.7(1)
C(4)	0.7533(4)	0.4863(6)	0.1745(5)	3.2(1)
C(5)	0.7463(4)	0.5529(6)	0.0705(5)	3.4(1)
C(6)	0.4594(4)	0.2454(6)	0.3382(5)	3.2(1)
C(7)	0.4886(5)	0.6555(6)	0.2271(6)	3.7(1)
C(8)	0.5463(5)	0.6280(6)	0.3272(5)	3.5(1)
C(9)	0.3663(4)	0.1996(5)	0.1751(5)	2.9(1)
C(10)	0.3685(4)	0.2730(5)	0.2762(5)	2.6(1)
C(11)	0.2939(4)	0.3644(5)	0.3164(5)	2.7(1)
C(12)	0.1967(4)	0.3732(5)	0.2542(5)	2.7(1)
C(13)	0.1622(5)	0.4852(5)	0.2170(5)	3.2(1)
C(14)	0.0718(5)	0.4940(6)	0.1588(5)	4.0(1)
C(15)	0.0145(5)	0.3920(7)	0.1363(5)	4.0(1)
C(16)	0.0478(5)	0.2795(6)	0.1723(6)	3.7(1)
C(17)	0.1402(5)	0.2712(6)	0.2314(5)	3.4(1)
C(18)	0.2535(4)	0.5133(5)	0.4549(5)	2.9(1)
C(19)	0.2819(5)	0.6331(6)	0.4674(6)	4.0(1)
C(20)	0.7794(6)	0.2151(6)	0.9731(6)	4.8(2)
C(21)	0.8675(6)	0.3273(6)	0.4225(6)	4.4(2)
C(22)	0.8954(5)	0.4469(6)	0.4335(5)	3.7(1)
C(23)	0.8362(5)	0.5263(6)	0.4941(5)	3.2(1)

Table 7
Crystal and intensity collection parameters for **2**

Formula	$C_{23}H_{18}FeHgN$
Crystal dimensions (mm)	0.19 × 0.15 × 0.12
Crystal system	Triclinic
Space group	$P\bar{1}$
M_r	588.29
a (Å)	13.994(2)
b (Å)	9.005(3)
c (Å)	9.084(2)
α (°)	110.30(3)
β (°)	72.71(2)
γ (°)	106.99(3)
V (Å^3)	1001.9
Z	2
D_c (g cm^{-3})	1.950
μ cm^{-1}	216.984
$F(000)$	560
Data collection range (°)	$1 \leqslant \theta \leqslant 60$
Number of unique data	3103
Number of observed data ($I > 3\sigma(I)$)	2656
R	0.072
R_w	0.078
$(\Delta/\sigma)_{max}$	0.01

Table 8
Final positional parameters for **2**

Atom	x	y	z	B (Å^2)
Hg	0.04887(5)	0.25910(7)	0.03519(8)	3.76(2)
Fe	0.1734(2)	0.3261(2)	−0.3488(3)	3.53(6)
Cl	0.0284(4)	0.1288(5)	0.2243(6)	6.0(1)
N	0.220(1)	0.529(1)	0.063(1)	4.1(3)
C(1)	0.219(1)	0.121(2)	−0.380(2)	5.9(5)
C(2)	0.301(1)	0.256(2)	−0.350(2)	4.8(4)
C(3)	0.321(2)	0.325(2)	−0.473(2)	6.1(6)
C(4)	0.256(2)	0.244(2)	−0.575(2)	7.8(6)
C(5)	0.192(1)	0.113(2)	−0.521(3)	6.7(6)
C(6)	0.0685(9)	0.364(2)	−0.140(2)	3.8(4)
C(7)	0.021(1)	0.322(2)	−0.268(2)	4.3(4)
C(8)	0.064(1)	0.432(2)	−0.359(2)	4.7(4)
C(9)	0.144(1)	0.552(2)	−0.286(2)	4.2(4)
C(10)	0.145(1)	0.511(1)	−0.147(2)	2.7(3)
C(11)	0.218(1)	0.592(1)	−0.040(2)	3.5(4)
C(12)	0.288(1)	0.748(1)	−0.062(2)	3.7(4)
C(13)	0.245(1)	0.885(2)	−0.010(2)	5.2(5)
C(14)	0.308(2)	1.030(2)	−0.040(3)	6.5(6)
C(15)	0.409(2)	1.035(2)	−0.119(2)	6.7(6)
C(16)	0.450(2)	0.900(2)	−0.176(2)	6.2(6)
C(17)	0.388(1)	0.755(2)	−0.148(2)	5.5(5)
C(18)	0.288(1)	0.595(2)	0.166(2)	3.2(3)
C(19)	0.277(1)	0.732(2)	0.301(3)	6.1(5)
C(20)	0.341(2)	0.786(2)	0.400(2)	5.8(5)
C(21)	0.420(1)	0.717(2)	0.382(2)	4.5(4)
C(22)	0.432(1)	0.582(2)	0.251(2)	4.7(4)
C(23)	0.370(1)	0.526(2)	0.150(2)	4.2(4)

drogen atoms were refined anisotropically, and difference Fourier synthesis led to the location of all hydrogen atoms in the structure. The largest features on a final difference map were 0.411 and −0.633 electrons Å^{-3} in height. The positional parameters are given in Table 6.

3.3. Single-crystal X-ray diffraction study of 2

Crystal (red–brown in colour) were prepared as described above. The crystal data are presented in Table 7. The diffraction intensities were collected by the ω–2θ method on the Enraf–Nonius CAD 4 diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). Data were corrected for the Lorentz and polarization effects, and also for absorption. The structure was solved by Patterson methods using the Enraf–Nonius SDP program package [12] on a PDD 11/44 computer. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in calculation positions. The largest features on a final difference map were 3.74 and −3.61 electrons Å^{-3} in height, near Hg. The positional parameters are given in Table 8.

The following supplementary data is available from the authors; H-atom coordinates, thermal parameters, and remaining bond angles for **1** and **2**.

Acknowledgements

We are grateful to the National Natural Science Foundation of China and the Natural Science Foundation of Henan Province for financial support of this work.

References

[1] S.Q. Huo, Y.J. Wu, X.A. Mao and H.Z. Yuan, *Tetrahedron, 50* (1994) 10467.
[2] Y.J. Wu, S.Q. Huo and Y. Zhu, *J. Organomet. Chem., 485* (1995) 161.
[3] Q. Liu, S. Cao, Y. Hu, M. Xin and J. Huang, *Jiegou Huaxue, 4* (1985) 178.
[4] L.G. Kuz'mina, N.G. Bkiy and Yu.T. Struchkov, *Usp. Khim., 44* (1975) 134.
[5] D. Grdenic, *Q. Rev. Chem. Soc., 19* (1965) 303.
[6] L.G. Kuz'mina, N.G. Bokiy, Yu.T. Struchikov, D.N. Kravtzov and E.M. Rokhlina, *Zh. Strukt. Khim., 15* (1974) 491.
[7] D. Grdenic, B. Kamenar and Z. Dodi, *Izv. Jugosl. Cent. Kristallogr., 2* (1976) 28.
[8] A. Bondi, *J. Phys. Chem., 68* (1964) 441.
[9] S.Q. Huo, Y.J. Wu, Y. Zhu and L. Yang, *J. Organomet. Chem., 470* (1994) 17.
[10] Y.J. Wu, S.Q. Huo, Y. Zhu and L. Yang, *J. Organomet. Chem., 481* (1994) 235.
[11] H.M. McConnell, *J. Chem. Phys., 27* (1957) 226.
[12] B.A. Frenz and Associate, Inc., College Station, TX, *SDP Program Package*, Enraf–Nonius, Delft, 1985.