Acta Cryst. (1993). C**49**, 791–793

1-(*N*,*N*-Dimethylferrocenylmethylamine)-2-methyl-3-(trimethylsilyl)-2,3-dicarba-1-plumba-*closo*-heptaborane(6)

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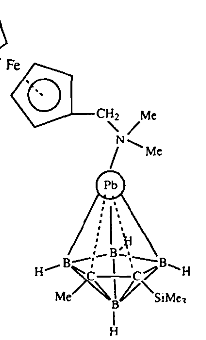
(*Received* 25 *March* 1992; *accepted* 8 *October* 1992)

Abstract

The title compound, 1-Pb[(η^5-C_5H_5)Fe{η^5-C_5H_4-$CH_2(CH_3)_2N$}]-2-(CH_3)-3-[Si$(CH_3)_3$]-2,3-$C_2B_4H_4$] (3) was crystallized in the monoclinic space group $P2_1/n$. The structure of this complex is quite similar to those found for the corresponding germa-, stanna- and plumbacarborane analogues of the formula 1-*M*[(η^5-C_5H_5)Fe{η^5-$C_5H_4CH_2(CH_3)_2N$}]-2,3-[Si$(CH_3)_3]_2$-2,3-$C_2B_4H_4$] [*M* = Sn (1); *M* = Ge and Pb (2)]. As in (1) and (2) the dihedral angles between the C_5H_5 and C_2B_3 planes in (3) are about 91°. This is the result of a slight rotation of the ferrocenyl ligand about the C(11)—C(21) bond making the Pb—C(12) bond a distance of closest approach and thus establishing the existence of secondary metal–C_5H_5 (π) interactions in the stabilization of these donor–acceptor complexes.

Comment

The coordination chemistry of *closo*-metallacarboranes of main-group elements has received much attention in recent years. These heterocarboranes form donor–acceptor complexes with monodentate, bidentate, bis(bidentate) and tridentate Lewis bases. One of the prominent structural features of these complexes has been the slippage of the heteroatom from η^5 to η^3 bonding (Hosmane & Maguire, 1988, 1990, 1991; Hosmane, 1991). However, only one structure has been reported for a monodentate Lewis base–metallacarborane complex, 1-Sn[(η^5-C_5H_5)Fe-{η^5-$C_5H_4CH_2(CH_3)_2N$}]-2,3-[Si$(CH_3)_3]_2$-2,3-$C_2B_4H_4$] [(1); Hosmane, Fagner, Zhu, Siriwardane, Maguire, Zhang, & Pinkston, 1989]. The X-ray structure shows two independent molecules in a unit cell. The most intriguing structural feature of these complexes is that in both molecules the ferrocenyl groups are not in positions of minimum steric interactions, but are in positions which are almost eclipsed relative to the stannacarboranes so that some of the cyclopentadienyl C atoms are well within the van der Waals radii of the Sn atoms. Thus, it may be that the ferrocenyl moiety is acting as more than just a pendant group that promotes single crystal formation. In addition, the change in the ^{119}Sn NMR chemical shift of the stannacarborane on complexation with the *N*,*N*-dimethylferrocenylmethylamine is in the opposite direction from those found for other Lewis base–stannacarborane complexes. It has been speculated that an extended C_2B_4-Sn-C_p-Fe-C_p interaction might contribute to this anomalous chemical shift behavior (Hosmane, Fagner, Zhu, Siriwardane, Maguire, Zhang & Pinkston, 1989). To our surprise, the same structural features were found for the corresponding Ge and Pb analogues, 1-*M*[(η^5-C_5H_5)Fe{η^5-$C_5H_4CH_2$-$(CH_3)_2N$}]-2,3-[Si$(CH_3)_3]_2$-2,3-$C_2B_4H_4$] [(2); Hosmane, Lu, Zhang, Maguire, Jia & Barreto, 1992]. Noting that both (1) and (2) carry a bulky $SiMe_3$ group on each cage C atom, the question arose whether the presence of a less bulky group such as Me on one of the cage C atoms would also yield the same configuration of the Lewis base, *N*,*N*-dimethylferrocenylmethylamine, in the complex such that it is in a position of maximum steric interaction. In order to test this hypothesis the title compound 1-Pb[(η^5-C_5H_5)Fe{η^5-$C_5H_4CH_2$-$(CH_3)_2N$}]-2-(CH_3)-3-[Si$(CH_3)_3$]-2,3-$C_2B_4H_4$] (3), in which one of the cage C atoms carries a methyl group, was synthesized as described by Hosmane, Lu, Zhang, Maguire, Jia & Barreto (1992) and its crystals were grown very slowly from a solution containing 95% anhydrous *N*,*N*-dimethylferrocenylmethylamine and 5% dry benzene. We report herein the results of the subsequent structural investigation.



(3)

The crystal structure reveals that the geometry of (3) is identical to that of (1) and (2), even though, unlike (1) and (2), it crystallizes in a space group other than $P\bar{1}$. The dihedral angles between the C_5H_5 and C_2B_3 planes are about 91°. Thus the orientation of the ferrocenyl ligand about the C(11)—C(21) bond makes the Pb—C(12) distance a closest non-bonded intramolecular contact [Pb···C(11) 3.378 (9) and Pb···C(12) 3.334 (9) Å; the other Pb···C(C_p) distances are > 4.0 Å]. An intermolecular interaction

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[3.723 (10) Å; (′) = 1 + x, y, z] also exists between Pb and C(19′) (see packing diagram in Fig. 2). Thus, the present work establishes the existence of the secondary metal–C_5H_5 (π) interactions in this type of adduct for complex stabilization and furthermore it provides a general structural pattern for these systems (Hosmane, Fagner, Zhu, Siriwardane, Maguire, Zhang & Pinkston, 1989; Hosmane, Lu, Zhang, Maguire, Jia & Barreto, 1992).

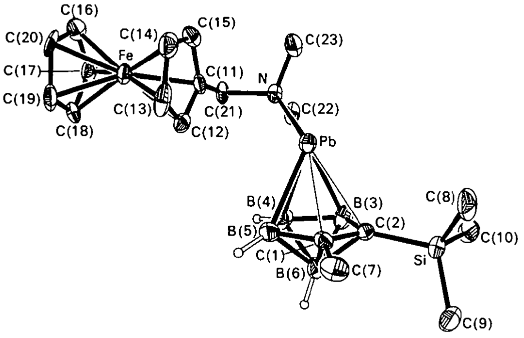

Fig. 1. View of the title compound (*SHELXTL-Plus*) with thermal ellipsoids drawn at 40% probability levels. The H atoms of the methyl groups and the ferrocenyl ligand are omitted for clarity. The cage H atoms are drawn as small circles of arbitrary radius.

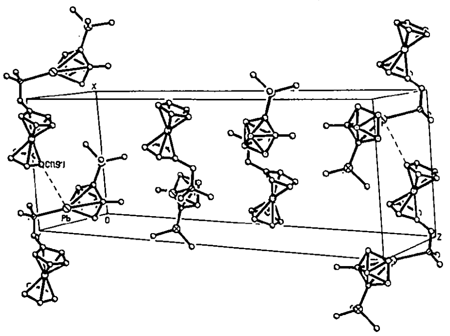

Fig. 2. Packing diagram of (3) showing the Pb···C(19′) intermolecular interaction.

Experimental

Crystal data

$C_{19}H_{33}B_4FeNPbSi$
M_r = 609.8
Monoclinic
$P2_1/n$
a = 10.070 (2) Å
b = 8.156 (1) Å
c = 28.820 (7) Å
β = 92.49 (2)°
V = 2364.8 (8) Å^3
Z = 4
D_x = 1.71 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 24 reflections
θ = 9–15°
μ = 7.64 mm^{-1}
T = 230 K
Plate
0.30 × 0.20 × 0.20 mm
Orange

Data collection

Siemens $R3m/V$ diffractometer
$\omega/2\theta$ scans
Absorption correction: Semi-empirical
$T_{\min}$ = 0.6066, $T_{\max}$ = 0.9807
5189 measured reflections
2846 observed reflections [$F>6.0\sigma(F)$]

$R_{\rm int}$ = 0.022
$\theta_{\max}$ = 27.0°
h = 0 → 12
k = 0 → 10
l = −36 → 36
3 standard reflections monitored every 150 reflections intensity variation: <1.36%

Refinement

Refinement on F
Final R = 0.039
wR = 0.042
S = 1.04
2846 reflections
244 parameters
H atoms: riding model, fixed U = 0.08 Å^2

$w = 1/[\sigma^2(F)+0.0004F^2]$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 1.11 e Å^{-3}
$\Delta\rho_{\min}$ = −1.06 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$U_{\rm eq}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U_{\rm eq}$
Pb	0.2099 (1)	0.1133 (1)	0.1331 (1)	0.032 (1)
Fe	−0.2666 (1)	0.3124 (2)	0.0888 (1)	0.033 (1)
Si	0.5264 (3)	−0.1769 (4)	0.1933 (1)	0.041 (1)
C(1)	0.2325 (9)	−0.1519 (10)	0.1915 (3)	0.031 (3)
C(2)	0.3555 (9)	−0.1496 (10)	0.1661 (3)	0.030 (3)
B(3)	0.3256 (12)	−0.1500 (16)	0.1121 (4)	0.043 (4)
B(4)	0.1602 (13)	−0.1634 (15)	0.1049 (5)	0.048 (4)
B(5)	0.1053 (12)	−0.1528 (14)	0.1592 (5)	0.044 (4)
B(6)	0.2378 (12)	−0.2881 (15)	0.1465 (5)	0.042 (4)
C(7)	0.2353 (11)	−0.1863 (14)	0.2432 (4)	0.051 (4)
C(8)	0.5638 (11)	−0.0042 (14)	0.2344 (4)	0.066 (5)
C(9)	0.5471 (11)	−0.3771 (14)	0.2239 (4)	0.062 (4)
C(10)	0.6525 (10)	−0.1710 (14)	0.1473 (4)	0.053 (4)
N	0.1499 (7)	0.2305 (9)	0.0482 (3)	0.027 (2)
C(11)	−0.0669 (8)	0.2776 (11)	0.0816 (3)	0.032 (3)
C(12)	−0.1165 (9)	0.1677 (12)	0.1155 (3)	0.036 (3)
C(13)	−0.1694 (10)	0.2604 (16)	0.1509 (4)	0.052 (4)
C(14)	−0.1547 (10)	0.4259 (14)	0.1393 (4)	0.050 (4)
C(15)	−0.0913 (9)	0.4398 (12)	0.0959 (3)	0.036 (3)
C(16)	−0.3960 (10)	0.4441 (14)	0.0467 (4)	0.045 (4)
C(17)	−0.3655 (9)	0.2954 (14)	0.0252 (4)	0.046 (4)
C(18)	−0.4049 (9)	0.1664 (13)	0.0553 (4)	0.041 (4)
C(19)	−0.4571 (9)	0.2369 (14)	0.0940 (4)	0.047 (4)
C(20)	−0.4534 (8)	0.4111 (14)	0.0898 (4)	0.046 (4)
C(21)	0.0036 (8)	0.2274 (12)	0.0393 (3)	0.031 (3)
C(22)	0.2153 (9)	0.1406 (13)	0.0114 (3)	0.043 (3)
C(23)	0.1986 (9)	0.4002 (13)	0.0490 (4)	0.045 (3)

Table 2. *Selected bond lengths* (Å), *angles* (°) *and torsion angles* (°)

Pb—Cnt(1)*	2.224	Fe—Cnt(2)†	1.652
Fe—Cnt(3)‡	1.653	Pb—C(1)	2.744 (9)
Pb—C(2)	2.743 (8)	Pb—B(3)	2.529 (13)
Pb—B(4)	2.443 (12)	Pb—B(5)	2.539 (12)
Pb—N	2.673 (7)	Fe—C(11)	2.050 (8)
Fe—C(12)	2.042 (9)	Fe—C(13)	2.048 (10)
Fe—C(14)	2.025 (11)	Fe—C(15)	2.051 (9)
Fe—C(16)	2.045 (10)	Fe—C(17)	2.052 (11)
Fe—C(18)	2.042 (10)	Fe—C(19)	2.027 (9)
Fe—C(20)	2.048 (9)	Si—C(2)	1.874 (9)
Si—C(8)	1.868 (12)	Si—C(9)	1.863 (12)
Si—C(10)	1.878 (11)	C(1)—C(2)	1.467 (13)

C(1)—B(5)	1.552 (15)	C(1)—B(6)	1.711 (16)
C(1)—C(7)	1.516 (14)	C(2)—B(3)	1.571 (15)
C(2)—B(6)	1.715 (15)	B(3)—B(4)	1.673 (18)
B(3)—B(6)	1.763 (18)	B(4)—B(5)	1.683 (20)
B(4)—B(6)	1.731 (18)	B(5)—B(6)	1.782 (17)
N—C(21)	1.485 (10)	N—C(22)	1.468 (12)
N—C(23)	1.469 (12)		
Cnt(1)—Pb—N	122.1	Pb—N—C(21)	109.6 (5)
Pb—N—C(22)	113.1 (5)	Pb—N—C(23)	105.1 (5)
C(2)—C(1)—B(5)	113.1 (9)	C(2)—C(1)—B(6)	64.8 (6)
B(5)—C(1)—B(6)	66.0 (7)	Si—C(2)—C(1)	124.7 (7)
Si—C(2)—B(3)	123.2 (7)	C(1)—C(2)—B(3)	111.4 (8)
Si—C(2)—B(6)	132.0 (6)	C(1)—C(2)—B(6)	64.5 (6)
B(3)—C(2)—B(6)	64.7 (7)	C(2)—B(3)—B(4)	105.7 (9)
C(2)—B(3)—B(6)	61.6 (7)	B(4)—B(3)—B(6)	60.5 (7)
B(3)—B(4)—B(5)	104.3 (9)	B(3)—B(4)—B(6)	62.4 (7)
B(5)—B(4)—B(6)	62.9 (8)	C(1)—B(5)—B(4)	105.2 (9)
C(1)—B(5)—B(6)	61.3 (7)	B(4)—B(5)—B(6)	59.9 (7)
C(1)—B(6)—C(2)	50.7 (6)	C(1)—B(6)—B(3)	92.5 (8)
C(2)—B(6)—B(3)	53.7 (6)	C(1)—B(6)—B(4)	96.6 (8)
C(2)—B(6)—B(4)	97.2 (8)	B(3)—B(6)—B(4)	57.2 (7)
C(1)—B(6)—B(5)	52.7 (6)	C(2)—B(6)—B(5)	92.2 (8)
B(3)—B(6)—B(5)	96.8 (8)	B)4)—B(6)—B(5)	57.2 (7)
C(2)—C(1)—C(7)	121.0 (8)	B(5)—C(1)—C(7)	124.7 (9)
B(6)—C(1)—C(7)	128.8 (8)	C(2)—Si—C(8)	109.4 (5)
C(2)—Si—C(9)	112.6 (4)	C(8)—Si—C(9)	110.3 (5)
C(2)—Si—C(10)	109.7 (5)	C(8)—Si—C(10)	107.7 (5)
C(9)—Si—C(10)	107.0 (5)	N—C(21)—C(11)	110.9 (7)
C(21)—N—C(22)	109.9 (7)	C(21)—N—C(23)	110.3 (7)
C(22)—N—C(23)	108.8 (7)		
Fe—C(11)—C(21)—N	175.1 (6)	C(11)—C(21)—N—Pb	40.2 (8)
C(21)—N—Pb—C(2)	118.7 (6)	N—Pb—C(2)—Si	101.9 (7)

*Centroid of ring C(1), C(2), B(3), B(4), B(5).
†Centroid of ring C(11), C(12), C(13), C(14), C(15).
‡Centroid of ring C(16), C(17), C(18), C(19), C(20).

The systematic absences (*h*0*l*, *h* + *l* odd) were consistent with the space group $P2_1/n$. Data were collected with a scan range of 1.20° plus $K\alpha$ separation and a variable scan speed of 5.00–25.00° $\min^{-1}$. Data were corrected for Lorentz, polarization and absorption effects, the latter correction being applied on the basis of the azimuthal scan data of 4 high-κ reflections with an increment of 10°. The structure was solved by heavy-atom methods with *SHELXTL-Plus* (Sheldrick, 1990). A full-matrix least-squares refinement was performed. All non-H atoms were refined anisotropically. The cage H atoms were located on difference Fourier maps while other H atoms were calculated. No H-atom parameters were refined. Diagrams were produced and most calculations performed using *SHELXTL-Plus*.

This work was supported by grants from the National Science Foundation (CHE-9100048), the Robert A. Welch Foundation (N-1016) and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55709 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1014]

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Acta Cryst. (1993). C**49**, 793–796

A Diphenylformamidinate-Bridged Terpyridineplatinum(II) Dimer

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(*Received* 3 *June* 1992; *accepted* 29 *September* 1992)

Abstract

The compound μ-*N*,*N*′-diphenylformamidinato-bis[2,2′,2″-terpyridineplatinum(II)] perchlorate monohydrate (1) is formed by reaction of diphenylformamidine and [Pt(tpy)Cl]Cl (tpy = terpyridine) in the presence of excess base. The two platinum centers are bridged by a single diphenylformamidinato ligand with the remaining coordination geometry completed by the terpyridine group. The platinum–platinum separation is 3.049 (1) Å.

Comment

We are presently investigating the effect of metal–metal separation on the spectroscopic properties of binuclear platinum–terpyridine complexes. The complex $[\{Pt(tpy)\}_2(\mu\text{-dpf})](ClO_4)_3$ (1) (dpf = *N*,*N*′-diphenylformamidinate, tpy = terpyridine) is deep red in color as compared to the orange pyrazolyl-bridged dimer (Bailey & Gray, 1992). The luminescence properties of these complexes are also dependent on the metal–metal interaction. The structural analysis of (1) is described herein.

Fig. 1 shows the cation with atom labels; Fig. 2 shows the contents of the unit cell viewed down the *a*

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† Contribution No. 8646.

0108-2701/93/040793-04$06.00