Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Carbonyl(η^5-cyclopentadienyl)(trimethylsilyl isocyanide)(triphenylphosphine)iron(II) trifluoromethanesulfonate dichloromethane hemisolvate

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Received 3 May 2005
Accepted 13 May 2005
Online 21 May 2005

In the title compound, $[Fe(C_5H_5)(C_4H_9NSi)(C_{18}H_{15}P)(CO)]$-$(CF_3SO_3)\cdot 0.5CH_2Cl_2$, the Fe^{II} atom is coordinated by carbonyl, triphenylphosphine, trimethylsilyl isocyanide and cyclopentadienyl ligands in a typical piano-stool structure. The Fe—C—N—Si arrangement is almost linear and the Fe—C, C—N and N—Si bond distances are 1.836 (3), 1.162 (4) and 1.792 (3) Å, respectively.

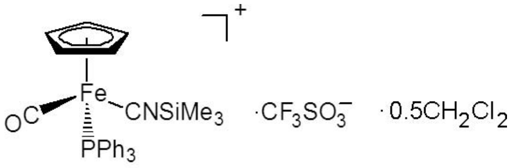
Key indicators

Single-crystal X-ray study
T = 203 K
Mean σ(C–C) = 0.006 Å
Disorder in solvent or counterion
R factor = 0.061
wR factor = 0.154
Data-to-parameter ratio = 18.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

$[FeCp(CO)_2(CNSiMe_3)]OTf$ (Cp is cyclopentadienyl and OTf is trifluoromethanesulfonate), (I), has been reported to be prepared from $[FeCp(CO)_2(CN)]$ and TMSOTf (trimethylsilyltrifluoromethanesulfonate) and was structurally characterized by X-ray diffraction (Nakazawa *et al.*, 2005). A similar reaction of $[FeCp(CO)(CN)(PPh_3)]$ with TMSOTf afforded the corresponding silyl isocyanide complex, *viz.* the title complex, $[FeCp(CO)(CNSiMe_3)(PPh_3)]OTf\cdot 0.5CH_2Cl_2$, (II) (Fig. 1).



(II)

A limited number of crystal structures have been reported to date for silyl isocyanide complexes: $[NEt_4]_2[Si\{(NC)(CO)_5Cr\}_6]$ (Fritz *et al.*, 1992), $[Re(dppe)_2Cl(CNSiMe_3)]$ (dppe

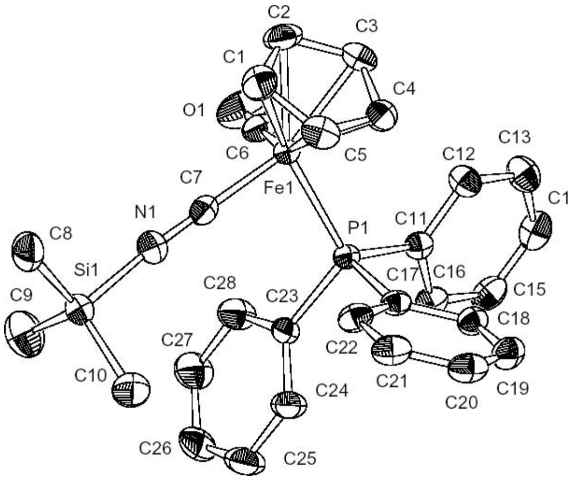


Figure 1
ORTEPII drawing (Johnson, 1976) of the cation of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

is diphenylphosphinoethane; da Silva *et al.*, 2000), [RhCp*(PMe$_3$)(^{i}Pr)(CNSiPh$_3$)][BAr$^f_4$] [Cp* is C$_5$Me$_5$ and Ar^f is C$_6$H$_3$(CF$_3$)$_2$-3,5; Taw *et al.*, 2002] and [FeCp(CO)-Me(CNSiPh$_3$)] (Nakazawa *et al.*, 2004).

The Fe—C—N—Si arrangement in (II) is almost linear [Fe—C—N = 177.3 (3)° and C—N—Si = 173.6 (3)°], as in other reported silyl isocyanide complexes, with the exception of [FeCp(CO)(Me)(CNSiPh$_3$)] [C—N—Si = 156.7 (5)°]. A comparison of bond distances in the Fe—C—N—Si portion of (II) with those of (I) reveals that the Fe—C bond of (II) [1.836 (3) Å] is slightly shorter than that of (I) [1.862 (4) Å]. The C—N and N—Si bond distances are comparable [C—N = 1.162 (4) Å for (II) and 1.157 (6) Å for (I); N—Si = 1.792 (3) Å for (II) and 1.794 (4) Å for (I)]. The P1—Fe1—C7 angle [88.5 (1)°] seems to show no steric repulsion between the PPh$_3$ and SiMe$_3$ ligands.

Experimental

TMSOTf (0.1 ml, 0.55 mmol) was added to a CH$_2$Cl$_2$ solution (3 ml) of [FeCp(CN)(CO)(PPh$_3$)] (100 mg, 0.23 mmol) prepared according to the literature method (Faller & Johnson, 1975). After the mixture was stirred for 1 h at 195 K, the solvent was removed under reduced pressure to give a yellow oil, which was washed with diethyl ether repeatedly and dried *in vacuo* to give [FeCp(CO)(CNSiMe$_3$)(PPh$_3$)]OTf, (II), as a pale-brown powder (140 mg, 0.21 mmol, 92%). Single crystals of (II) were obtained by solvent diffusion at 253 K over a few days from a CH$_2$Cl$_2$ layer containing (II) and an overlayer of hexane. IR (CH$_2$Cl$_2$, cm^{-1}): ν_{CO} 1998, ν_{CN} 2097; ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.03 (*s*, SiMe$_3$, 6H), 0.16 (*s*, SiMe$_3$, 3H), 4.78 (*s*, Cp, 5H), 7.45 (*m*, Ph, 15H); ^{13}C NMR (100.3 MHz, CDCl$_3$): δ −0.5 (*s*, SiMe$_3$), 1.9 (*s*, SiMe$_3$), 85.5 (*s*, Cp), 129.2 (*d*, *J* = 10.6 Hz, Ph), 131.6 (*d*, *J* = 3.1 Hz, Ph), 132.5 (*d*, *J* = 49.0 Hz, Ph) 132.7 (*d*, *J* = 10.6 Hz, Ph), 154.8 (*d*, *J* = 22.3 Hz, CN), 213.7 (*d*, *J* = 26.1 Hz, CO); ^{31}P NMR (161.7 MHz, CDCl$_3$): δ 67.5 (*s*).

Crystal data

[Fe(C$_5$H$_5$)(C$_4$H$_9$NSi)(C$_{18}$H$_{15}$P)(CO)](CF$_3$SO$_3$)·0.5CH$_2$Cl$_2$
M_r = 701.98
Triclinic, $P\overline{1}$
a = 9.429 (2) Å
b = 13.055 (3) Å
c = 13.510 (3) Å
α = 95.995 (4)°
β = 100.673 (4)°
γ = 96.272 (4)°
V = 1611.0 (6) Å^3
Z = 2
D_x = 1.447 Mg m^{-3}
Mo Kα radiation
Cell parameters from 6485 reflections
θ = 3.1–27.5°
μ = 0.75 mm^{-1}
T = 203.2 K
Needle, yellow
0.47 × 0.11 × 0.09 mm

Data collection

Rigaku/MSC Mercury CCD diffractometer
ω scans
Absorption correction: multi-scan (Jacobson, 1998)
T_{min} = 0.839, T_{max} = 0.934
15 438 measured reflections
7155 independent reflections
5918 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 27.5°
h = −12 → 12
k = −16 → 14
l = −17 → 13

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.061
$wR(F^2)$ = 0.154
S = 1.04
7155 reflections
388 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0697P)^2 + 2.9827P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.03 e Å^{-3}
$\Delta\rho_{min}$ = −0.84 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Fe1—C6	1.760 (4)	Fe1—C3	2.113 (3)
Fe1—C7	1.836 (3)	Fe1—P1	2.2283 (9)
Fe1—C1	2.099 (4)	Si1—N1	1.792 (3)
Fe1—C5	2.102 (3)	O1—C6	1.142 (4)
Fe1—C2	2.103 (3)	N1—C7	1.162 (4)
Fe1—C4	2.113 (3)		
C6—Fe1—C7	96.63 (16)	C7—N1—Si1	173.6 (3)
C6—Fe1—P1	93.12 (11)	N1—C7—Fe1	177.3 (3)
C7—Fe1—P1	88.48 (10)		

H atoms were refined using a riding model, with C—H = 0.95 Å, and fixed individual displacement parameters [U_{iso}(H) = U_{eq}(C)]. For the solvent molecule, the two carbon positions were refined as a disordered model with C atoms having 0.5 occupancy.

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2000); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXL97*; software used to prepare material for publication: *TEXSAN*.

This work was supported by a Grant-in-Aid (No. 15205010) and by a Grant-in-Aid for Science Research on Priority Areas (No. 16033250, Reaction Control of Dynamic Complexes) from the Ministry of Education, Culture, Sports, Science and Technology, Japan, by a Sasagawa Scientific Research Grant from the Japan Science Society, and by the Yamada Science Foundation.

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