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Transmetallation reaction of cyclomercurated anils of benzoylferrocene with metallic tin.
X-ray crystal structure of $[SnCl_2\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CPh{=}NC_6H_4\text{-}4\text{-}CH_3)\}_2]$

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Abstract

The transmetallation reaction of cyclomercurated anils of benzoylferrocene $[HgCl\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CPh{=}NAr)\}]$ (Ar = substituted phenyl groups) with metallic tin was carried out in refluxing xylene to give dichlorobisferrocenyltin(IV) $[SnCl_2\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CPh{=}NAr)\}_2]$. The composition and structure of products were characterized by elemental analysis, IR, ^{1}H-NMR and 2D NOESY spectra. The molecular structure of $[SnCl_2\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CPh = NC_6H_4\text{-}4\text{-}CH_3)\}_2]$ was determined by single crystal X-ray analysis. The distances of N and Sn are 2.519(3) and 2.501(3) Å, respectively, shorter than the sum of van der Waals radii of N and Sn (3.6 Å), indicating an intramolecular coordination of N and Sn. The ^{119}Sn-NMR spectra were recorded, and a satisfactory linear relationship was found to exist between the ^{119}Sn shifts (δ) and Hammett substituent constants.

Keywords: Transmetallation; Mercury; Tin; Ferrocene; Anils

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1. Introduction

Organomercury (II) compounds have received renewed interest in these years because of their ability to accommodate essentially all important organic functional groups, remarkable chemical and thermal stability, simple preparation and the ease with which they undergo transmetallation reaction to form other useful organometallics [1]. In our previous paper has been reported that mercurated shiff bases can be used as transmetallation reagents for the synthesis of other organometallic compounds and particularly that the reaction of shiff-base-type arylmercury compounds with metallic tin leads to dichlorobisaryltin (IV) [2–4].

Organotin compounds have attracted considerable attention recently for their anti-tumour activity, environmental effect, and industrial application [5–7]. More recently, the syntheses and structures of dialkyltin esters of ferrocenecarboxylic acid and 1,1′-ferrocenedicarboxylic acid have been reported, together with the finding that dibutyltin ferrocenecarboxylate oxide adopts an oxo-bridging dimer structure made with four anisobidentate bridging carboxylate groups as ligands [8]. Though some organotin compounds containing a $Sn(Fc)_2$ fragment have been reported [9], to the best of our knowledge, no synthesis of organotin compounds containing not only a $Sn(Fc)_2$ fragment but also N → Sn intramolecular coordination has ever been reported so far.

In the present paper, further insight into transmetallation reaction and organotin compounds is provided in the descriptions of the synthesis of dichlorobisferro-

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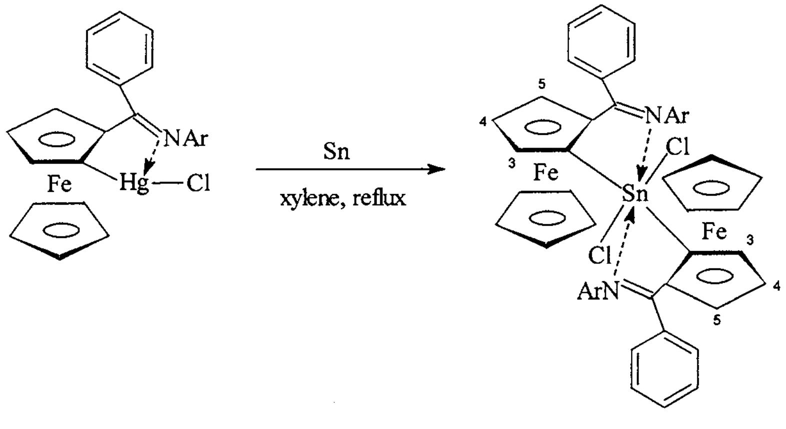
cenyltin (IV) via transmetallation reaction of the mercurated anils of benzoylferrocene with metallic tin in refluxing xylene as well as the study of the structure and ^{119}Sn-NMR.



1 **2**

Ar = p-$CH_3OC_6H_4$ (**a**), p-$CH_3C_6H_4$ (**b**), C_6H_5 (**c**), p-ClC_6H_4 (**d**), p-BrC_6H_4 (**e**), m-$CH_3C_6H_4$ (**f**), m-ClC_6H_4 (**g**), m-BrC_6H_4 (**h**).

2. Results and discussion

2.1. Transmetallation reaction

Transmetallation reaction of cyclomercurated anils of benzoylferrocene [HgCl{(η^5-C_5H_5)Fe(η^5-C_5H_3CPh=NAr)}] **1** [10] with metallic tin was carried out by a previously published procedure [2]. Dichlorobisferrocenyltins [$SnCl_2${(η^5-C_5H_5)Fe(η^5-C_5H_3CPh=NAr)}$_2$] **2** were produced as red air-stable crystals which have been characterized by elemental analysis, IR and ^{1}H-NMR spectra.

The influence of different substituents of N-phenyl ring on the yields of the reaction did not cause obvious regularities. However, when the N-phenyl was changed to N-naphthyl or the substituent on N-phenyl was *meta* nitro, no product was formed by treating them with metallic tin in refluxing xylene for 24 h. This is tentatively imputed to the steric hindrance and strong electron-withdrawing group which decreased the electron population of the imino nitrogen atom and the stability of the molecule.

2.2. Spectral properties of transmetallation products

The IR spectral features of **2** are similar to those described in our previous report on mercurated anils of benzoylferrocene [10]. As shown in Table 1, the C=N absorption of **2** are shifted to lower frequency by 32–54 cm^{-1} in comparison with those of the corresponding anils of benzoylferrocene [(η^5-C_5H_5)Fe(η^5-C_5H_3CPh=NAr)] **3**, indicating that nitrogen is coordinated to tin through its lone pair electrons [11]. By comparison of the C=N absorption of **2** with **1** and corresponding cyclopalladated compounds [Pd{(η^5-C_5H_5)Fe(η^5-C_5H_3CPh=NAr)}Cl(PPh_3)] **4** [4], it can be concluded that the intramolecular N → Sn coordination in **2** was stronger than the intramolecular N → Hg coordination in **1** but weaker than the intramolecular N → Pd coordination in the corresponding palladated derivatives **4**.

The ^{1}H-NMR spectra of **2** were completely consistent with a homoannular 1,2-disubstituted structures. Two dimensional NOESY was measured for **2f** to assign the three broad singlets at 3.99, 4.26 and 4.80 ppm. It was confirmed that the upfield singlet at 3.99 ppm corresponding to the protons 5, owing to the appearance of the negative cross-peak representing the nuclear overhauser effect (NOE) between protons 5 and the protons of the C-phenyl ring. The singlet at 4.26 ppm represents the resonance of protons 4, because of the appearance of the NOE cross peak between protons 5 and protons 4. Accordingly, the singlet at 4.80 ppm can be attributed to protons 3. In addition, it has been found in

Table 1
The C=N stretching frequencies (cm^{-1}) for compounds **3**, **1**, **2** and **4**[a]

	a	b	c	d	e	f	g	h
3[b]	1614	1616	1600	1616	1616	1616	1614	1614
1[b]	1604	1590	1590	1590	1590	1590	1580	1590
2	1566	1571	1568	1562	1567	1570	1570	1570
4[c]	1554	1532	1532	1532	1534	1542	1542	1542

[a] **3**: anils of benzoylferrocene; **1**, **2** and **4**: corresponding mercurated, stannated and palladated compounds respectively.
[b] The data are cited from [10].
[c] The data are cited from [4].

Table 2
^{119}Sn-NMR chemical shifts δ (ppm) for compounds **2**

	a	**b**	**c**	**d**	**e**	**f**	**g**	**h**
δ (ppm)	388.03	389.91	394.82	404.76	405.30	390.49	406.48	406.75

its ^{1}H NMR spectrum that half of hexane per molecule was contained in compound **2b**, which has been certified by elemental analysis and X-ray structure. The ^{1}H-NMR spectra of **2e**–**2h** show that one or half of a dichloromethane per molecule was contained.

The ^{119}Sn-NMR spectra of **2a**–**2h** were recorded and the ^{119}Sn chemical shifts (δ) are listed in Table 2. The ^{119}Sn shifts (δ) show obvious dependence on the nature of the substituents in the N-phenyl ring, with lower frequency shifts resulting from electron-donating groups and with higher frequency shifts resulting from electron-withdrawing groups. Such a trend is in consistence with that of the imino carbons and ferrocenyl carbons 2 of substituted ferrocene for compounds **1** [12], opposition to that was found in the ^{199}Hg- and ^{195}Pt-NMR [13,14]. Satisfactory linear correlation between ^{119}Sn shifts (δ) and Hammett substituent constant σ_p and σ_m [15] was obtained (Eq. (1))

$$\delta = 395.45 + 32.27\sigma \quad r = 0.977 \quad n = 8 \tag{1}$$

In general, there are two pathway for the substituents of the N-phenyl ring to affect the tin: one is the transmission of electronic effects through the C=N bond and Cp ring, and the other involves the N → Sn intramolecular coordination, which has been demonstrated by crystal structure (Fig. 1). It is possible that the substituents affected the tin essentially by way of N → Sn interaction, rather than through the C=N bond together with Cp ring owing to the nonplanar nature of the N-phenyl ring with respect to the Cp ring or the C–C=N–C plane.

2.3. *X-ray crystal structure of* ***2b***

The X-ray crystal structure of **2b** was determined in order to provide further structural information of compounds **2**. Fig. 1 shows the ORTEP view of the molecular structure of **2b**. Atomic coordinates are listed in Table 3; selected bond lengths and bond angles are listed in Table 4. As shown in Fig. 1 and Table 4, the coordination sphere of tin atom was a highly distorted octahedron composed of two chlorine atoms and two coordinated imino nitrogen atoms in the equatorial plane and two *trans*-positioned ferrocenyl group in the axial sites. The angles 163.36° for N(1)–Sn–Cl(2), 162.02° for N(2)–Sn–Cl(1) and 155.4° for C(10)–Sn–C(30) showed smaller distortion than in dichlorobis[2-(benzylideneamino)-5-tolyl]tin(IV) [2], in which the corresponding angles were 152.7, 156.3 and 139.3°. The tin atom was bonded covalently to two chloride atoms and two carbon atoms of the substituted Cp rings. The C–Sn and Cl–Sn bond distances (average values of 2.11 and 2.45 Å, respectively) were well within the range of values obtained in similar complexes of tin [2,5,7,16]. The distances between N and Sn were almost the same (2.519 Å for Sn–N(1) and 2.501 Å for Sn–N(2)), much shorter than the sum of the van der Waals radii for Sn and N (about 3.6 Å) [17], suggesting the presence of significant N → Sn intramolecular coordination interaction. The C=N bond lengths of 1.296(5) Å (N(1)–C(11)) and 1.303(5) Å (N(2)–C(35)) were longer than those found in {(phenylimino)phenylmethyl}ferrocene (1.27 Å) and 2-chloromercurio-1-[{(phenylimino)phenylmethyl}ferrocene] (1.282 Å) [18], but similar to those determined for cyclopalladated and cycloplatinated ferrocenylketimines (1.296 and 1.293 Å, respectively) [11,19], in which the N → Pd and N → Pt intramolecular coordination were stronger than N → Hg intramolecular coordination. This phenomenon is consistent with the IR spectra.

The Sn, N(1), C(11), C(6), C(10) and Sn, N(2), C(35), C(34), C(30) were essentially coplanar respectively with largest deviation of 0.078 Å for C(10) and −0.104 Å for C(30) from the corresponding least-square plane. The dihedral angle between the two planes was 72.41°. The arrangements of the C-phenyl and N-phenyl rings as well as the Cp rings were similar to that in compounds **1** [18], except that the N-phenyl rings formed smaller dihedral angles of 50.46 and 56.92° with the plane of C=N bond. The angles between the substituted Cp rings and the C=N plane were only 6.79 and 7.06°.

As mentioned in spectral section, half of hexane per molecule was contained in compound **2b**, which could be observed from its unit cell diagram.

3. Experiment details

3.1. *Materials and instruments*

Melting points were determined on a WC-1 microscopic apparatus and are uncorrected. Elemental analyses were determined with a Carlo Erba 1106 Elemental Analyzer. IR spectra were recorded on a Perkin-Elmer FT-IR 1730 spectrophotometer. ^{1}H-NMR spectra were recorded on Bruker DPX-400 spectrometer, using $CDCl_3$ as a solvent and TMS as an internal standard. 2D-NOESY spectrum was recorded on a Bruker DPX-

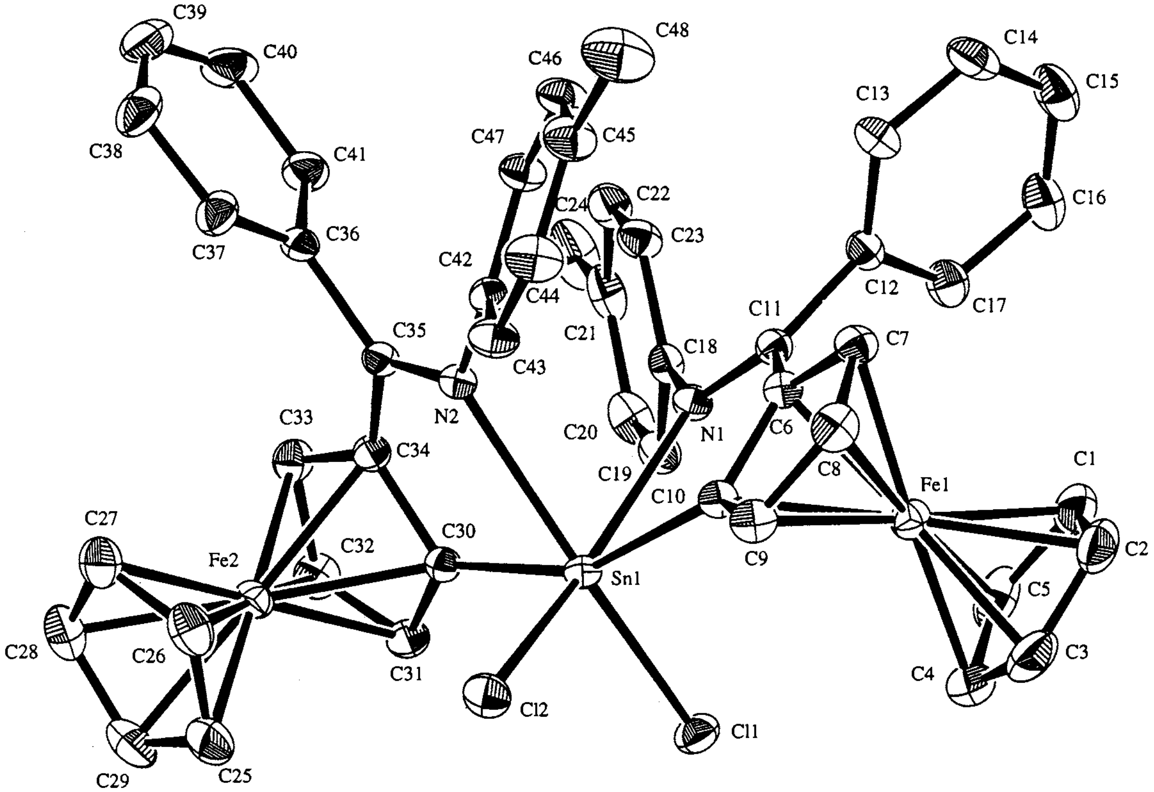


Fig. 1. ORTEP view of the molecular structure of compound **2b**, with thermal ellipsoids drawn at the 20% probability level. Hydrogen atoms and half of hexane molecule are omitted for clarity.

400 spectrometer in $CDCl_3$ at room temperature with a mixing time of 250 ms. ^{119}Sn-NMR spectra were recorded using $SnCl_4$ in D_2O as an external standard. The operating frequency was 149.11 MHz and the routine acquisition parameters used were as follows: pulse width, 5.00 μs, acquisition time 0.09 s, spectral width 89686.1 Hz. Some of the compounds were crystallized as solvates from dichloromethane or hexane, and their compositions were determined by elemental analyses and calibrated on the basis of ^1H-NMR.

All solvents were dried according to the standard methods and metallic tin was purified according to the literature [20]. The mercurated anils of benzoylferrocene **1** were prepared according to the literature procedures [10].

*3.2. Preparation of the compounds **2***

*3.2.1. General procedure for the synthesis of compounds **2***

Suspensions of **1** (0.15 mmol) and powder metallic tin (0.0825 mmol) were refluxed in dry xylene (10 ml) for 5–14 h. After removing the metallic mercury by filtration, the solvents were evaporated in vacuo. The resulting crude products were recrystallized from dichloromethane-hexane to give red crystals **2**. The compounds prepared according to this procedure were characterized as follows.

*3.2.1.1. $[SnCl_2\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CPh{=}NC_6H_4OCH_3\text{-}4)\}_2]$ (**2a**).* Yield 76%. M.p. 168–170°C (dec.). Anal. Found: C, 59.22; H, 3.83; N, 2.81. $C_{48}H_{40}N_2Cl_2Fe_2O_2Sn$. Calc.: C, 58.94; H, 4.12; N, 2.86%. IR (KBr pellet): 1606, 1584, 1566, 1503, 1435, 1242, 1106, 1002, 826, 743, 702 cm^{-1}. ^1H-NMR: δ 3.71(s, 6H, OCH_3), 4.00(bs, 2H, H-5), 4.27(bs, 2H, H-4), 4.35(s, 10H, C_5H_5), 4.81(bs, 2H, H-3), 6.50(bs, 8H, N–Ar–H), 7.00(d, 4H, H-α, $J = 6.4$ Hz), 7.24(m, 6H, H-β,γ) ppm.

*3.2.1.2. $[SnCl_2\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CPh{=}NC_6H_4CH_3\text{-}4)\}_2]$ (**2b**).* Yield 77%. M.p. > 232°C (dec.). Anal. Found: C, 61.76; H, 4.66; N, 2.75. $C_{48}H_{40}N_2Cl_2Fe_2Sn \cdot 0.5C_6H_{14}$. Calc.: C, 61.92; H, 4.79; N, 2.83%. IR (KBr pellet): 1605, 1586, 1571, 1505, 1435, 1107, 1004, 828, 730, 711 cm^{-1}. ^1H-NMR: δ 2.17(s, 6H, CH_3), 3.99(bs, 2H, H-5), 4.22(bs, 2H, H-4), 4.35(s, 10H, C_5H_5), 4.74(bs, 2H, H-3), 6.44(d, 4H, N–Ar–H, $J = 7.2$ Hz), 6.76(d, 4H, N–Ar–H, $J = 7.6$ Hz), 7.04(d, 4H, H-α, $J = 7.2$ Hz), 7.25(m, 6H, H-β,γ) ppm.

*3.2.1.3. $[SnCl_2\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CPh{=}NC_6H_5)\}_2]$ (**2c**).* Yield 82%. M.p. > 270°C (dec.). Anal. Found: C, 60.24; H, 3.99; N, 3.00. $C_{46}H_{36}N_2Cl_2Fe_2Sn$. Calc.: C, 60.18; H, 3.95; N, 3.05%. IR (KBr pellet): 1586, 1568,

Table 3
Atomic coordinates and equivalent isotropic thermal parameters for **2b**

Atom	x	y	z	B_{eq}
Sn	0.143717(9)	0.31910(2)	0.77577(1)	2.8926(6)
Fe(1)	0.06772(2)	0.50714(4)	0.66106(4)	3.66(1)
Fe(2)	0.21553(2)	0.12077(4)	0.87836(3)	3.51(1)
Cl(1)	0.18829(4)	0.45676(7)	0.82341(7)	4.51(3)
Cl(2)	0.11206(5)	0.29874(8)	0.86656(7)	4.81(3)
N(1)	0.1536(1)	0.3306(2)	0.6600(2)	3.01(7)
N(2)	0.1185(1)	0.1665(2)	0.7172(2)	3.04(7)
C(1)	0.0849(3)	0.6125(3)	0.6093(4)	6.7(2)
C(2)	0.0474(2)	0.6374(3)	0.6233(4)	6.6(2)
C(3)	0.0584(3)	0.6356(4)	0.6966(4)	6.8(2)
C(4)	0.1022(3)	0.6098(4)	0.7261(3)	6.4(2)
C(5)	0.1186(2)	0.5965(3)	0.6743(5)	6.5(2)
C(6)	0.0808(1)	0.3787(3)	0.6316(2)	3.18(9)
C(7)	0.0368(1)	0.4065(3)	0.5911(2)	3.82(10)
C(8)	0.0145(2)	0.4204(3)	0.6386(3)	4.6(1)
C(9)	0.0438(2)	0.4033(3)	0.7067(3)	4.1(1)
C(10)	0.0853(1)	0.3761(3)	0.7038(2)	3.23(9)
C(11)	0.1185(1)	0.3609(3)	0.6113(2)	3.03(9)
C(12)	0.1152(1)	0.3860(3)	0.5388(2)	3.39(9)
C(13)	0.0830(2)	0.3505(3)	0.4811(2)	4.3(1)
C(14)	0.0786(2)	0.3832(4)	0.4145(3)	5.8(1)
C(15)	0.1061(2)	0.4521(4)	0.4076(3)	6.1(2)
C(16)	0.1383(2)	0.4865(4)	0.4642(3)	5.6(2)
C(17)	0.1437(2)	0.4538(3)	0.5309(3)	4.3(1)
C(18)	0.1920(1)	0.3030(3)	0.6466(2)	3.19(9)
C(19)	0.2327(2)	0.3339(3)	0.6903(2)	3.9(1)
C(20)	0.2404(2)	0.3064(4)	0.6798(3)	4.6(1)
C(21)	0.2681(2)	0.2458(4)	0.6251(3)	4.7(1)
C(22)	0.2281(2)	0.2135(3)	0.5835(3)	4.7(1)
C(23)	0.1895(2)	0.2412(3)	0.5931(2)	3.9(1)
C(24)	0.3098(2)	0.2149(5)	0.6137(4)	7.1(2)
C(25)	0.1973(2)	0.1421(4)	0.9631(3)	5.9(2)
C(26)	0.1662(2)	0.0862(4)	0.9134(3)	5.2(1)
C(27)	0.1878(2)	0.0049(4)	0.9037(3)	5.6(1)
C(28)	0.2325(2)	0.0112(4)	0.9471(3)	6.1(2)
C(29)	0.2383(2)	0.0955(4)	0.9842(3)	6.2(2)
C(30)	0.1985(1)	0.2297(2)	0.8087(2)	2.91(8)
C(31)	0.2434(1)	0.2380(3)	0.8539(2)	3.74(10)
C(32)	0.2665(2)	0.1579(3)	0.8466(3)	4.3(1)
C(33)	0.2369(2)	0.0977(3)	0.7967(2)	3.8(1)
C(34)	0.1943(1)	0.1425(3)	0.7730(2)	3.14(9)
C(35)	0.1516(1)	0.1109(3)	0.7262(2)	3.06(9)
C(36)	0.1485(1)	0.0171(3)	0.6927(2)	3.45(9)
C(37)	0.1207(2)	−0.0501(3)	0.7018(3)	4.6(1)
C(38)	0.1193(2)	−0.1378(3)	0.6730(4)	6.1(1)
C(39)	0.1445(2)	−0.1563(4)	0.6341(4)	6.9(2)
C(40)	0.1717(2)	−0.0902(4)	0.6233(3)	6.6(2)
C(41)	0.1744(2)	−0.0028(3)	0.6542(3)	4.6(1)
C(42)	0.0757(1)	0.1518(3)	0.6684(2)	3.15(9)
C(43)	0.0404(2)	0.1674(3)	0.6889(3)	4.4(1)
C(44)	−0.0019(2)	0.1620(4)	0.6409(3)	5.4(1)
C(45)	−0.0106(2)	0.1416(4)	0.5715(3)	5.3(1)
C(46)	0.0248(2)	0.1248(4)	0.5513(3)	5.1(1)
C(47)	0.0674(2)	0.1298(3)	0.5983(2)	4.0(1)
C(48)	−0.0568(2)	0.1384(6)	0.5180(4)	8.5(2)
C(49)	0.5224(9)	0.384(1)	0.775(3)	27(2)
C(50)	0.530(1)	0.390(2)	0.852(1)	26(1)
C(51)	0.5818(6)	0.391(1)	0.898(1)	19.8(9)

1505, 1431, 1109, 1002, 831, 768, 736, 705, 696 cm^{-1}. ^{1}H-NMR: 4.01(bs, 2H, H-5), 4.23(bs, 2H, H-4), 4.36(s, 10H, C_5H_5), 4,77(bs, 2H, H-3), 6.58(d, 4H, N–Ph–H, $J = 7.2$ Hz), 6.86(t, 2H, N–Ph–H, $J = 7.2$ Hz), 6.97(t, 4H, N–Ph–H, $J = 7.2$ Hz), 7.03(d, 4H, H-α, $J = 7.2$ Hz), 7.24(m, 6H, H-β,γ) ppm.

3.2.1.4. $[SnCl_2\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CPh{=}NC_6H_4Cl\text{-}4)\}_2]$ (**2d**). Yield 80%. M.p. 188–190°C (dec.). Anal. Found: C, 52.39; H, 3.14; N, 2.38. $C_{46}H_{34}N_2Cl_4Fe_2Sn \cdot CH_2Cl_2$. Calc.: C, 52.66; H, 3.39; N, 2.61%. IR (KBr pellet): 1605, 1583, 1562, 1434, 1108, 1004, 837, 735, 702 cm^{-1}. ^{1}H-NMR: 4.10(bs, 2H, H-5), 4.33(t, 2H, H-4, $J = 2.0$ Hz), 4.38(s, 10H, C_5H_5), 4.73(bs, 2H, H-3), 5.30(s, 2H, CH_2Cl_2), 6.48(d, 4H, N–Ar–H, $J = 8.4$ Hz), 6.94(d, 4H, N–Ar–H, $J = 8.4$ Hz), 7.02(d, 4H, H-α, $J = 7.2$ Hz), 7.28(m, 6H, H-β,γ) ppm.

3.2.1.5. $[SnCl_2\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CPh{=}NC_6H_4Br\text{-}4)\}_2]$ (**2e**). Yield 79%. M.p. 156–158°C (dec.). Anal. Found: C, 49.64; H, 3.35; N, 2.23. $C_{46}H_{34}N_2Br_2Cl_2Fe_2Sn \cdot 0.5CH_2Cl_2$. Calc.: C, 49.94; H, 3.15; N, 2.51%. IR (KBr pellet): 1584, 1567, 1435, 1107, 1004, 831, 733, 699 cm^{-1}. ^{1}H-NMR: 4.11(bs, 2H, H-5), 4.34(t, 2H, H-4, $J = 2.0$ Hz), 4.38(s, 10H, C_5H_5), 4.72(bs, 2H, H-3), 5.30(s, 1H, $0.5CH_2Cl_2$), 6.42(d, 4H, N–Ar–H, $J = 8.0$ Hz), 7.02(d, 4H, H-α, $J = 7.2$ Hz), 7.09(d, 4H, N–Ar–H, $J = 8.4$ Hz), 7.28(m, 6H, H-β,γ) ppm.

3.2.1.6. $[SnCl_2\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CPh{=}NC_6H_4CH_3\text{-}3)\}_2]$ (**2f**). Yield 82%. M.p. > 250°C (dec.). Anal. Found: C, 58,64; H, 4.20; N, 2.71. $C_{48}H_{40}N_2Cl_2Fe_2Sn \cdot 0.5CH_2Cl_2$. Calc.: C, 58.92; H, 4.18; N, 2.83%. IR (KBr pellet): 1601, 1584, 1565, 1436, 1107, 1004, 876, 827, 789, 733, 709, 689cm^{-1}. ^{1}H-NMR: 2.16(s, 6H, CH_3), 3.99(bs, 2H, H-5), 4.26(bs, 2H, H-4), 4.36(s, 10H, C_5H_5), 4.80(bs, 2H, H-3), 5.30(s, 1H, $0.5CH_2Cl_2$), 6.21(d, 2H, N–Ar–H, $J = 7.6$ Hz), 6.50(s, 2H, N–Ar–H), 6.67(d, 2H, N–Ar–H, $J = 7.6$ Hz), 6.81(t, 2H, N–Ar–H, $J = 7.6$ Hz), 7.02(d, 4H, H-α, $J = 7.6$ Hz), 7.26(m, 6H, H-β,γ) ppm.

3.2.1.7. $[SnCl_2\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CPh{=}NC_6H_4Cl\text{-}3)\}_2]$ (**2g**). Yield 82%. M.p. 178–180°C (dec.). Anal. Found: C, 52.98; H, 3.43; N, 2.57. $C_{46}H_{34}N_2Cl_4Fe_2Sn \cdot CH_2Cl_2$. Calc.: C, 52.66; H, 3.39; N, 2.61%. IR (KBr pellet): 1585, 1570, 1432, 1107, 1004, 918, 873, 834, 786, 730, 709, 699cm^{-1}. ^{1}H-NMR: 4.12(bs, 2H, H-5), 4.34(bs, 2H, H-4), 4.37(s, 10H, C_5H_5), 4.79(bs, 2H, H-3), 5.30(s, 2H, CH_2Cl_2), 6.43(s, 2H, N–Ar–H), 6.52(d, 2H, N–Ar–H, $J = 6.4$ Hz), 6.85(d, 2H, N–Ar–H, $J = 7.2$ Hz), 6.93(t, 2H, N–Ar–H, $J = 7.6$ Hz), 7.07(d, 4H, H-α, $J = 6.8$ Hz), 7.29(m, 6H, H-β,γ) ppm.

Table 4
Selected bond lengths (Å) and bond angles (°) for **2b**

Bond lengths					
Sn–Cl(1)	2.446(1)	N(1)–C(11)	1.296(5)	C(21)–C(24)	1.525(7)
Sn–Cl(2)	2.454(1)	N(1)–C(18)	1.432(5)	C(34)–C(35)	1.452(6)
Sn–N(1)	2.519(3)	N(2)–C(35)	1.301(5)	C(35)–C(36)	1.504(5)
Sn–N(2)	2.501(3)	N(2)–C(42)	1.411(5)	C(45)–C(48)	1.513(8)
Sn–C(10)	2.113(4)	C(6)–C(11)	1.456(6)	C(49)–C(50)	1.51(5)
Sn–C(30)	2.108(4)	C(11)–C(12)	1.499(6)	C(50)–C(51)	1.63(3)
Bond angles					
Cl–Sn–Cl(2)		98.31(4)	Sn–N(2)–C(42)		122.9(2)
Cl(1)–Sn–N(1)		93.74(8)	C(35)–N(2)–C(42)		124.5(3)
Cl(1)–Sn–N(2)		162.02(8)	C(10)–C(6)–C(11)		120.5(4)
Cl(1)–Sn–C(10)		102.8(1)	Sn–C(10)–Fe(1)		133.8(2)
Cl(1)–Sn–C(30)		93.1(1)	Sn–C(10)–C(6)		117.6(3)
Cl(2)–Sn–N(1)		163.36(9)	Sn–C(10)–C(9)		134.9(3)
Cl(2)–Sn–N(2)		96.10(8)	N(1)–C(11)–C(6)		116.1(4)
Cl(2)–Sn–C(10)		93.4(1)	N(1)–C(11)–C(12)		125.2(4)
Cl(2)–Sn–C(30)		102.9(1)	N(1)–C(18)–C(19)		119.1(4)
N(1)–Sn–N(2)		74.6(1)	N(1)–C(18)–C(23)		121.6(4)
N(1)–Sn–C(10)		72.7(1)	Sn–C(30)–Fe(2)		132.3(2)
N(1)–Sn–C(30)		87.8(1)	Sn–C(30)–C(31)		135.2(3)
N(2)–Sn–C(10)		87.0(1)	Sn–C(30)–C(34)		117.2(3)
N(2)–Sn–C(30)		73.1(1)	N(2)–C(35)–C(34)		116.7(3)
C(10)–Sn–C(30)		155.4(2)	N(2)–C(35)–C(36)		124.9(4)
Sn–N(1)–C(11)		112.0(3)	N(2)–C(42)–C(43)		118.6(4)
Sn–N(1)–C(18)		125.6(3)	N(2)–C(42)–C(47)		122.6(4)
C(11)–N(1)–C(18)		122.4(3)	C(30)–C(34)–C(35)		120.3(4)
Sn–N(2)–C(35)		111.2(3)	C(49)–C(50)–C(51)		110(2)

*3.2.1.8. [$SnCl_2\{(\eta^5$-$C_5H_5)Fe(\eta^5$-$C_5H_3CPh{=}NC_6H_4Br$-$3)\}_2$] (**2h**).* Yield 87%. M.p. 164–168°C (dec.). Anal. Found: C, 50.40; H, 3.58; N, 2.18. $C_{46}H_{34}N_2Br_2Cl_2Fe_2Sn \cdot 0.5CH_2Cl_2$. Calc.: C, 49.94; H, 3.15; N, 2.51%. IR (KBr pellet): 1585, 1570, 1431, 1107, 1004, 912, 870, 834, 786, 729, 707, 697 cm^{-1}. ^1H-NMR: 4.13(bs, 2H, H-5), 4.35(t, 2H, H-4, $J = 2.4$ Hz), 4.37(s, 10H, C_5H_5), 4.80(bs, 2H, H-3), 5.30(s, 1H, $0.5CH_2Cl_2$), 6.57(s, 2H, N–Ar–H), 6.58(d, 2H, N–Ar–H, $J = 7.2$ Hz), 6.87(t, 2H, N–Ar–H, $J = 8.0$ Hz), 7.01(d, 2H, N–Ar–H, $J = 8.0$ Hz), 7.07(d, 4H, H-α, $J = 6.8$ Hz), 7.28(m, 6H, H-β,γ) ppm.

3.3. X-ray crystal structure determination for **2b**

3.3.1. Crystal data of **2b**

$C_{51}H_{47}Cl_2Fe_2N_2Sn$, $Mr = 989.24$, monoclinic, $C2/c$(No.15), $a = 32.610(7)$, $b = 14.415(2)$, $c = 20.56(1)$ Å, $\beta = 111.105(2)°$, $V = 9015(4)$ Å^3, $Z = 8$, $D_{calc} = 1.457$g cm^{-3}, $F(000) = 4024.00$, $\lambda = 0.71070$ Å, $\mu(Mo{-}K_\alpha) = 13.39$ cm^{-1}.

3.3.2. Data collection

Red prismatic crystal of **2b** with approximate dimensions of 1.30 × 0.20 × 0.30 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS-IV imaging plate area detector with graphite monochramated Mo–K_α radiation. The data were collected to a maximum 2θ value of 55.0°. A total of 42 3.00° oscillation images were collected, each being exposed for 5.0 min. The crystal-to-detector distance was 110.00 mm with the detector at the zero swing position. Readout was performed in the 0.100 mm pixel mode. A total of 8069 reflections was collected; 6194 reflections were considered as observed applying the conditions $I > 3.00\sigma(I)$. Data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient $= 3.87800 \times 10^{-8}$).

3.3.3. Structure solution and refinement

The structure was solved by direct methods [21] and expanded using Fourier techniques. All calculations were performed using the teXsan crystallographic software package [22]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final R factors were 0.037 ($Rw = 0.051$). The maximum and minimum peaks on the final difference Fourier map corresponded to 0.36 and -0.71 e^- Å^{-3}, respectively.

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