

A Ferrocenyl-Backboned Unsymmetric O,C-Coordinating Ligand and Its Tin Derivatives

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Dedicated to Professor Heinrich Lang on the occasion of his 60th birthday

The syntheses of the phosphonyl-substituted ferrocenyl stannane $\text{Fe}[\{\eta^5\text{-C}_5\text{H}_3\text{-1-SnPh}_3\text{-2-P(O)(O-}i\text{Pr)}_2\}\{\eta^5\text{-C}_5\text{H}_4\text{P(O)(O-}i\text{Pr)}_2\}]$ (**1**) and its iodine derivative $\text{Fe}[\{\eta^5\text{-C}_5\text{H}_3\text{-1-SnPh}_2\text{-2-P(O)(O-}i\text{Pr)}_2\}\{\eta^5\text{-C}_5\text{H}_4\text{P(O)(O-}i\text{Pr)}_2\}]$ (**2**) are reported. The syntheses of the corresponding salts $\text{Fe}[\{\eta^5\text{-C}_5\text{H}_3\text{-1-SnPh}_2\text{-2-P(O)(O-}i\text{Pr)}_2\}\{\eta^5\text{-}$

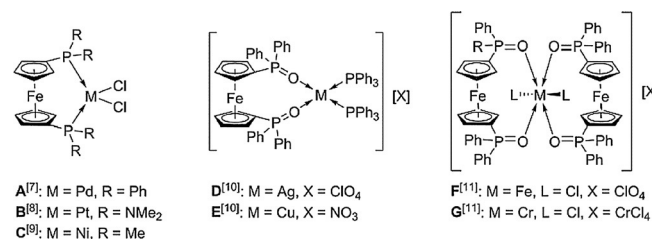
$\text{C}_5\text{H}_4\text{P(O)(O-}i\text{Pr)}_2\}\text{X}$ (**3**, $\text{X}=\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4$, **4**, $\text{X}=\text{ClO}_4$, **5**, $\text{X}=\text{HgI}_3$), respectively, are also described. The compounds are characterized by elemental analyses, ^1H , ^{13}C , ^{31}P , ^{119}Sn NMR and IR spectroscopy, electrospray ionization mass spectrometry, and, except for **4** and **5**, single-crystal X-ray diffraction analyses.

1. Introduction

In recent decades, the variety of ferrocene derivatives has grown intensely and application of such ferrocene derivatives in numerous areas of chemistry is well reported in literature.^[1] In particular, 1,1'-disubstituted ferrocenes have found applications in asymmetric catalysis, biochemistry, and material sciences and as chelating ligand systems.^[2] As a consequence, a huge number of so-called ferrocenyl-backboned chelate ligands have been developed in coordination chemistry.^[3] One of the most frequently employed bidentate ligand systems involves phosphorus-substituted ferrocene derivatives. 1,1'-bis-(diphenylphosphino)ferrocene (dppf), for instance, has attracted considerable attention because of its application in several metal-catalyzed reactions.^[4–6]

Among these ligands, phosphane- and phosphonyl-substituted ferrocenes have been investigated and their complexes with several metal cations have been explored. Some representative examples are shown in Scheme 1.^[7–9]

In 1979, Hayashi and co-workers prepared the first ferrocene-based bidentate coordination complex **A** through the simple treatment of dppf with PdCl_2 .^[7] A similar approach was used by Gimeno et al. for the syntheses of compounds **D** and **E**, consisting of phosphonyl moieties that coordinate the cen-



Scheme 1. Selected complexes of 1,1'-disubstituted ferrocenes with phosphane and phosphonyl moieties.

tral metal center, respectively.^[10] Zhang and Hor used 1,1'-bis-(diphenylphosphinoxy)ferrocene (dppfO₂) as ligand to investigate the complexation behavior of 3d metals, yielding several six-coordinate complexes with octahedral geometry.^[11a]

In the last years, there has been considerable activity concerning main group element cations.^[11b–m] Prominent representatives among these are intramolecularly coordinated organotin derivatives,^[11n–r] in which the positive charge at the tin centers is stabilized by donor atoms through Lewis acid–Lewis base interactions.

In context with our ongoing studies on O,C,O-coordinating pincer-type ligands^[12] and phosphonyl-substituted ferrocenes,^[13] including their main group element derivatives, as well as with related work by others,^[14] we herein present the syntheses and structures of organotin-substituted derivatives of the recently reported 1,1'-bis(diiso-propoxyphosphonyl)-ferrocene **H**^[15] and the corresponding donor-stabilized triorganotin cations. To the best of our knowledge, the ionic complexes are, based on 1,1'-disubstituted ferrocene backboned systems, the first examples, where the metal atom is covalently bound to the cyclopentadienyl ring and donor-stabilized by P=O moieties.

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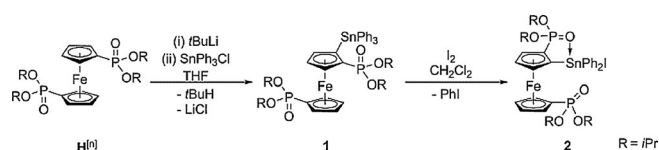
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2. Results and Discussion

2.1. Synthesis of Bis(diisopropoxyphosphonyl)-Substituted Ferrocenyl Stannane (1) and Corresponding Organotiniodide Derivative (2)

The reaction in THF of the in situ generated 1,1'-bis(diisopropoxyphosphonyl)-ferrocenyllithium, 1,1'-Fc{P(O)(O-*i*Pr)}₂Li, with triphenyltin chloride, SnPh₃Cl, gave the bis(diisopropoxy)ferrocenyl stannane Fe{[η⁵-C₅H₅-1-SnPh₃-2-P(O)(O-*i*Pr)}₂{η⁵-C₅H₄P(O)(O-*i*Pr)} (1) as orange solid material. Subsequent reaction of this compound with elemental iodine provided the corresponding triorganotiniodide derivative Fe{[η⁵-C₅H₅-1-SnPh₂-2-P(O)(O-*i*Pr)}₂{η⁵-C₅H₄P(O)(O-*i*Pr)} (2) as a red powder (Scheme 2).



Scheme 2. Synthesis of Fe{[η⁵-C₅H₅-1-SnPh₃-2-P(O)(O-*i*Pr)}₂{η⁵-C₅H₄P(O)(O-*i*Pr)} (1) and Fe{[η⁵-C₅H₅-1-SnPh₂-2-P(O)(O-*i*Pr)}₂{η⁵-C₅H₄P(O)(O-*i*Pr)} (2).

Single crystals of 1 and 2 suitable for X-ray diffraction analysis were obtained from the corresponding saturated hot *iso*-hexane solutions. The molecular structures are shown in Figure 1 and Figure 2, respectively, and selected interatomic distances and angles are given in the captions.

Compounds 1 and 2 crystallized in the triclinic space group *P*-1 with two molecules in the unit cell. The Sn(1) atom in 1 is [4+1]-coordinated by C(1), C(41), C(51), and O(1), and adopts a distorted tetrahedral environment. The overall geometry is similar to other previously reported P=O→Sn coordinated tetraorganotin compounds such as (3aR,7aR)-2-ferrocenyl-3a,4,5,6,7,7a-octahydro-1,3-dimethyl-1,3,2-benzodiazaphosphole 2-oxide^[13] [hereafter referred to as (*R,R*)-FcP(O)(DMC-DA)SnPh₃]. The O(1)–Sn(1) distance of 3.042(4) Å is shorter than the sum of the van der Waals radii of these elements (4.05 Å^[16]) and indicates a weak, probably mainly electrostatic, O→Sn interaction. In compound 2, the Sn(1) atom is penta-coordinated and exhibits a distorted trigonal-bipyramidal environment, where O(1) and I(1) occupy the axial and C(1), C(31), and C(41) the equatorial positions. As expected, the O(1)–Sn(1) distance of 2.424(2) Å in compound 2 is, compared to 1, shorter and reflects the enhanced Lewis acidity of the tin atom. As a result of the intramolecular P=O→Sn coordination, the Sn(1)–I(1) distance is longer than the sum of the covalent radii of tin and iodine atoms (2.73 Å^[17a]).

A ³¹P NMR spectrum of 1 in CDCl₃ (Figure S1 in the Supporting Information) revealed two singlet resonances at δ = 21.7 and 24.2 ppm [²J(³¹P–^{117/119}Sn) = 6.9 Hz]. In the corresponding ¹¹⁹Sn NMR spectrum (Figure S2 in the Supporting Information), a doublet resonance at δ = –117 ppm [²J(¹¹⁹Sn–³¹P) = 7 Hz] was observed. An electrospray ionization mass spectrum (hereafter referred to as ESI MS) in the positive mode revealed, in addition

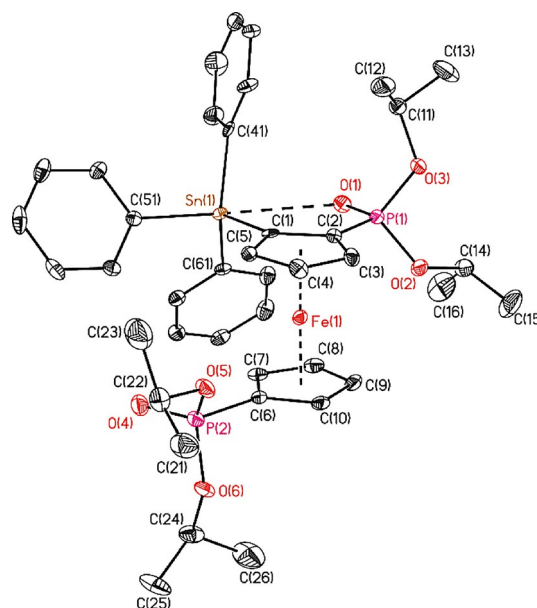


Figure 1. Displacement ellipsoid (30% probability level) plot of the asymmetric unit of Fe{[η⁵-C₅H₅-1-SnPh₃-2-P(O)(O-*i*Pr)}₂{η⁵-C₅H₄P(O)(O-*i*Pr)} (1) in the crystal. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn(1)–O(1) 3.042(4), Sn(1)–C(1) 2.132(4), Sn(1)–C(41) 2.131(5), Sn(1)–C(51) 2.159(5), Sn(1)–C(61) 2.150(5), P(1)–O(1) 1.461(3), P(1)–O(2) 1.576(4), P(1)–O(3) 1.578(3); C(41)–Sn(1)–O(1) 76.67(2), C(1)–Sn(1)–O(1) 70.84(2), C(61)–Sn(1)–O(1) 81.09(2), C(51)–Sn(1)–O(1) 172.05(1), C(41)–Sn(1)–C(1) 112.60(2), C(41)–Sn(1)–C(61) 112.42(2), C(1)–Sn(1)–C(61) 118.29(2), C(41)–Sn(1)–C(51) 104.15(2), C(1)–Sn(1)–C(51) 101.85(2), C(61)–Sn(1)–C(51) 105.60(3).

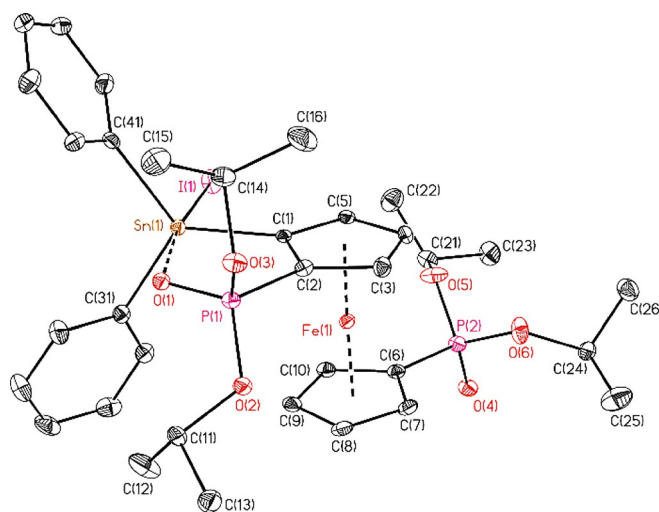


Figure 2. Displacement ellipsoid (30% probability level) plot of the asymmetric unit of Fe{[η⁵-C₅H₅-1-SnPh₂-2-P(O)(O-*i*Pr)}₂{η⁵-C₅H₄P(O)(O-*i*Pr)} (2) in the crystal. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn(1)–I(1) 2.8124(3), Sn(1)–O(1) 2.424(2), Sn(1)–C(1) 2.131(3), Sn(1)–C(31) 2.134(3), Sn(1)–C(41) 2.171(3), P(1)–O(1) 1.493(2), P(1)–O(2) 1.552(2), P(1)–O(3) 1.572(2); C(1)–Sn(1)–C(31) 121.71(1), C(1)–Sn(1)–C(41) 119.71(1), C(31)–Sn(1)–C(41) 113.54(1), C(1)–Sn(1)–O(1) 77.67(9), C(31)–Sn(1)–O(1) 83.45(1), C(41)–Sn(1)–O(1) 86.86(1), C(1)–Sn(1)–I(1) 95.41(8), C(31)–Sn(1)–I(1) 96.98(9), C(41)–Sn(1)–I(1) 100.25(9), O(1)–Sn(1)–I(1) 171.96(5).

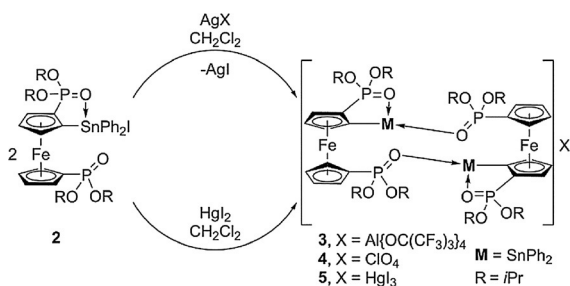
to the minor intense mass cluster centered at *m/z* 864 [(*M* + *H*)⁺] (10%), a major mass cluster at *m/z* 787 that is as-

signed to $[(M-Ph)^+]$ (100%) and a minor mass cluster at m/z 1748 that is assigned to $[(2M+K)^+]$ (30%).

A ^{31}P NMR spectrum of **2** in $CDCl_3$ (Figure S6 in the Supporting Information) showed two sharp singlet resonances at $\delta = 21.4$ and 29.5 ppm. For the signal at 29.5 ppm, unresolved $^{117/119}Sn$ satellites [$^2J(^{31}P-^{117/119}Sn) = 55$ Hz] were observed. The ^{119}Sn NMR spectrum (Figure S7 in the Supporting Information) showed a doublet resonance at $\delta = -160$ [$^2J(^{119}Sn-^{31}P) = 55$ Hz]. An ESI MS revealed a mass cluster centered at m/z 1213 $[(M-I)^+]$ (100%) and a mass cluster of minor intensity at m/z 745 that is assigned to $[(M-I-iPr)^+]$ (10%).

2.2. Synthesis of Ionic Complexes 3–5

Reactions of **2** in dichloromethane with $Ag[Al(OC(CF_3)_3)_4]$ (for **3**), $AgClO_4$ (for **4**), and HgI_2 (for **5**), in equimolar ratios, provided the corresponding ionic tin complexes **3–5** (Scheme 3).



Scheme 3. Syntheses of the organotin compounds **3–5**.

Single crystals of **3**, as its dichloromethane solvate **3-CH₂Cl₂**, suitable for X-ray diffraction analysis, were obtained from its solution in dichloromethane at $-30^\circ C$. The molecular structure is shown in Figure 3 (selected interatomic distances and angles are given in the captions).

Compound **3** crystallized as a centrosymmetric dimer in the monoclinic space group $P2_1/n$ with four molecules in the unit cell. The Sn(1) atom is pentacoordinated and shows a distorted trigonal-bipyramidal environment, in which the oxygen atoms occupy the axial positions and the carbon atoms occupy the equatorial positions. The O(4)–Sn(1)–O(1) angle is $172.4(3)^\circ$ and differs only slightly from 180° . Interestingly, the Sn(1)–O(1) distance of $2.294(7)$ Å is longer than the Sn(1)–O(1) distance of $2.202(6)$ Å, reflecting the superior donor capacity of the intramolecular coordination of $C_{cp}(O-iPr)_2P=O$ in the *ortho*-position versus the intermolecular coordinating $C_{cp}(O-iPr)_2P=O$ moiety. Compared to the triorganotin(IV) triflate salt $[FcP(O)(DMCDA)SnPh_2(OPPh_3)]OTf^{[13]}$ [Sn(1)–O(1) $2.2491(19)$ Å], the $P=O \rightarrow Sn$ coordination is much stronger at a Sn(1)–O(1) distance of $2.202(6)$ Å.

A ^{31}P NMR spectrum of a solution of compound **3** in CD_2Cl_2 (Figure S8 in the Supporting Information) displayed two sharp resonances at $\delta = 25.0$ [$J(^{31}P-^{117/119}Sn) = 71.9$ Hz] and 30.7 ppm [$J(^{31}P-^{117/119}Sn) = 93.9$ Hz], being high-frequency shifted in comparison to the resonance of **2** ($\delta = 21.4$ and 29.5 ppm). A ^{119}Sn spectrum (Figure S9 in the Supporting Information) of the

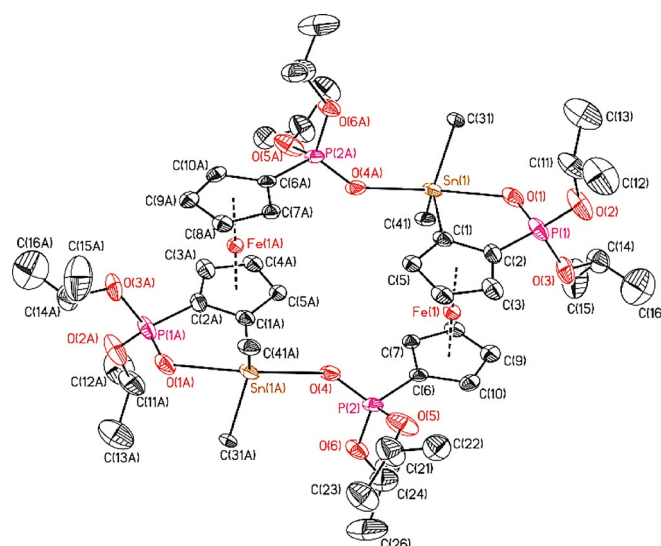


Figure 3. Displacement ellipsoid (30% probability level) plot of the molecular structure of $Fe[\eta^5-C_5H_5-1-SnPh_2-2-P(O)(O-iPr)_2]\{\eta^5-C_5H_4P(O)(O-iPr)_2\}Al(OC(CF_3)_3)_4$ (**3-CH₂Cl₂**). Hydrogen atoms, phenyl carbon atoms except C_i, and the counteranions are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn(1)–O(1) 2.294(7), Sn(1)–O(4) 2.202(6), Sn(1)–C(1) 2.112(9), Sn(1)–C(41) 2.127(4), Sn(1)–C(31) 2.129(11), Sn(1)–C(31) 2.134(3), P(1)–O(1) 1.500(8), P(1)–O(2) 1.552(7), P(1)–O(3) 1.546(8); C(1)–Sn(1)–C(41) 116.6(3), C(1)–Sn(1)–C(31) 111.0(5), C(41)–Sn(1)–C(31) 128.7(5), C(1)–Sn(1)–O(1) 80.6(3), C(41)–Sn(1)–O(1) 91.6(2), C(31)–Sn(1)–O(1) 78.0(5), C(1)–Sn(1)–O(4) 92.0(3), C(41)–Sn(1)–O(4) 93.0(3), C(31)–Sn(1)–O(4) 78.0(5), O(4)–Sn(1)–O(1) 172.4(3).

same sample revealed a doublet-of-doublet resonance at $\delta = -186$ ppm [$J(^{119}Sn-^{31}P) = 75$ Hz, $J(^{119}Sn-^{31}P) = 96$ Hz]. In addition, the ^{31}P and ^{119}Sn NMR spectra showed additional resonances of low intensity (8%) at $\delta = 24.1$, 30.4, and -193.3 ppm, respectively, indicating partial hydrolysis of **3** under the experimental conditions employed.

The 1H , ^{13}C , ^{31}P , and ^{119}Sn NMR spectra of **4** and **5** (see the Experimental Section) confirmed the identity of these compounds in solution. There is no change of the NMR data upon replacement of the aluminate anion in **3** by the perchlorate and triiodidomercurate anions in **4** and **5**, respectively. The molecular structure of compound **5**, as determined by single-crystal X-ray diffraction analysis, revealed it to be composed of a dinuclear dication similar to that in **3** and two HgI_3^- anions (see the ball-and-stick image in Figure S11). As result of poor crystal quality and incomplete refinement, no details of its structure are discussed.

The ESI MS (positive mode) of **3**, **4**, and **5** each showed a major mass cluster centered at m/z 787 that could be assigned to the cationic species $[(M-X)^+]$. In case of the mercury-containing compound **4**, a mass cluster centered at m/z 1390 of less than 5% intensity, and indicative of a dimer fragment, was observed but not assigned. The data suggest, with caution, that the cations in **3–5** are monomeric instead of dimeric. A molecular mass determination by osmometry was not possible under the experimental conditions available, as the compounds immediately hydrolyze upon contact with air moisture, giving an insoluble precipitate that does not melt until $400^\circ C$ as well as $1,1'-Fc(P(O)(O-iPr)_2)_2$ (**H**), as unambigu-

ously evidenced by using ^{31}P NMR spectroscopy. The ESI MS in the negative mode revealed mass clusters of the corresponding counter anions (**3**, m/z 967 $[(\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4)^-]$; **4**, m/z 99 $[(\text{ClO}_4)^-]$; **5**, m/z 583 $[(\text{HgI}_3)^-]$).

3. Conclusions

We have presented monostannylated 1,1'-bis(phosphonyl)-substituted ferrocene derivatives. The degree of $\text{P}=\text{O} \rightarrow \text{Sn}$ coordination depends on the substituent pattern at the tin atom with rather weak interaction for SnPh_3 in **1** to strong interaction for SnPh_2I in **2**. Most importantly, for SnPh_2^+ , a bicentric dication **3** is formed through head-to-tail dimerization involving both phosphonyl moieties. The preferred formation of a salt consisting of a dication and two anions over a salt composed of a monocation and an anion is likely to result in a gain of lattice energy. Other examples for such an effect have recently been reported.^[18]

Experimental Section

General Methods

Reactions were carried out in an inert atmosphere of argon by using standard Schlenk techniques. The solvents were dried by using standard methods and freshly distilled before use. Silver aluminate $\text{AgAl}\{\text{OC}(\text{CF}_3)_3\}_4$ was prepared as reported in the literature.^[17b] The NMR experiments were carried out on Bruker DRX 500, Bruker DRX 400 or Bruker DPX 600 spectrometers at ambient temperature unless otherwise stated. Chemical shifts (δ) were given in ppm and referenced to the solvent signals with the usual values calibrated against tetramethylsilane (^1H , ^{13}C), 85% phosphoric acid (^{31}P), and tetramethylstannane (^{119}Sn). The correct assignment of the ^1H and ^{13}C NMR resonances for compound **1** was ensured by obtaining ^1H , ^{13}C -HSQC, ^1H , ^1H -COSY, and ^1H , ^{13}C -HMBC NMR spectra (Figures S3–S5 in the Supporting Information). Elemental analyses were performed on a LECO-CHNS-932 analyzer. Melting points were uncorrected and were measured on a Büchi M-560. IR spectra of solids were recorded on a PerkinElmer Spectrum Two (ATR). All compounds were dried in vacuo (0.01 mm Hg) prior to analyses. The electrospray mass spectra were recorded on a Thermoquest-Finnigan instrument by using CH_3CN or CH_2Cl_2 as a mobile phase.

Crystallography

Intensity data for crystals of compounds **1** and **2** were collected on an XcaliburS CCD diffractometer (Oxford Diffraction) by using $\text{MoK}\alpha$ radiation at 173 K and for crystals of compound **3** on an APEX-II CCD diffractometer (Bruker Corporation) using $\text{Mo K}\alpha$ radiation at 100 K. The structures were solved with direct methods by using SHELXS-2014/7^[19] and refinements were carried out against F2 by using SHELXL-2014/7.^[19,20] The C–H hydrogen atoms were positioned with idealized geometry and refined by using a riding model. All non-hydrogen atoms were refined by using anisotropic displacement parameters. The carbon atoms of the *iso*-propoxy groups C11, C12, C13 and C21, C22, C23, respectively, in compound **1** are affected by disorder and refined by a split model over two positions (occupancy values 50:50). The carbon atoms of the phenyl ring C31 to C36 in compound **3** are affected by disorder and refined by a split model over two positions (occupancy values 50:50).^[21]

Synthesis of $\text{Fe}\{\{\eta^5\text{-C}_5\text{H}_5\text{-1-SnPh}_3\text{-2-P(O)(O-}i\text{Pr)}_2\}\{\eta^5\text{-C}_5\text{H}_4\text{P(O)(O-}i\text{Pr)}_2\}\}$ (**1**)

A solution of $t\text{BuLi}$ (9.8 mL, 1.9 M in pentane, 18.67 mmol) was added to $1,1'\text{-Fc}\{\text{P(O)(O-}i\text{Pr)}_2\}_2$ (6.4 g, 12.44 mmol) in THF (150 mL) at -78°C . The reaction mixture was stirred for 1 h at -50°C . The resulting suspension was cooled to -78°C and SnPh_3Cl (7.20 g, 18.67 mmol) was added. The mixture was warmed to room temperature over a period of 8 h and then quenched with water (50 mL). The mixture was extracted with Et_2O (3×50 mL), the organic phase was dried over MgSO_4 , and the solvent was evaporated under reduced pressure. The compound was then purified by silica column chromatography using *n*-hexane/THF (1:1) to yield 7.78 g (73%) of **1** as an orange powder. Storage of the saturated *iso*-hexane solution of **1** for 24 h at 5°C gave orange crystals.

Mp: $215.5\text{--}216.5^\circ\text{C}$. Anal. calcd. for $\text{C}_{40}\text{H}_{50}\text{FeO}_6\text{P}_2\text{Sn}$ (863.34 g mol^{-1}): C 55.65; H 5.84. Found: C 55.8; H 5.8. ^1H NMR (400.3 MHz, CDCl_3): $\delta = 0.74$ [d, 3H, OCHCH_3 , $^3J(\text{H-}^1\text{H}) = 5.9$ Hz], 0.88 [d, 3H, OCHCH_3 , $^3J(\text{H-}^1\text{H}) = 5.9$ Hz], 1.23 [d, 3H, OCHCH_3 , $^3J(\text{H-}^1\text{H}) = 5.4$ Hz], 1.33 (m, 9H, OCHCH_3), 1.40 [d, 3H, OCHCH_3 , $^3J(\text{H-}^1\text{H}) = 5.9$ Hz], 1.47 [d, 3H, OCHCH_3 , $^3J(\text{H-}^1\text{H}) = 5.9$ Hz], 3.73 (m, 1H, OCHCH_3), 4.10, 4.42 (s, 2H, Cp- $H3'$, Cp- $H4'$), 4.39, 4.56 (s, 2H, Cp- $H2'$, Cp- $H5'$), 4.53 (s, 1H, Cp- $H3$), 4.67, 4.69 (m, 2H, OCHCH_3), 4.74 (s, 1H, Cp- $H5$), 4.84 (s, 1H, Cp- $H4$), 4.86 (m, 1H, OCHCH_3), 7.37 (m, 9H, Ph- H_m , Ph- H_p), 7.83 ppm [m, 6H, Ph- H_o , $^3J(\text{H-}^{117}\text{Sn}) = 45.0$ Hz, $^3J(\text{H-}^{119}\text{Sn}) = 56.2$ Hz]. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3): $\delta = 23.4$ [d, OCHCH_3 , $^3J(^{13}\text{C-}^{31}\text{P}) = 4$ Hz], 23.7 [d, OCHCH_3 , $^3J(^{13}\text{C-}^{31}\text{P}) = 4$ Hz], 23.9 [d, OCHCH_3 , $^3J(^{13}\text{C-}^{31}\text{P}) = 2$ Hz], 24.0 [d, OCHCH_3 , $^3J(^{13}\text{C-}^{31}\text{P}) = 2$ Hz], 24.0 [d, OCHCH_3 , $^3J(^{13}\text{C-}^{31}\text{P}) = 2$ Hz], 24.1 [d, OCHCH_3 , $^3J(^{13}\text{C-}^{31}\text{P}) = 4$ Hz], 24.1 (ps, OCHCH_3), 69.9 (d, Cp-C2, $^1J(^{13}\text{C-}^{31}\text{P}) = 215$ Hz), 70.1 (d, OCHCH_3 , $^3J(^{13}\text{C-}^{31}\text{P}) = 6$ Hz), 70.2 (d, OCHCH_3 , $^3J(^{13}\text{C-}^{31}\text{P}) = 6$ Hz), 70.3 (d, Cp-C4, $^3J(^{13}\text{C-}^{31}\text{P}) = 6$ Hz), 72.3 (d, Cp-C2' or Cp-C5', $^2J(^{13}\text{C-}^{31}\text{P}) = 15$ Hz), 73.2 (d, Cp-C2' or Cp-C5', $^2J(^{13}\text{C-}^{31}\text{P}) = 15$ Hz), 74.1 (d, Cp-C3' or Cp-C4', $^3J(^{13}\text{C-}^{31}\text{P}) = 14$ Hz), 75.0 (d, Cp-C3' or Cp-C4', $^3J(^{13}\text{C-}^{31}\text{P}) = 14$ Hz), 74.4 (d, Cp-C1', $^1J(^{13}\text{C-}^{31}\text{P}) = 215$ Hz), 75.5 (d, Cp-C5, $^3J(^{13}\text{C-}^{31}\text{P}) = 15$ Hz), 80.7 [d, Cp-C3, $^3J(^{13}\text{C-}^{31}\text{P}) = 17$ Hz], 128.2 [s, Ph-C m , $^3J(^{13}\text{C-}^{117/119}\text{Sn}) = 53$ Hz], 128.5 [s, Ph-C p , $^4J(^{13}\text{C-}^{117/119}\text{Sn}) = 10$ Hz], 137.6 [s, Ph-C o , $^2J(^{13}\text{C-}^{117/119}\text{Sn}) = 39$ Hz], 140.0 ppm (s, Ph-Ci). $^{31}\text{P}\{^1\text{H}\}$ NMR (162.0 MHz, CDCl_3): $\delta = 22.4$ (s), 24.2 [s, $J(^{31}\text{P-}^{117/119}\text{Sn}) = 7$ Hz]. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (149.2 MHz, CDCl_3): $\delta = -117$ [d, $J(^{119}\text{Sn-}^{31}\text{P}) = 7$ Hz]. ESI-MS, positive mode: $m/z = 1748$ [$2\text{M} + \text{K}$] $^+$, 887 [$\text{M} + \text{Na}$] $^+$, 887 [$\text{M} - \text{Ph}$] $^+$. IR: $\nu(\text{P}=\text{O}) = 1236\text{ cm}^{-1}$, 1244 cm^{-1} .

Synthesis of $\text{Fe}\{\{\eta^5\text{-C}_5\text{H}_5\text{-1-SnPh}_2\text{-2-P(O)(O-}i\text{Pr)}_2\}\{\eta^5\text{-C}_5\text{H}_4\text{P(O)(O-}i\text{Pr)}_2\}\}$ (**2**)

To a solution of **1** (2.0 g, 2.32 mmol) in CH_2Cl_2 (100 mL), I_2 (0.588 g, 2.32 mmol) in small portions was added over a period of 1 h at room temperature. The reaction mixture was stirred for an additional 24 h. The solution was evaporated giving 2.07 g (98%) of compound **2** as a red powder. Crystallization from hot *n*-hexane yielded dark-red crystals that were suitable for X-ray diffraction analysis.

Mp: $196.3\text{--}197.3^\circ\text{C}$. Anal. calcd. for $\text{C}_{34}\text{H}_{45}\text{FeO}_6\text{P}_2\text{Sn}$ (913.13 g mol^{-1}): C 44.72; H 4.97. Found: C 44.8; H 5.0. ^1H NMR (400.3 MHz, CDCl_3): $\delta = 0.76$ [d, 3H, OCHCH_3 , $^3J(\text{H-}^1\text{H}) = 5.9$ Hz], 0.90 [d, 3H, OCHCH_3 , $^3J(\text{H-}^1\text{H}) = 5.9$ Hz], 1.25 [d, 3H, OCHCH_3 , $^3J(\text{H-}^1\text{H}) = 5.4$ Hz], 1.30 [m, 3H, OCHCH_3 , $^3J(\text{H-}^1\text{H}) = 6.4$ Hz], 1.39 [d, 3H, OCHCH_3 , $^3J(\text{H-}^1\text{H}) = 2.9$ Hz], 1.41 [d, 3H, OCHCH_3 , $^3J(\text{H-}^1\text{H}) = 2.9$ Hz], 1.45 [d, 3H, OCHCH_3 , $^3J(\text{H-}^1\text{H}) = 6.4$ Hz], 1.49 [d, 3H, OCHCH_3 , $^3J(\text{H-}^1\text{H}) = 6.4$ Hz], 3.74 (m, 1H, OCHCH_3), 4.10 (m, 1H,

Cp-H3' or Cp-H4'), 4.39 (m, 1H, Cp-H2' or Cp-H5'), 4.42 (m, 1H, Cp-H3' or Cp-H4'), 4.53 (s, 1H, Cp-H3), 4.56 (m, 1H, Cp-H2' or Cp-H5'), 4.63 (m, 1H, OCHCH₃), 4.74 (s, 1H, Cp-H5), 4.79 (m, 1H, OCHCH₃), 4.84 (s, 1H, Cp-H4), 4.86 (m, 1H, OCHCH₃), 7.28 (m, 4H, Ph-H_m), 7.49 (m, 2H, Ph-H_p), 7.80 [m, 2H, Ph-H, ³J(¹H-¹¹⁷Sn)=61.6 Hz, ³J(¹H-¹¹⁹Sn)=75.3 Hz], 8.44 ppm [m, 2H, Ph-H_o, ³J(¹H-¹¹⁷Sn)=65.5 Hz, ³J(¹H-¹¹⁹Sn)=80.7 Hz]. ¹³C{¹H} NMR (100.7 MHz, CDCl₃): δ=23.2 [d, OCHCH₃, ³J(¹³C-³¹P)=4 Hz], 23.4 [d, OCHCH₃, ³J(¹³C-³¹P)=4 Hz], 23.9 [d, OCHCH₃, ³J(¹³C-³¹P)=4 Hz], 24.0 (ps, OCHCH₃), 24.0 [d, OCHCH₃, ³J(¹³C-³¹P)=4 Hz], 24.1 [d, OCHCH₃, ³J(¹³C-³¹P)=4 Hz], 24.2 [d, OCHCH₃, ³J(¹³C-³¹P)=3 Hz], 24.3 [d, OCHCH₃, ³J(¹³C-³¹P)=4 Hz], 70.4 (d, OCHCH₃, ³J(¹³C-³¹P)=6 Hz], 70.5 [d, OCHCH₃, ³J(¹³C-³¹P)=6 Hz], 70.7 [d, Cp-C2, ¹J(¹³C-³¹P)=183 Hz], 71.8 [d, OCHCH₃, ³J(¹³C-³¹P)=5.8 Hz], 72.7 [d, Cp-C4, ³J(¹³C-³¹P)=6 Hz], 73.8 [d, Cp-C2' or Cp-C5', ²J(¹³C-³¹P)=15 Hz], 74.0 [d, Cp-C2' or Cp-C5', ²J(¹³C-³¹P)=15 Hz], 74.1 [d, Cp-C3' or Cp-C4', ³J(¹³C-³¹P)=14 Hz], 74.4 [d, Cp-C1', ¹J(¹³C-³¹P)=215 Hz], 75.0 [d, Cp-C3' or Cp-C4', ³J(¹³C-³¹P)=14 Hz], 75.5 [d, Cp-C5, ³J(¹³C-³¹P)=15 Hz], 80.7 [d, Cp-C3, ²J(¹³C-³¹P)=17 Hz], 128.3 (s, Ph-C_m), 135.8 [l, Ph-C_p, ⁴J(¹³C-^{117/119}Sn)=14 Hz], 137.6 [s, Ph-C_o, ²J(¹³C-^{117/119}Sn)=56 Hz], 139.3 ppm (s, Ph-C_i). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ=21.4 (s), 29.5 [s, ³J(³¹P-^{117/119}Sn)=55 Hz]. ¹¹⁹Sn{¹H} NMR (149.2 MHz, CDCl₃): δ=-160 ppm [d, ¹J(¹¹⁹Sn-³¹P)=55 Hz]. ESI-MS, positive mode: *m/z*=787 [M-]⁺, 745 [M-*iPr*]⁺. IR ν(P=O)=1211 cm⁻¹, 1237 cm⁻¹.

Synthesis of Fe[η⁵-C₅H₃-1-SnPh₂-2-P(O)(O-*iPr*)₂]{η⁵-C₅H₄P(O)(O-*iPr*)₂}[Al{OC(CF₃)₃}]₃ (3)

To a solution of Ag[Al(OC(CF₃)₃)₄] (0.25 g, 0.24 mmol) in CH₂Cl₂ (5 mL), **2** (0.22 g, 0.24 mmol) was added at room temperature. After the reaction mixture had been stirred for an additional 1 h, the solution was filtered. Crystallization from CH₂Cl₂ at -30 °C yielded 0.38 g (92%) of **3**·CH₂Cl₂ as orange crystals that were suitable for X-ray diffraction analysis. The crystals were dried in vacuo (1.5 mm Hg) for 5 h at 30 °C to remove the dichloromethane solvate.

Mp: 133.1–135.0 °C. Anal. calcd. for C₅₀H₄₅AlF₃₆FeO₁₀P₂Sn (1753.33 g mol⁻¹): C 34.25; H 2.59. Found: C 34.9; H 2.9. ¹H NMR (600.3 MHz, CD₂Cl₂): δ=0.55 [d, 3H, OCHCH₃, ³J(¹H-¹H)=6.3 Hz], 0.88 [d, 3H, OCHCH₃, ³J(¹H-¹H)=6.3 Hz], 0.98 [d, 3H, OCHCH₃, ³J(¹H-¹H)=6.3 Hz], 1.08 [m, 3H, OCHCH₃, ³J(¹H-¹H)=5.9 Hz], 1.15 [d, 3H, OCHCH₃, ³J(¹H-¹H)=6.3 Hz], 1.35 [d, 3H, OCHCH₃, ³J(¹H-¹H)=5.9 Hz], 1.47 (d, 3H, OCHCH₃, ³J(¹H-¹H)=6.6 Hz], 1.49 [d, 3H, OCHCH₃, ³J(¹H-¹H)=6.3 Hz], 3.83 (m, 1H, OCHCH₃), 4.4 (m, 7H, Cp-H), 4.92 (m, 1H, OCHCH₃), 5.09 (m, 2H, Cp-H), 7.54 (m, 8H, Ph-H), 8.03 (m, 2H, Ph-H). ¹³C{¹H} NMR (150.9 MHz, CD₂Cl₂): δ=22.9 [d, OCHCH₃, ³J(¹³C-³¹P)=4 Hz], 23.3 [d, OCHCH₃, ³J(¹³C-³¹P)=4 Hz], 23.5 [d, OCHCH₃, ³J(¹³C-³¹P)=3 Hz], 23.6 [d, OCHCH₃, ³J(¹³C-³¹P)=4 Hz], 23.7 [d, OCHCH₃, ³J(¹³C-³¹P)=6 Hz], 24.0 [d, OCHCH₃, ³J(¹³C-³¹P)=6 Hz], 24.4 [d, OCHCH₃, ³J(¹³C-³¹P)=3 Hz], 25.0 [d, OCHCH₃, ³J(¹³C-³¹P)=4 Hz], 64.9 [d, Cp-C2, ¹J(¹³C-³¹P)=219 Hz], 71.7 [d, Cp-C1', ¹J(¹³C-³¹P)=209 Hz], 74.2 [d, Cp-C3' or Cp-C4', ³J(¹³C-³¹P)=17 Hz], 75.0 [d, OCHCH₃, ³J(¹³C-³¹P)=7 Hz], 75.2 [d, OCHCH₃, ³J(¹³C-³¹P)=7 Hz], 75.4 [d, Cp-C3' or Cp-C4', ³J(¹³C-³¹P)=14 Hz], 76.2 (pt, Cp-C4, Cp-C2', Cp-C5'), 76.5 [d, Cp-C5, ³J(¹³C-³¹P)=8 Hz], 78.8 (pt, Cp-C3' or Cp-C4'), 82.7 [d, Cp-C3, ²J(¹³C-³¹P)=13 Hz], 121.9 [q, ¹J(¹³C-¹⁹F)=293 Hz], 129.9 (s, Ph-C_p), 135.5 (s, Ph-C_m), 136.5 (s, Ph-C_o), 141.9 (s, Ph-C_i). ¹⁹F{¹H} NMR (564.8 MHz, CD₂Cl₂): δ=-75.7 (s). ³¹P{¹H} NMR (243.0 MHz, CD₂Cl₂): δ=25.0 [s, ³J(³¹P-^{117/119}Sn)=93.9 Hz], 30.7 ppm [s, ³J(³¹P-^{117/119}Sn)=71.9 Hz]. ¹¹⁹Sn{¹H} NMR (223.9 MHz, CD₂Cl₂): δ=-186 ppm [dd, ¹J(¹¹⁹Sn-³¹P)=96 Hz], ¹J(¹¹⁹Sn-³¹P)=75 Hz, ¹J(¹¹⁹Sn-³¹P)=96 Hz]. ESI-MS, positive mode: *m/z*=787 [M-Al(OC(CF₃)₃)₄]⁺, 745 [M-Al(OC(CF₃)₃)₄-2-*iPr*]⁺, 667 [M-Al(OC(CF₃)₃)₄-2-*iPr*]⁺, 625 [M-

Al(OC(CF₃)₃)₄-P(O)(O*iPr*)₂]⁺; negative mode: *m/z*=967 [Al(OC(CF₃)₃)₄]⁻. IR ν(P=O)=1136 cm⁻¹, 1207 cm⁻¹.

Upon contact with moisture (from laboratory atmosphere) a colorless precipitate was formed. It was filtered off. It is not soluble in THF, OEt₂, hexane, MeOH, toluene, and water and does not melt until 400 °C. A ³¹P{¹H} NMR spectrum of the filtrate showed a singlet resonance at δ=21.7 ppm, indicating formation of the phosphoryl-substituted ferrocene **H**.

Synthesis of Fe[η⁵-C₅H₃-1-SnPh₂-2-P(O)(O-*iPr*)₂]{η⁵-C₅H₄P(O)(O-*iPr*)₂}]ClO₄ (4)

To a solution of AgClO₄ (0.11 g, 0.52 mmol) in CH₂Cl₂ (5 mL), **2** (0.48 g, 0.52 mmol) was added at room temperature. After the reaction mixture had been stirred for an additional 10 mins, the solution was filtered and evaporated under reduced pressure giving 0.45 g (98%) of **4** as a brown solid.

Mp: 99.4–100.2 °C. Anal. calcd. for C₃₄H₄₅ClFeO₁₀P₂Sn (885.68 g mol⁻¹): C 46.11; H 5.12. Found: C 45.4; H 5.2. ¹H NMR (600.3 MHz, CD₂Cl₂): δ=0.55 [d, 3H, OCHCH₃, ³J(¹H-¹H)=6.2 Hz], 0.86 [d, 3H, OCHCH₃, ³J(¹H-¹H)=6.2 Hz], 0.97 [d, 3H, OCHCH₃, ³J(¹H-¹H)=6.2 Hz], 1.10 [d, 3H, OCHCH₃, ³J(¹H-¹H)=6.2 Hz], 1.21 [d, 3H, OCHCH₃, ³J(¹H-¹H)=6.2 Hz], 1.40 [d, 3H, OCHCH₃, ³J(¹H-¹H)=6.2 Hz], 1.50 (m, 6H, OCHCH₃), 4.50 (unresolved, 11H, Cp-H and OCHCH₃), 7.48 (m, 8H, Ph-H), 8.01 ppm (m, 2H, Ph-H). ¹³C{¹H} NMR (150.9 MHz, CD₂Cl₂): δ=23.0 [d, OCHCH₃, ³J(¹³C-³¹P)=4 Hz], 23.3 [d, OCHCH₃, ³J(¹³C-³¹P)=4 Hz], 23.5 [d, OCHCH₃, ³J(¹³C-³¹P)=3 Hz], 23.8 [d, OCHCH₃, ³J(¹³C-³¹P)=6 Hz], 23.9 [d, OCHCH₃, ³J(¹³C-³¹P)=6 Hz], 24.1 [d, OCHCH₃, ³J(¹³C-³¹P)=6 Hz], 24.2 [d, OCHCH₃, ³J(¹³C-³¹P)=4 Hz], 25.1 [d, OCHCH₃, ³J(¹³C-³¹P)=3 Hz], 64.8 [d, Cp-C2, ¹J(¹³C-³¹P)=219 Hz], 71.3 [d, Cp-C1', ¹J(¹³C-³¹P)=209 Hz], 74.0 [d, Cp-C3' or Cp-C4', ³J(¹³C-³¹P)=18 Hz], 74.7 [d, OCHCH₃, ³J(¹³C-³¹P)=6 Hz], 75.2 [d, OCHCH₃, ³J(¹³C-³¹P)=8 Hz], 75.7 [d, Cp-C3' or Cp-C4', ³J(¹³C-³¹P)=15 Hz], 76.0 (m, Cp-C4, Cp-C2', Cp-C5'), 76.3 [d, Cp-C5, ³J(¹³C-³¹P)=8 Hz], 78.6 (pt, Cp-C3' or Cp-C4'), 82.8 [d, Cp-C3, ²J(¹³C-³¹P)=14 Hz], 129.9 (s, Ph-C_p), 135.4 (s, Ph-C_m), 136.4 (s, Ph-C_o), 142.0 ppm (s, Ph-C_i). ³¹P{¹H} NMR (243.0 MHz, CD₂Cl₂): δ=5.2 [s, ³J(³¹P-^{117/119}Sn)=95.4 Hz], 30.9 ppm [s, ³J(³¹P-^{117/119}Sn)=71.9 Hz]. ¹¹⁹Sn{¹H} NMR (223.9 MHz, CD₂Cl₂): δ=-187 [dd, ¹J(¹¹⁹Sn-³¹P)=74 Hz, ¹J(¹¹⁹Sn-³¹P)=97 Hz]. ESI-MS, positive mode: *m/z*=787 [M-ClO₄]⁺, 745 [M-ClO₄-2-*iPr*]⁺, 667 [M-ClO₄-2-*iPr*]⁺, 625 [M-ClO₄-P(O)(O*iPr*)₂]⁺; negative mode: *m/z*=99 [ClO₄]⁻. IR ν(P=O)=1143 cm⁻¹, 1211 cm⁻¹.

Synthesis of Fe[η⁵-C₅H₃-1-SnPh₂-2-P(O)(O-*iPr*)₂]{η⁵-C₅H₄P(O)(O-*iPr*)₂}]HgI₃ (5)

To a solution of **2** (0.20 g, 0.22 mmol) in CH₂Cl₂ (5 mL), HgI₂ (0.10 g, 0.22 mmol) was added at room temperature. After the reaction mixture had been stirred for an additional 10 mins, the solution was evaporated under reduced pressure giving 0.28 g (94%) of **5** as a red-brown oil.

Anal. calcd. for C₃₄H₄₅FeHgI₃O₆P₂Sn (1367.53 g mol⁻¹): C 29.86; H 3.32. Found: C 30.1; H 3.5. ¹H NMR (600.3 MHz, CD₂Cl₂): δ=0.56 [d, 3H, OCHCH₃, ³J(¹H-¹H)=6.3 Hz], 0.88 [d, 3H, OCHCH₃, ³J(¹H-¹H)=6.3 Hz], 0.97 [d, 3H, OCHCH₃, ³J(¹H-¹H)=6.3 Hz], 1.12 [d, 3H, OCHCH₃, ³J(¹H-¹H)=5.9 Hz], 1.21 [d, 3H, OCHCH₃, ³J(¹H-¹H)=6.3 Hz], 1.51 (m, 6H, OCHCH₃), 1.51 [d, 3H, OCHCH₃, ³J(¹H-¹H)=6.6 Hz], 4.50 (unresolved, 11H, Cp-H and OCHCH₃), 7.48 (m, 8H, Ph-H), 8.01 ppm (m, 2H, Ph-H). ¹³C{¹H} NMR (150.9 MHz, CD₂Cl₂): δ=22.9 [d, OCHCH₃, ³J(¹³C-³¹P)=4 Hz], 23.3 [d, OCHCH₃, ³J(¹³C-³¹P)=

4 Hz], 23.5 [d, OCHCH₃, ³J(¹³C–³¹P)=3 Hz], 23.6 [d, OCHCH₃, ³J(¹³C–³¹P)=4 Hz], 23.7 [d, OCHCH₃, ³J(¹³C–³¹P)=6 Hz], 24.0 [d, OCHCH₃, ³J(¹³C–³¹P)=6 Hz], 24.4 [d, OCHCH₃, ³J(¹³C–³¹P)=3 Hz], 25.0 [d, OCHCH₃, ³J(¹³C–³¹P)=4 Hz], 64.9 [d, Cp-C2, ¹J(¹³C–³¹P)=219 Hz], 71.7 [d, Cp-C1', ¹J(¹³C–³¹P)=209 Hz], 74.2 [d, Cp-C3' or Cp-C4', ³J(¹³C–³¹P)=17 Hz], 75.0 [d, OCHCH₃, ³J(¹³C–³¹P)=7 Hz], 75.2 [d, OCHCH₃, ³J(¹³C–³¹P)=7 Hz], 75.4 [d, Cp-C3' or Cp-C4', ³J(¹³C–³¹P)=14 Hz], 76.2 (pt, Cp-C4, Cp-C2', Cp-C5'), 76.5 [d, Cp-C5, ³J(¹³C–³¹P)=8 Hz], 78.8 (pt, Cp-C3' or Cp-C4'), 82.7 [d, Cp-C3, ²J(¹³C–³¹P)=13 Hz], 129.9 (s, Ph-C_p), 135.4 (s, Ph-C_m), 136.3 (s, Ph-C_o), 141.8 ppm (s, Ph-C). ³¹P{¹H} NMR (243.0 MHz, CD₂Cl₂): δ=25.2 [s, J(³¹P–¹¹⁷

¹¹⁹Sn)=93.9 Hz], 30.9 ppm [s, J(³¹P–¹¹⁷/¹¹⁹Sn)=71.9 Hz]. ¹¹⁹Sn{¹H} NMR (223.9 MHz, CD₂Cl₂): δ=–187 ppm [dd, J(¹¹⁹Sn–³¹P)=74 Hz, J(¹¹⁹Sn–³¹P)=97 Hz]. ESI-MS, positive mode: m/z=787 [M–HgI₃]⁺, 745 [M–HgI₃–2·iPr]⁺, 667 [M–HgI₃–2·O(iPr)]⁺, 625 [M–HgI₃–P(O)(O(iPr))₂]⁺; negative mode: m/z=583 [HgI₃][–], 127 [I][–]. IR ν(P=O)=1213 cm^{–1}, 1240 cm^{–1}.

Keywords: ferrocene · phosphorus · tin · weakly coordinating anions · X-ray diffraction

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