

Metal Atom Synthesis of (η^6 -Toluene)(η^2 -ethene)iron(σ^1 -stannandiyls): Unusual Iron(0) Complexes

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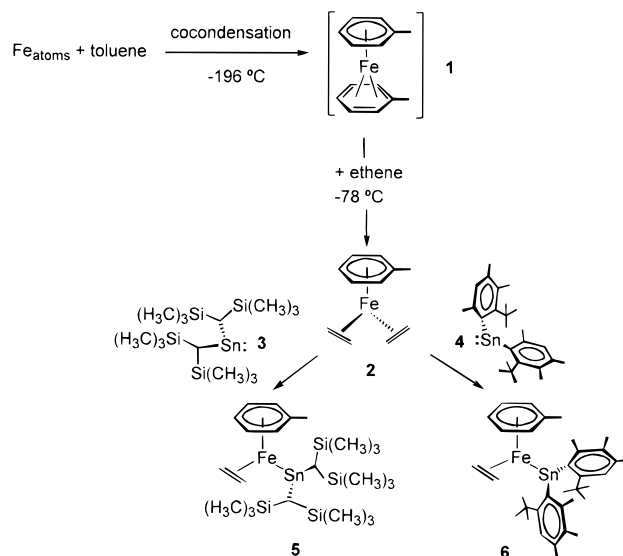
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Over the last two decades Klabunde has demonstrated the peculiar stabilizing ability of electron-demanding σ -element bonds in SiCl_3 , SiF_3 , and C_6F_5 ligands when combined with the electron-donating ability of the η^6 -arene group in late transition metal chemistry (Fe, Co, Ni).^{1,2} However, there are very few well-characterized Fe arene complexes containing main group elements. Examples described so far are (η^6 -arene)Fe(H_2)(SiX_3) (arene = benzene, toluene, *p*-xylene; X = Cl, F) bearing iron exclusively in unusual +IV formal oxidation state.² None of these complexes display π arene reactivity. Stannylenes or stannandiyls $:\text{SnR}_2$ are unique 2 e σ -donor main group metal ligands which in contrast to electron-demanding σ ligands such as SiX_3 (X = Cl, F) or C_6F_5 on the other hand offer a high σ -donor capability in bonds to transition metals.³ The apparent difference of what is known concerning the stabilizing σ ligand environments in π -arene iron chemistry and for complexation properties of low-valent stannylenes SnR_2 toward transition metal fragments prompted us to investigate this obviously contradictory reactivity pattern in more depth.

We developed a multistep direct reaction sequence starting from metal atoms and toluene and reacted "toluene solvated iron atoms" in two consecutive further reactions, first with ethene gas and then with Lappert's or Weidenbruch's stannylenes SnR_2 (R = $\text{CH}(\text{SiMe}_3)_2$ ⁴ or aryl = 2-*tert*-butyl-4,5,6-trimethylphenyl⁵) to form the title compounds **5** and **6** in good yields (Scheme 1), a new class of low-valent π -arene iron(0) complexes which are reactive toward π -arene exchange.

Iron vapor (4 g) was co-deposited with excess toluene (150 mL) at -196°C over 4 h at 10^{-3} Torr. During warming to -30°C the reactor was backfilled with ethene gas to a pressure of approximately 760 Torr causing the initially brown green matrix to melt and become orange, indicating the formation of thermolabile [$(\eta^6$ -toluene)(η^2 -ethene) $_2$ Fe].⁶ The resulting solution

Scheme 1



containing **2** was filtered through Celite under ethene atmosphere at -78°C to remove any excess of iron metal. To this solution 3 g of SnR_2 (R = *tert*-butyl-4,5,6-trimethylphenyl or R = $\text{CH}(\text{SiMe}_3)_2$) dissolved in 20 mL of ether was added causing a color change to intense purple red upon warming to -20°C . The toluene was removed in a vacuum at -15°C and the purple to almost black residue gave purple black crystals of **5** and **6** in 50 and 65% yield (based on individual stannylene SnR_2 added) upon recrystallization from ether or pentane at -78°C . Crystalline **5** and **6** are stable under nitrogen at room temperature only for very short periods of time. However, long-term stability (months) can be achieved at temperatures below 0°C under ethene atmosphere.

The spectroscopic data⁷ (^1H , ^{13}C NMR, ^{119}Sn) obtained for **5** and **6** did fully substantiate their isostructural constitution. The molecular structure of **6** was determined by X-ray crystallography.⁸ The Fe atom is trigonal planar coordinated and 0.095 Å out of plane built by the center of the η^6 -toluene, the η^2 -ethene, and the Sn atom. With respect to the Sn–Fe axis the aryl ligands adopt a local C_2 -symmetry. (Figure 1).

The Fe–Sn bond is 2.4362(10) Å and one of the shortest so far reported for transition metals to tin (record low for Fe–Sn =

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(7) Spectroscopic data for **5**, **6**, and **9–11**. **5**: $\text{C}_{35}\text{H}_{50}\text{FeSn}$ [645.39]. ^1H -NMR (300 MHz, C_7D_8 , -20°C) δ 7.16, 7.11 (s, 2H, =CH), 5.57, 5.18, 4.41 (s, 1H, m, 2H, m, 2H, $\text{C}_6\text{H}_5\text{CH}_3$), 2.67, 2.40 (m, 4H, C_2H_4), 3.20, 3.14, 2.20, 2.12, 1.78 (s, 6H, s, 6H, 2s, 6H), 1.44 (s, 3H, $\text{C}_6\text{H}_5\text{CH}_3$), 1.25, 0.94 ppm (s, 18H, *t*Bu). ^{13}C -NMR (75 MHz, C_7D_8 , -20°C) δ 165.8, 158.9, 152.4, 151.8, 141.1, 140.3, 135.7, 135.3, 133.9, 133.5 (C-aryl), 127.2, 126.9 (CH-aryl), 95.9, 85.8, 84.6, 83.2 ($\text{C}_6\text{H}_5\text{CH}_3$), 37.3 (C_2H_4), 34.3, 32.9 (C(CH $_3$) $_3$), 32.4, 32.2 (C(CH $_3$) $_3$), 16.0 ($\text{C}_6\text{H}_5\text{CH}_3$), 24.4, 24.0, 26.3, 25.9, 14.2, 13.9 ppm (CH $_3$ -aryl). ^{119}Sn (C_7D_8 , -20°C) δ 1231.6 ppm (in addition a minor intensity signal at 1237.7 ppm was observed). **6**: $\text{C}_{23}\text{H}_{30}\text{FeSi}_2\text{Sn}$ [613.63]. ^1H -NMR (300 MHz, C_7D_8 , -20°C) δ 5.85, 5.30, 4, 32 (s, 1H, 2, 2H, s, 2H, $\text{C}_6\text{H}_5\text{CH}_3$), 2.47, 2.11 (s, 4H, C_2H_4), 1.65 (s, 2H, CH), 0.31 ppm (s, 36H, Si(CH $_3$) $_3$). ^{13}C -NMR (75 MHz, C_7D_8 , -20°C) δ 97.4 (*ipso*- $\text{C}_6\text{H}_5\text{CH}_3$), 85.2, 83.3 (*o,m*- $\text{C}_6\text{H}_5\text{CH}_3$), 81.6 (*o,m*- $\text{C}_6\text{H}_5\text{CH}_3$), 45.2 (C_2H_4), 26.3 ($\text{C}_6\text{H}_5\text{CH}_3$), 25.2 (CH), 4.23 ppm (Si(CH $_3$) $_3$). ^{119}Sn (C_7D_8 , -20°C): no signal detected. **8** and **9** can be separated by chromatography on Al_2O_3 , however, not completely. **8**: MS (EI, 70 eV) [1014]-(4), M^+ , [999](1), $\text{M}^+ - \text{CH}_3$, [930](1), $\text{M}^+ - 3\text{CO}$, [494](14), [FeSn{CH(TMS) $_2$ } $_2$] $^+$. IR (KBr) $\tilde{\nu}$ 1808 vs (CO). ^{13}C -NMR (75 MHz, C_6D_6 , 27°C) δ 229.9, 90: MS (EI 70 eV) 606(1) M^+ , [Fe(CO) $_4$ Sn{CH(SiMe $_3$) $_2$ } $_2$] $^+$, [578](2) $\text{M}^+ - \text{CO}$; [550](2) $\text{M}^+ - 2\text{CO}$, [494](9) $\text{M}^+ - 4\text{CO}$, 28(100) CO. IR (KBr) $\tilde{\nu}$ 2000, 1960, 1919 (s, m, vs) Fe(CO) $_4$. ^{13}C -NMR (75 MHz, C_6D_6 , 27°C) δ 226.8. **10**: MS (EI 70 eV) [587](3) [$\text{M}^+ - \text{CO}(\text{H})$] [tol-FeSn{CH(TMS) $_2$ } $_2$] + H] $^+$, [494](2) [Fe-Sn{CH(TMS) $_2$ } $_2$] $^+$, [439](2) [Sn{CH(TMS) $_2$ } $_2$] $^+$, [28]-(46) CO. ^1H -NMR (300 MHz, C_6D_6 , 27°C) δ 5.25 (s, 1H), 5.10 (m, 2H), 4.97 (m, 2H), 1.83 (s, 3H, tol-CH $_3$), 1.29 (s, 2H, CH), 0.32 ppm (s, 36H, SiMe $_3$). ^{13}C -NMR (75 MHz, C_6D_6 , 27°C) δ 215.5 (CO), 96.9, 86.3, 84.7, 83.5 (all tol), 43.0 (CH), 21.6 (CH $_3$ -tol), 4.2 ppm (Me $_3$ Si). Anal. Calcd for $\text{C}_{22}\text{H}_{46}\text{FeOSi}_4\text{Sn}$: 613.60. Found: C, 42.91; H, 7.65; Fe, 9.27. Calcd: C, 43.06; H, 7.57; Fe, 9.10.

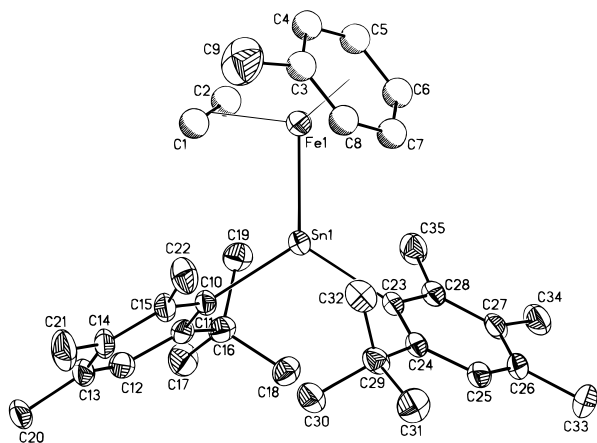


Figure 1. Molecular structure of **6** (50% ellipsoids) in the crystal with the atom labeling scheme. The disordered, isotropically refined atoms are displayed as balls. Selected bond length [Å] and angles (deg) are as follows: Sn–Fe 2.4362(10), Sn–C11 2.253(6), Sn–C23 2.251(6); C10–Sn–Fe 122.96(14), C23–Sn–Fe 122.70(14), C23–Sn–C10 114.3(2).

2.408(1) Å, found in $[(\text{CO})_4\text{Fe}-\{\text{SnOC}_6\text{H}_2'\text{Bu}_2-2,6\text{-Me-4}\}_2]$.^{3d,9,10} The modest stability of **5** and **6** apparently relies on their closed shell 18 e electron configuration. If toluene is considered to occupy three coordination sites and the ethene and σ -bonded SnR_2 ligands occupy two sites then **5**, **6**, and **8** are five-coordinate compounds. Introducing fluorinated ligands instead of hydrogen is known to be a powerful tool in stabilizing organometallics.¹¹ An intriguing proposition would be a H vs F substitution of ethylene in **5** or **6**, as the superior π -accepting ability introduced by such a substitution¹¹ is expected to confer greater stability to the resulting complexes than ethylene itself. However, attempts to stabilize compound **5** or **6** in such a way up to ambient conditions has not proven successful so far. Employing partially fluorinated 1,2-difluoroethene instead of ethene in reaction Scheme 1 did not produce **5**[F₂] or **6**[F₂].

Of special interest to us was the quest for π arene lability of **5** and **6**. This rarely reported reactivity pattern in arene iron chemistry¹² would close a gap in π arene exchange studies of late transition metal arene complexes of Co and Ni known so far.¹

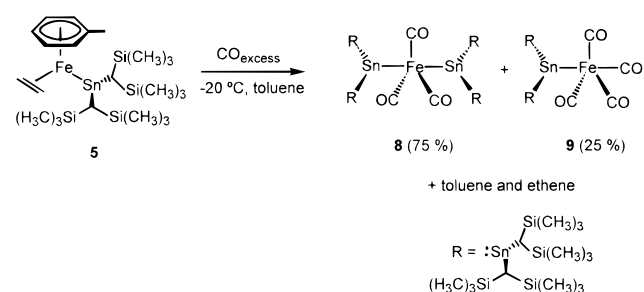
(8) Crystal data: single crystals of **6** are crystallized from diethyl ether, crystal dimensions $0.37 \times 0.34 \times 0.26 \text{ mm}^3$, purple black, measured on a Siemens SMART-CCD diffractometer (three-axis platform) with Mo K α radiation at 200 K. Cell dimensions $a = 10.2722(2) \text{ \AA}$, $b = 19.5738(3) \text{ \AA}$, $c = 18.0423(3) \text{ \AA}$, $\beta = 104.462(10)^\circ$, $V = 3512.74(10) \text{ \AA}^3$; monoclinic crystal system, $Z = 4$, $d_{\text{calc}} = 1.255 \text{ g cm}^{-3}$, $\mu = 1.145 \text{ mm}^{-1}$, space group $P2_1/n$, data collection of 23177 intensities ($2\theta_{\text{max}} = 50^\circ$, $0.3^\circ \omega$ -scans 120 frames at $\phi = 0^\circ$, four runs $0.3^\circ \phi$ -scans with 600 frames at angles 135, 143, 156, and 169° in ω , more than 97% of the data covered), absorption correction with Siemens SADABS (R_{merge} before/after 0.1230/0.0729, max/min equivalent transmission 1.00/0.51), 5682 independent and 4582 "observed" data ($F_o \geq 4\sigma(F)$), structure solution with direct methods (Siemens-SHELXTL-Plus Vers. 5.03) and refined on F^2 (Siemens SHELXL-97) (326 parameters). The atoms C(1)–C(8) were found to be disordered with respect to a local pseudomirror plane passing through C9, Fe1, and Sn1 and were refined isotropically with $1/2$ occupation factors. A disordered ether molecule is located around the inversion center in b. Hydrogen atom positions were calculated and refined as riding groups with the 1.2-fold (1.5 for methyl groups) isotropic U values. $R1 = 0.0641$, $wR2 = 0.1772$, $w^{-1} = \sigma^2(F_o^2) + (0.096P)^2 + 7.88P$, where $P = [(\text{max } F_o^2) + (2F_c^2)]/3$, GOF = 1.057, max/min residual electron density 1.876–0.517 e \AA^{-3} close to the heavy atoms.

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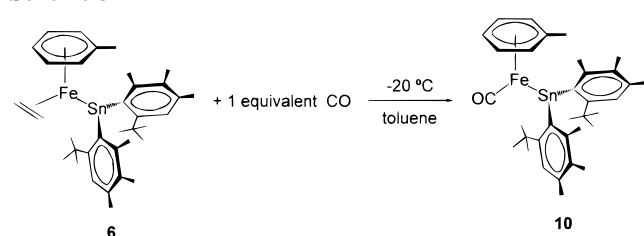
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Scheme 2



Scheme 3



5 reacts with an excess of CO gas at -20°C in toluene solution by substitution of both ethene and arene ligands and formation of the two stable carbonyl complexes **8** and **9** in a 1:1 ratio (Scheme 2). The substitution proceeds irreversibly, which is in contrast to reversible π arene lability in related complex $(\eta^6\text{-toluene})\text{Ni}(\text{SiCl}_3)_2$.^{1b,d}

If only 1 equiv of CO is added at -20°C , only ethene is selectively substituted and stable red crystals of **10**⁷ are formed in nearly quantitative yield (Scheme 3). NMR spectra of **10** lack the characteristic signals of π bonded ethene but still possess the characteristic signal pattern for the η^6 -coordinated toluene ligand. In addition the carbonyl resonance at 216 ppm is found in ^{13}C NMR and ν_{CO} is detected at 2022 cm^{-1} (vs) in IR.

The direct metal vapor approach offers a valuable synthetic pathway to a new class of 18e mixed arene iron/tin half-sandwich complexes (arene)Fe(SnR₂)(ethene). The subtle equilibrium of synergistic interactions established by the presence of ethene and SnR₂ stannylene ligands to iron seems the prime stability factor, but it is also the main reactivity enhancing factor in this new type of π arene iron chemistry. At this time our most important conclusion is that under the right conditions mixed Fe(0)/Sn(II) group metal 18e complexes can be moderately stable but still reactive enough to allow arene reactivity under very mild, yet unexpected conditions.

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Supporting Information Available: Tables of data collection information, atomic coordinates, anisotropic displacement parameters, bond length, bond angles, and structure factor amplitudes of $[(\eta^6\text{-toluene})(\eta^2\text{-ethene})\text{Fe}-\text{Sn}(\text{tert-butyl-4,5,6-trimethyl-phenyl})_2]$ **6** (PDF). This material is available free of charge via the Internet at <http://pub.acs.org>.

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