



## Communication

# Selective benzylic C–H activation of solvent toluene and *m*-xylene by an iron–tin cluster complex: $\text{Fe}_2(\mu\text{-SnBu}^t)_2(\text{CO})_8$

Lei Zhu<sup>a</sup>, Veeranna Yempally<sup>a</sup>, Derek Isrow<sup>a</sup>, Perry J. Pellechia<sup>b</sup>, Burjor Captain<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, University of Miami, Coral Gables, FL 33124, USA

<sup>b</sup> Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC, USA

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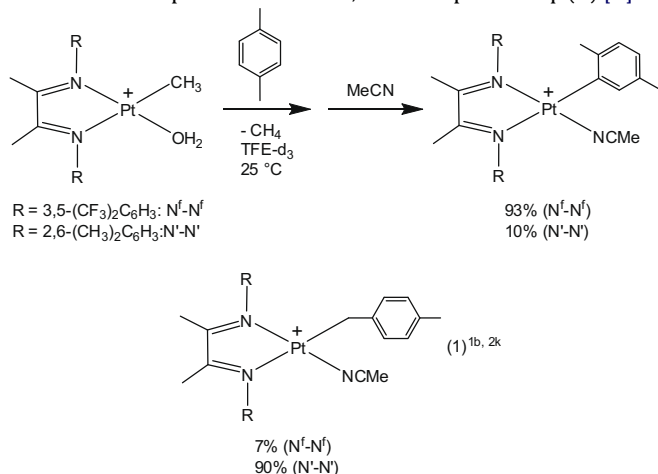
## ABSTRACT

The bimetallic cluster complex  $\text{Fe}_2(\mu\text{-SnBu}^t)_2(\text{CO})_8$ , **1**, selectively activates the benzylic C–H bond in solvent toluene at reflux conditions to afford the complex  $\text{Fe}_2[\mu\text{-SnBu}^t(\text{CH}_2\text{Ph})]_2(\text{CO})_8$ , **3**, where two of the  $\text{Bu}^t$  groups in **1** have been replaced with benzyl groups. Similarly **1** also activates the benzylic C–H bond in solvent *m*-xylene to yield complexes  $\text{Fe}_2[\mu\text{-SnBu}^t(m\text{-CH}_2\text{PhMe})]_2(\text{CO})_8$ , **4**,  $\text{Fe}_2[\mu\text{-SnBu}^t(m\text{-CH}_2\text{PhMe})][\mu\text{-Sn}(m\text{-CH}_2\text{PhMe})_2](\text{CO})_8$ , **5**, and  $\text{Fe}_2[\mu\text{-Sn}(m\text{-CH}_2\text{PhMe})_2]_2(\text{CO})_8$ , **6**, where two, three and four of the  $\text{Bu}^t$  groups in **1** have been replaced by *m*-tolyl groups, respectively. A mechanism based on a radical pathway is proposed for the C–H activation by **1**.

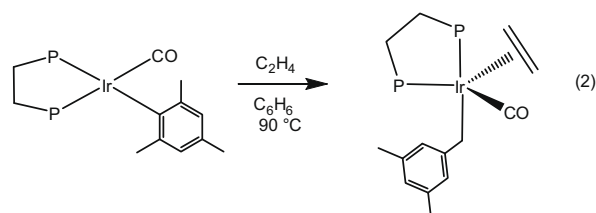
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## 1. Introduction

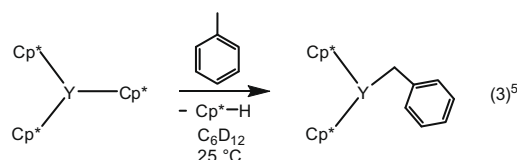
The activation of the carbon–hydrogen bond in organic molecules for the purpose of functionalization by transition metal complexes has always been one of the fore-fronts of chemical research [1]. Selective C–H activation is especially important when the substrate contains both  $sp^2$  hybridized aryl C–H bonds as well as  $sp^3$  hybridized aliphatic C–H bonds. It has been shown that transition metal complexes are capable of activating both the aryl C–H as well as the aliphatic C–H bonds, for example see Eq. (1) [2].



There are also instances that demonstrate an aryl C–H to aliphatic C–H (benzylic C–H) [3] rearrangement and vice versa [4] in iridium complexes, for example see Eq. (2).



Recent studies have shown that even some cyclopentadienyl complexes of Ytterbium and Gadolinium can also activate C–H bonds, Eq. (3) [5]. The most common main group elements known to metalate arene rings are those of complexes containing Tl [6] and Pb [7]. Tin has also been shown to selectively activate the aryl C–H bonds in alkylaromatic compounds. For example, the complex “( $\text{CF}_3\text{COO}$ )<sub>4</sub>Sn” [8] activates the aryl C–H bond in benzene as well as in *p*-xylene.



Recently, a bimetallic Ir–Sn complex was shown to be a catalyst for the alkylation of arenes, which proceeds via aryl C–H activation of the arene substrate at an Ir center [9]. We have now found that the bimetallic Fe–Sn cluster  $\text{Fe}_2(\mu\text{-SnBu}^t)_2(\text{CO})_8$ , **1**, is capable of

\* Corresponding author. Tel.: +1 305 284 3059.

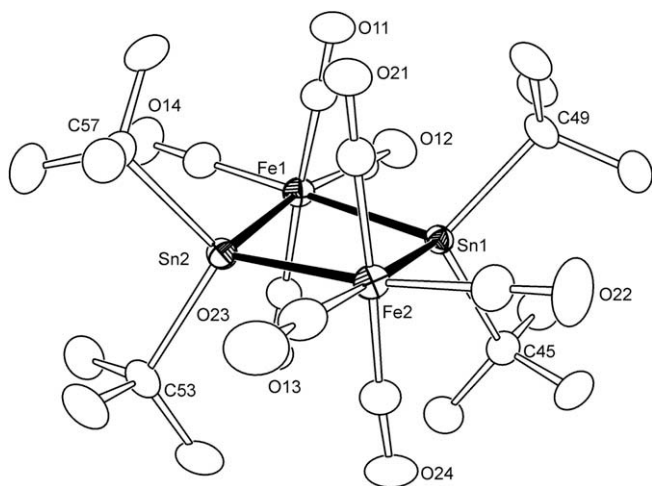
E-mail address: captain@miami.edu (B. Captain).

selectively activating only the benzylic C–H bond in toluene and *m*-xylene, and propose a radical mechanism for the reaction. This is the first example of selective benzylic C–H activation of alkylaromatic compounds at Sn centers, and we wish to report our preliminary findings in this communication.

## 2. Results and discussion

The bimetallic cluster complex **1** was obtained from the reaction of  $\text{Fe}_2(\text{CO})_9$  and  $\text{Bu}_3\text{SnH}$  at 97 °C in 41% yield. Compound **1** was prepared several years ago from the reaction of  $\text{Na}_2\text{Fe}(\text{CO})_4$  and  $\text{Bu}_2\text{SnCl}_2$  in 50% yield and its structure was formulated accurately based on infrared spectroscopy and molecular weight measurements [10]. We have obtained the structure of compound **1** by single crystal X-ray diffraction and its molecular structure is shown in Fig. 1. The structure is essentially the same as the dimethyl tin analog  $\text{Fe}_2(\mu\text{-SnMe}_2)_2(\text{CO})_8$ , **2** [11]. The two iron atoms which are apart by 4.225(1) Å (4.153(1) Å in molecule 2, there are two molecules in the asymmetric unit) are non-bonding, and is similar to the iron–iron non-bonding distance in **2**, 4.139(15) Å. The electron count around each iron atom is 18.

Interestingly, when the reaction of  $\text{Fe}_2(\text{CO})_9$  and  $\text{Bu}_3\text{SnH}$  was carried out in refluxing toluene solvent (110 °C), compound **1** was not formed, instead the new compound  $\text{Fe}_2[\mu\text{-SnBu}^t(\text{CH}_2\text{Ph})]_2(\text{CO})_8$ , **3** was obtained in 4% yield. Compound **3** was characterized by a combination of IR, NMR and single crystal X-ray diffraction analyses. An ORTEP showing the molecular structure of compound **3** is shown in Fig. 2. Compound **3** is very similar to the structure of **1** except that one  $\text{Bu}^t$  group on each of the Sn atoms in **1** has been replaced with a benzyl group from the solvent toluene. Indeed when compound **1** is dissolved in toluene solvent and heated to reflux, compound **3** is obtained as the sole metal complex product in 21% yield. As seen in Fig. 2 the benzyl groups are located *trans* to each other, however  $^1\text{H}$  NMR after TLC work-up indicates the presence of another resonance which is attributed to the *cis* isomer which we are not able to separate by chromatography. The relative proportions of the *trans* and *cis* isomer by  $^1\text{H}$  NMR are approximately in a 50:50 ratio. However, the *trans* isomer can be obtained in pure form by fractional crystallizations at –20 °C from a methylene chloride/hexane solvent mixture. We have been unable to obtain a crystal structure of this *cis* isomer at this time.

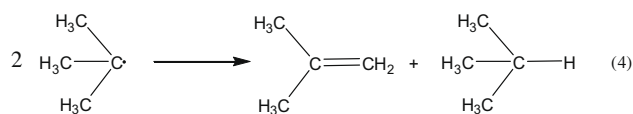


**Fig. 1.** An ORTEP of the molecular structure of  $\text{Fe}_2(\mu\text{-SnBu}_3)_2(\text{CO})_8$ , **1** showing 30% probability thermal ellipsoids. Selected bond distances (in Å) are as follows: (molecule 1) Sn(1)–Fe(1) = 2.7216(9), Sn(1)–Fe(2) = 2.7074(9), Sn(2)–Fe(1) = 2.7156(9), Sn(2)–Fe(2) = 2.7288(9), (molecule 2) Sn(3)–Fe(3) = 2.7248(10), Sn(3)–Fe(4) = 2.7236(10), Sn(4)–Fe(3) = 2.7207(11), Sn(4)–Fe(4) = 2.7106(9).

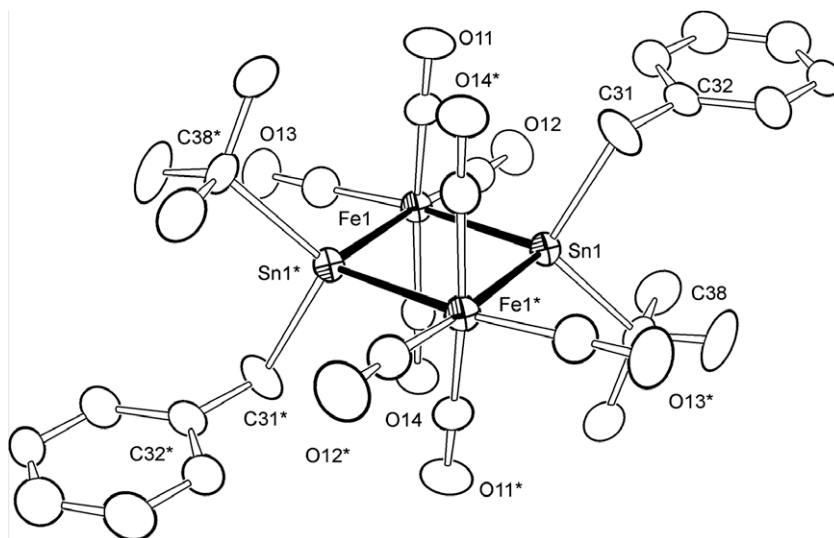
To further investigate the ability of complex **1** to activate the alkyl groups in alkylaromatic compounds, we investigated the reaction of **1** with *m*-xylene. When a solution of **1** in *m*-xylene solvent was heated to reflux, the compound,  $\text{Fe}_2[\mu\text{-SnBu}^t(m\text{-CH}_2\text{PhMe})]_2(\text{CO})_8$ , **4**, was obtained in 20% yield, see Fig. 3. Like in compound **3**, compound **4** has replaced one of the  $\text{Bu}^t$  groups on each of the two Sn atoms with a *m*-tolyl (tolyl =  $\text{CH}_2\text{PhMe}$ ) group. The *m*-tolyl groups are *trans* with respect to each other. In addition to **4** where two  $\text{Bu}^t$  groups were replaced, this reaction afforded compounds  $\text{Fe}_2[\mu\text{-SnBu}^t(m\text{-CH}_2\text{PhMe})][\mu\text{-Sn}(m\text{-CH}_2\text{PhMe})_2](\text{CO})_8$ , **5**, and  $\text{Fe}_2[\mu\text{-Sn}(m\text{-CH}_2\text{PhMe})_2]_2(\text{CO})_8$ , **6**, in 19% and 8% yields, respectively. For compound **5** three of the  $\text{Bu}^t$  groups have been replaced by *m*-tolyl groups, see Fig. 3, and in **6** all of the  $\text{Bu}^t$  groups in **1** have been replaced with *m*-tolyl groups, see Fig. 4. The reason multiple addition products with *m*-xylene solvent were obtained is probably due to the higher boiling point of *m*-xylene (139 °C) to that of toluene (110 °C).

The reaction of **1** with solvents toluene and *m*-xylene furnished products which were a result of activation of the benzylic C–H bond. We have not seen any evidence for products that may have been formed as a result of aryl C–H activation. When the reaction of **1** in refluxing toluene was carried out in the presence of a radical scavenger TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) for 1 h, compound **3** was not formed and all of the starting **1** was consumed. Furthermore, light is not required to generate the radical species in solution as we found no significant difference in the rate of formation for **3** when the reaction of **1** in refluxing toluene was carried out in the dark verses when this reaction was performed under hood light. The effect of toluene- $d_8$  on the reaction was investigated and only trace amount of **3** was found. Only when this reaction was sealed in a Parr reactor and heated to 150 °C were we able to obtain the desired product where two of the  $\text{Bu}^t$  groups in **1** had been replaced by two deuterated benzyl groups.  $^1\text{H}$  NMR shows it is a mixture of two isomers like compound **3**, and X-ray diffraction analysis of **3-d**<sub>14</sub> for crystals obtained from a methylene chloride/hexane solvent mixture at –20 °C, revealed the structure of the *cis* isomer, see SI for an ORTEP of **3-d**<sub>14</sub>. This observation is consistent with the mechanism in which C–H bond activation plays a prominent role.

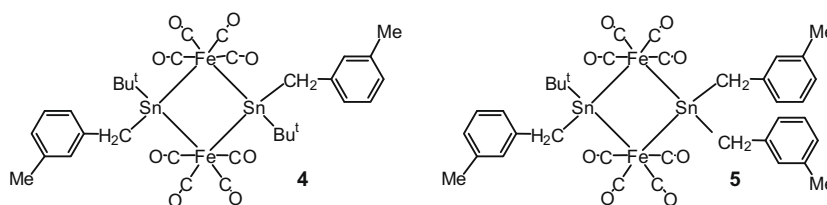
To detect the formation of isobutane- $d_1$  ( $\text{D-Bu}^t$ ), compound **1** in toluene- $d_8$  was sealed in an NMR tube under partial vacuum and heated at 150 °C for 2 h. The  $^2\text{H}\{^1\text{H}\}$  NMR spectrum of the reaction mixture showed a singlet at 1.63 ppm confirming appropriately formation of isobutane- $d_1$  ( $\text{D-Bu}^t$ ). However, it should be noted that the  $^1\text{H}$  NMR spectrum showed large amounts of non-deuterated isobutane, which made it very difficult to detect isobutane- $d_1$  ( $\text{D-Bu}^t$ ), as well as isobutylene. The observance of non-deuterated isobutane in the reaction mixture can be explained due to the possibility that two  $\text{Bu}^t$  radicals can transform to isobutylene and isobutane by losing and gaining one hydrogen atom, respectively, see Eq. (4). Pryor and Tang also observed disproportionation of  $\text{Bu}^t$  radicals (generated from photolysis of AIB (azoisobutane) in neat toluene and substituted toluene) to isobutene and isobutane [12]. Since the yield of the reaction is only 21%, we can account for the mass balance only by the fact that there is a lot of decomposition, thus it is not surprising that large quantities of isobutane and isobutylene were observed.



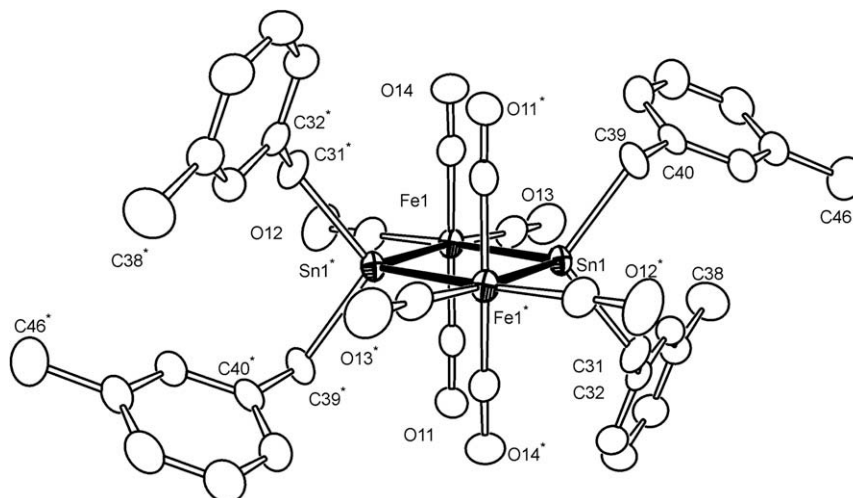
As possible control experiments, there was no reaction of  $\text{Fe}_2(\text{CO})_9$  in refluxing toluene, and the same was observed when  $\text{Bu}_2\text{SnCl}_2$  was refluxed in toluene, or when  $\text{Bu}_3\text{SnH}$  was heated in toluene at 95 °C. Furthermore, when  $\text{Bu}_3\text{SnH}$  in toluene was heated at reflux,



**Fig. 2.** An ORTEP of the molecular structure of  $\text{Fe}_2[\mu\text{-SnBu}^t(\text{CH}_2\text{Ph})]_2(\text{CO})_8$ , **3** showing 30% probability thermal ellipsoids. Selected bond distances (Å) are as follows: (molecule 1)  $\text{Sn}(1)\text{-Fe}(1) = 2.6749(10)$ ,  $\text{Sn}(1)\text{-Fe}(1)^* = 2.6958(11)$ , (molecule 2)  $\text{Sn}(2)\text{-Fe}(2) = 2.6837(10)$ ,  $\text{Sn}(2)\text{-Fe}(2)^* = 2.6951(10)$ .



**Fig. 3.** Line structures for compounds **4** and **5**. See supplementary material for ORTEPs of the molecular structures of compounds **4** and **5**.

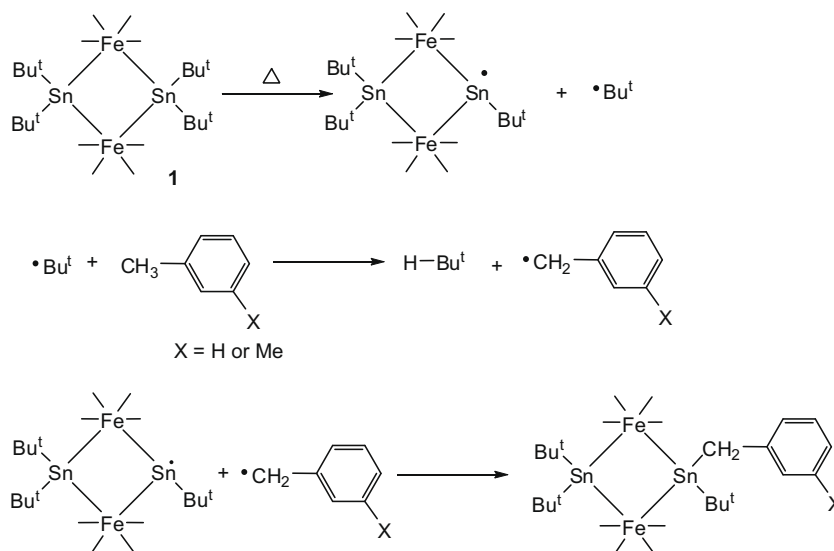


**Fig. 4.** An ORTEP of the molecular structure of  $\text{Fe}_2[\mu\text{-Sn}(m\text{-CH}_2\text{PhMe})_2]_2(\text{CO})_8$ , **6** showing 30% probability thermal ellipsoids. Selected bond distances (Å) are as follows: (molecule 1)  $\text{Sn}(1)\text{-Fe}(1) = 2.6340(3)$ ,  $\text{Sn}(1)\text{-Fe}(1)^* = 2.6901(3)$ ,  $\text{Sn}(1)\text{-Fe}(1) = 2.6901(3)$ ,  $\text{Sn}(1)\text{-Fe}(1)^* = 2.6340(3)$ .

no reaction was observed after 1.5 h, however, after prolonged time (over 3 h) the  $^1\text{H}$  NMR spectrum of the reaction mixture was full of a number of products, which we have not been able to identify. The role of the Fe-cluster framework we believe is to provide stability of the Sn radical that is produced in the first step by cleavage of the Sn–C bond in the mechanism of this reaction.

Based on these observations a radical mechanism is proposed, see Scheme 1, with the first step being homolysis of the Sn–C bond in **1** to expel a  $\text{Bu}^t$  radical. Alternatively, compound **1** which is a di-

mer comprised of two  $[\text{Fe}(\mu\text{-SnBu}^t)_2(\text{CO})_4]$  units could transform to the monomer by cleavage of a Fe–Sn bond. Marks et al. have shown that homolysis of the Fe–Sn bond in **1** is facile and reversible in coordinating solvents such as THF, pyridine, acetone and others, while homolysis of the Fe–Sn bond was not observed in non-coordinating solvents such as benzene or cyclohexane [10]. We thus suspect that the dimer does remain intact in solution as toluene and *m*-xylene are non-coordinating solvents. The next step is the abstraction of a hydrogen atom from the methyl group by the



Scheme 1.

Bu<sup>t</sup> radical to form isobutane, and the benzyl or *m*-tolyl radical. The presence of isobutane was detected by <sup>1</sup>H NMR. The benzyl or *m*-tolyl radical then combines with the tin radical in the Fe<sub>2</sub>Sn<sub>2</sub> cluster complex to yield the benzylic C–H activated complex. This process is then repeated to replace another Bu<sup>t</sup> group with a benzyl or *m*-tolyl group.

It is interesting that the bimetallic FeSn cluster Fe<sub>2</sub>(μ-SnBu<sup>t</sup>)<sub>2</sub>(CO)<sub>8</sub> reacts with solvents toluene and *m*-xylene to afford compounds containing benzyl or *m*-tolyl groups. It is proposed that the Bu<sup>t</sup> radical expelled from **1** attacks the benzylic C–H bond in toluene and *m*-xylene. There is evidence in the literature that Bu<sup>t</sup> radicals can abstract hydrogens from toluene and substituted toluenes [12,13]. Thus, it should be possible to selectively activate the benzylic C–H bond in other alkyl aromatic compounds as well. Preliminary work now underway has also shown similar reactivity with *ortho* and *para*-xylene solvent. Bimetallic catalytic systems have attracted much attention because their catalytic properties are often superior to that of their components [14]. It has been proposed that the different metals may exhibit “synergy” or bifunctional cooperativity such that one metal performs one role in a catalytic reaction and the other performs a second function.

### 3. Experimental

#### 3.1. Synthesis of Fe<sub>2</sub>[μ-SnBu<sup>t</sup>(CH<sub>2</sub>Ph)]<sub>2</sub>(CO)<sub>8</sub>, **3**

A 30 mg amount of Fe<sub>2</sub>(CO)<sub>9</sub> (0.082 mmol), 50 mg amount of Bu<sub>3</sub>SnH (0.17 mmol) and 10 mL of toluene were charged into a 50 mL 3-neck flask. The reaction was heated to reflux for 3 h, at which time IR showed complete consumption of the starting material. The solvent was removed *in vacuo* and the product was separated by TLC by using hexane solvent to yield 3.1 mg (yield 4%) of colorless product, **3**. <sup>1</sup>H NMR indicates the presence of another resonance which is attributed to the *cis* isomer, which we are not able to separate by chromatography. IR ν<sub>CO</sub> (cm<sup>-1</sup> in hexane) for the mixture: 2044 (vs), 1998 (m), 1979 (s). By means of fractional crystallizations at -20 °C from a methylene chloride/hexane solvent mixture, 5 mg of pure *trans*-Fe<sub>2</sub>[μ-SnBu<sup>t</sup>(CH<sub>2</sub>Ph)]<sub>2</sub>(CO)<sub>8</sub> is separated from 40 mg of the mixture. Spectral data for *trans*-**3**: IR ν<sub>CO</sub> (cm<sup>-1</sup> in hexane): 2044 (vs), 1997 (m), 1992 (w), 1980 (s). <sup>1</sup>H NMR (toluene-d<sub>8</sub>, in ppm, 400 MHz): δ = 7.27–6.98 (m, 10H, Ph), 3.44 (s, 4H, CH<sub>2</sub>, <sup>2</sup>J<sub>Sn-H</sub> = 34 Hz), 1.31 (s, 18H, CH<sub>3</sub>, <sup>3</sup>J<sub>117Sn-H</sub> = 94 Hz, <sup>3</sup>J<sub>119Sn-H</sub> =

97 Hz). Elemental Anal. Calc.: C, 41.43; H, 3.71. Found: C, 41.12; H, 3.97%.

#### 3.2. Synthesis of Fe<sub>2</sub>[μ-SnBu<sup>t</sup>(*m*-CH<sub>2</sub>PhMe)]<sub>2</sub>(CO)<sub>8</sub>, **4**, Fe<sub>2</sub>[μ-SnBu<sup>t</sup>(*m*-CH<sub>2</sub>PhMe)][μ-Sn(*m*-CH<sub>2</sub>PhMe)]<sub>2</sub>(CO)<sub>8</sub>, **5**, and Fe<sub>2</sub>[μ-Sn(*m*-CH<sub>2</sub>PhMe)]<sub>2</sub>(CO)<sub>8</sub>, **6**

A 30 mg amount of Fe<sub>2</sub>(μ-SnBu<sup>t</sup>)<sub>2</sub>(CO)<sub>8</sub> (0.037 mmol) was dissolved in 7 mL of *m*-xylene in a 100 mL 3-neck flask. The reaction was heated to reflux for 100 min. The solvent was removed *in vacuo* and the product was separated by TLC by using hexane solvent to yield in order of elution 6.9 mg (yield 20%) of pale yellow Fe<sub>2</sub>[μ-SnBu<sup>t</sup>(*m*-CH<sub>2</sub>PhMe)]<sub>2</sub>(CO)<sub>8</sub>, **4**, 6.7 mg (yield 19%) of pale yellow Fe<sub>2</sub>[μ-SnBu<sup>t</sup>(*m*-CH<sub>2</sub>PhMe)][μ-Sn(*m*-CH<sub>2</sub>PhMe)]<sub>2</sub>(CO)<sub>8</sub>, **5**, and 3.1 mg (yield of 8.3%) of colorless Fe<sub>2</sub>[μ-Sn(*m*-CH<sub>2</sub>PhMe)]<sub>2</sub>(CO)<sub>8</sub>, **6**. Spectral data for **4**: IR ν<sub>CO</sub> (cm<sup>-1</sup> in hexane): 2043 (vs), 1996 (m), 1992 (m, sh), 1979 (s), 1955 (w). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, in ppm, 300 MHz): δ = 7.13–6.85 (m, 8H, Ph), 3.51 (s, 4H, CH<sub>2</sub>, <sup>2</sup>J<sub>Sn-H</sub> = 34 Hz), 3.49 (s, 4H, CH<sub>2</sub>, <sup>2</sup>J<sub>Sn-H</sub> = 34 Hz), 2.20 (s, 6H, CH<sub>3</sub>), 2.15 (s, 6H, CH<sub>3</sub>), 1.33 (s, 18H, CH<sub>3</sub>, <sup>3</sup>J<sub>Sn-H</sub> = 95 Hz), 1.32 (s, 18H, CH<sub>3</sub>, <sup>3</sup>J<sub>Sn-H</sub> = 95 Hz). Note: This is a mixture of *cis*- and *trans*-isomers. Elemental Anal. Calc.: C, 42.81; H, 4.04. Found: C, 42.99; H, 3.80%. Spectral data for **5**: IR ν<sub>CO</sub> (cm<sup>-1</sup> in hexane): 2065 (w), 2045 (vs), 2006 (m), 1997 (m), 1979 (s), 1955 (w). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, in ppm, 300 MHz): δ = 7.13–6.84 (m, 12H, Ph), 3.44 (s, 2H, CH<sub>2</sub>, <sup>2</sup>J<sub>Sn-H</sub> = 35 Hz), 3.42 (s, 2H, CH<sub>2</sub>, <sup>3</sup>J<sub>Sn-H</sub> = 39 Hz), 3.33 (s, 2H, CH<sub>2</sub>, <sup>3</sup>J<sub>Sn-H</sub> = 38 Hz), 2.18 (s, 9H, CH<sub>3</sub>), 1.30 (s, 9H, CH<sub>3</sub>, <sup>3</sup>J<sub>Sn-H</sub> = 96 Hz). Elemental Anal. Calc.: C, 45.71; H, 3.83. Found: C, 45.67; H, 3.54%. Spectral data for **6**: IR ν<sub>CO</sub> (cm<sup>-1</sup> in hexane): 2068 (w), 2049 (vs), 2009 (m), 2003 (m), 1979 (s), 1955 (w). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, in ppm, 300 MHz): δ = 7.13–6.85 (m, 16H, Ph), 3.28 (s, 8H, CH<sub>2</sub>, <sup>2</sup>J<sub>Sn-H</sub> = 38.6 Hz), 2.17 (s, 12H, CH<sub>3</sub>). Elemental Anal. Calc.: C, 48.34; H, 3.65. Found: C, 48.62; H, 3.12%.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.09.024.

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