Organometallics **1996,** *15,* 4707−4713

Transition Metal Stannyl Complexes. 11.[1] Chelated ((Phosphinoalkyl)stannyl)iron Complexes by Intramolecular Oxidative Addition of Tin−Phenyl or Tin−Methyl Groups

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Received May 30, 1996[⊗]

Reaction of $Fe_2(CO)_9$ with $Ph_2P(CH_2)_nSnR_2R'$ ($n = 2$, $R' = Ph$, $SnR_2 = SnPh_2$, SnPhMe, $R' = Me$, $SnR_2 = SnMe_2$; $n = 1$, 3, $SnR_2R' = SnPh_3$) results in the formation of $(CO)_{5-x}Fe[PPh_2(CH_2)_nSnR_2R']_x$ ($x = 1, 2$). Upon UV irradiation, the chelated (phosphinoalkyl)stannyl complexes $(CO)_3(R')\overline{FePPh_2(CH_2)_nSn}R_2$ are obtained by intramolecular oxidative addition of the Sn−R′ group. The complexes *mer*-$(CO)_3(H)(R'_3Si)FePPh_2(CH_2)_3SnPh_3$ ($SiR'_3 = SiMePh_2$, $Si(OMe)_3$) are formed at −50 °C from $(CO)_4Fe(H)SiR'_3$ and $Ph_2P(CH_2)_2SnPh_3$. While the $SiMePh_2$ derivative is converted to the chelated complex $(CO)_3(Ph)\overline{FePPh_2(CH_2)_2Sn}Ph_2$ by $HSiMePh_2$ elimination upon heating, the $Si(OMe)_3$ derivative does not give the intramolecular oxidative addition. Photochemical reaction of $(CO)_3(Ph)\overline{FePPh_2(CH_2)_2Sn}Ph_2$ with $Ph_2P(CH_2)_2SnPh_3$ gives the substitution product $(CO)_2(Ph)\overline{Fe[PPh_2(CH_2)_2Sn}Ph_2]PPh_2(CH_2)_2SnPh_3$. While a second oxidative addition to the iron center by the dangling $SnPh_3$ group is not possible, the Sn−Ph group readily adds to a $(Ph_3P)_2Pt$ fragment to give $(CO)_2(Ph)\overline{Fe[PPh_2(CH_2)_2Sn}Ph_2]PPh_2(CH_2)_2SnPh_2Pt(Ph)(PPh_3)_2$. The related complex $(CO)_3(H)[(MeO)_3Si]FePPh_2(CH_2)_2SnPh_2Pt(Ph)(PPh_3)_2$ is similarly obtained from $(CO)_3(H)[(MeO)_3Si]FePPh_2(CH_2)_2SnPh_3$.

The electronic and steric factors governing the oxidative addition of E−H groups (E = Si, Ge, Sn) to transition metal centers were intensively investigated and are well understood. Contrary to this, the oxidative addition of $R_3E{-}E'R'_3$ (E′ = main group 4 element)[3] has only recently gained increased attention. While E−H groups are readily added to a large number of metal complex fragments, the electronic and steric requirements are more stringent for the addition of $R_3E{-}E'R'_3$. Unactivated Sn−C bonds, such as Sn−Ph or Sn−Me, are readily added to $[(Ph_3P)_2Pt]$, for example, to give the complexes *cis*-$(Ph_3P)_2Pt(R')SnR_3$[4] but are not added to less reactive metal complex fragments, such as $[(CO)_4Fe]$. The formation of $[(CO)_4Fe(\mu\text{-}SnR_2)]_2$ from iron carbonyls and tetraorganostannanes $SnR_xR'_{4-x}$ was only observed for special groups R′ and special combinations of R and R′.[5]

Apart from electronic and steric factors, oxidative addition reactions are promoted by "chelate assistance", as has initially been shown by Stobart et al. for the Si−H bonds of $R_2P(CH_2)_nSiR'_2H$.[6] Facilitated oxidative addition of Si−Si bonds was recently also observed for $Ph_2P(CH_2)_2$-substituted disilanes ($Ph_2P(CH_2)_2SiMe_2SiR_3$[7] and $[Ph_2P(CH_2)_2SiMe_2]_2$[8]). The corresponding distannanes, $[Ph_2P(CH_2)_nSnMe_2]_2$, were earlier used for the preparation of chelated (phosphinoalkyl)stannyl complexes of Pt(II).[9] Chelate-assisted oxidative additions of Sn−C bonds to Pd and Pt centers were earlier reported by us.[10] In the present paper we describe the oxidative addition of Sn−Me or Sn−Ph bonds of $Ph_2P(CH_2)_nSnR_3$ to the less reactive $[Fe(CO)_4]$ fragments. A preliminary report was published earlier.[11]

Results and Discussion

Previous experiments of Grobe and Möller had shown that thermal reaction (160 °C) of $Fe(CO)_5$ or $Fe_2(CO)_9$ with $Me_2PCH_2CH_2SnMe_3$ results in the formation of both the monophosphane complex $(CO)_4FePMe_2CH_2$-

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[⊗] Abstract published in *Advance ACS Abstracts*, October 1, 1996.

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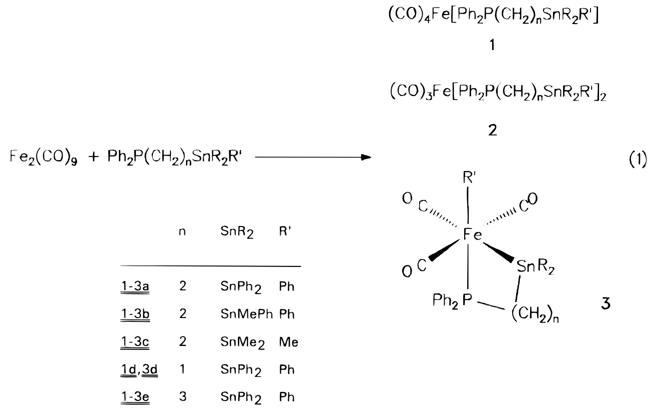
S0276-7333(96)00424-4 CCC: $12.00

CH_2SnMe_3 and the bis(phosphane) complex $(CO)_3Fe(PMe_2CH_2CH_2SnMe_3)_2$.[12] When we reacted a toluene solution of $Fe_2(CO)_9$ with the derivatives $Ph_2PCH_2CH_2SnR_2R'$ ($SnR_2R' = SnPh_3$, $SnPh_2Me$, $SnMe_3$) in a 2:1 ratio, we got not only the corresponding phosphane complexes **1a**−**c** and **2a**−**c** but in each case also minor amounts of a third metal complex, which turned out to be the oxidative addition products **3a**−**c** (eq 1). When a 1:1 ratio of the reactants was employed, a considerable amount of $Ph_2PCH_2CH_2SnR_2R'$ remained unreacted and had to be separated from the reaction mixture by reaction with MeI and precipitation of the phosphonium salt.



	n	SnR_2	R'
1-3a	2	$SnPh_2$	Ph
1-3b	2	SnMePh	Ph
1-3c	2	$SnMe_2$	Me
1d,3d	1	$SnPh_2$	Ph
1-3e	3	$SnPh_2$	Ph

The bis(phosphane) complexes **2a**−**c** were isolated by column chromatography, while the mono(phosphane) complexes **1a**−**c** and the oxidative addition products **3a**−**c** were eluted in one zone. We separated the $SnPh_3$ derivative **1a**, which was obtained as a yellow powder being stable in air for a short time. The complexes **2** are slightly less soluble in hydrocarbons than **1**. The IR and NMR spectra of **1** are typical for trigonal-bipyramidal $(CO)_4FeL$ complexes with an axial ligand L. The $^{31}P\{^1H\}$ NMR spectra of **2** show a signal at 80.5 ppm (**2a**) or 80.6 ppm (**2c**) for the chemically equivalent phosphorus nuclei. Due to the different tin isotopes, ABX-type spectra were observed, with a $^2J_{PFeP}$ coupling constant of 31 Hz for **2a**. A similar value (32 Hz) was previously observed for *trans*-$(CO)_3Fe(PPh_3)(PMePh_2)$. Therefore, the complexes **2** also have the *trans*-geometry, although the appearance of one weak and two strong ν(CO) bands of equal intensity [**2a**, 1940 (w), 1882 (s), 1876 (s) cm^{-1}; **2c**, 1939 (w), 1884 (s), 1872 (s) cm^{-1}] indicates that the trigonal-bipyramidal geometry is severely distorted.

For the deliberate synthesis of **3a**, a toluene solution of the mono(phosphane) complex **1a** was irradiated with UV light. There was quantitative conversion of **1a** after 2 h. The synthesis of **3a** was then simplified by irradiating the mixture of complexes obtained by the thermal reaction of $Fe_2(CO)_9$ with $Ph_2PCH_2CH_2SnPh_3$ (2:1 ratio) after removal of unreacted $Fe_2(CO)_9$. Within a few hours the IR bands of **2a** disappeared. Irradiation was continued until **1a** was also consumed. This procedure gives **3a** in a higher overall yield (71%) and does not require the separation of **1a** from the byproducts. The chelate complexes **3b,c** were similarly prepared by irradiating the reaction mixtures of $Fe_2(CO)_9$ with $Ph_2PCH_2CH_2SnR_2R'$ after removal of the bis(phosphane) complexes (**2b,c**) by column chromatography.

The complexes **3** are the intramolecular oxidative addition products of a Sn−Ph or Sn−Me group to the iron center of coordinatively unsaturated $[(CO)_3FePPh_2CH_2CH_2SnR_2R']$. The latter compound is obviously photochemically formed from either **2** (abstraction of a phosphane ligand) or **1** (abstraction of a CO ligand). The formation of **3b** shows, as expected,[4] that oxidative addition of a Sn−Ph bond is more favorable (for electronic reasons) than that of a Sn−Me bond. We cannot rule out that there is also oxidative addition of the Sn−Me bond to a minor extent, because we observed an additional minor signal at 75.2 ppm in the ^{31}P NMR spectrum of the reaction mixture of $Fe_2(CO)_9$ with $Ph_2PCH_2CH_2SnMePh_2$, which could be due to the Fe−Me isomer. The preparation of **3c** shows that the iron center, in principle, is reactive enough for the chelate-assisted oxidative addition of a Sn−Me group.

The thermal stability of **3** depends to a very high degree on the substituents at tin. While **3a,b** are remarkably stable against reductive elimination, even at elevated temperatures, **3c** is very labile and completely decomposes already at −25 °C within 24 h. The main decomposition product is $Ph_2PCH_2CH_2SnMe_3$, formed by initial reductive elimination of the Sn−Me bond. Since oxidative addition and reductive elimination are reverse processes, the facile elimination of the Sn−Me group in **3c** is consistent with the less pronounced tendency to oxidatively add to the metal, compared with Sn−Ph groups.

We also probed the effect of the ring size on the oxidative addition by thermally reacting $Ph_2PCH_2SnPh_3$ and $Ph_2PCH_2CH_2CH_2SnPh_3$ with $Fe_2(CO)_9$. Reaction of $Ph_2PCH_2CH_2CH_2SnPh_3$ proceeded as that of $Ph_2PCH_2CH_2SnPh_3$; i.e., the phosphane complexes **1e** and **2e** and the oxidative addition product **3e** were formed. Thermal reaction of $Ph_2PCH_2SnPh_3$ with $Fe_2(CO)_9$ only yielded the mono(phosphane) complex **1d**. Toluene solutions of the isolated complexes **1d** and **1e** were irradiated by UV light. The oxidative addition product **3e** was formed from **1e** within 3 h in high yields. There was no significant difference to the reaction of **1a**, and particularly no indication for the oxidative addition of the $Sn-CH_2$ bond (which would have resulted in a five-membered Fe−P−C−C−C metallacycle and a $SnPh_3$ ligand). Contrary to that, the reaction of **1d** was less straightforward. There was no further change in the IR spectrum of the reaction mixture after 7 h of irradiation, although some starting compound was left. This indicates an equilibrium between the oxidative addition and reductive elimination products. The ^{31}P NMR spectrum showed that the oxidative addition product **3d** was formed, but there was also a great number of byproducts. This is not unexpected, because the formation of a four-membered metallacycle is less favorable than of five- or six-membered ones. The same trend has been observed for the tendency to form chelate complexes of nickel with $Ph_2P(CH_2)_nPPh_2$ ($n = 1 \ll n = 2 \approx n = 3$).[13]

The complexes **3** were isolated as yellow solids, soluble in common organic solvents. The ν(CO) bands in the infrared spectra show the *mer* arrangement of the three

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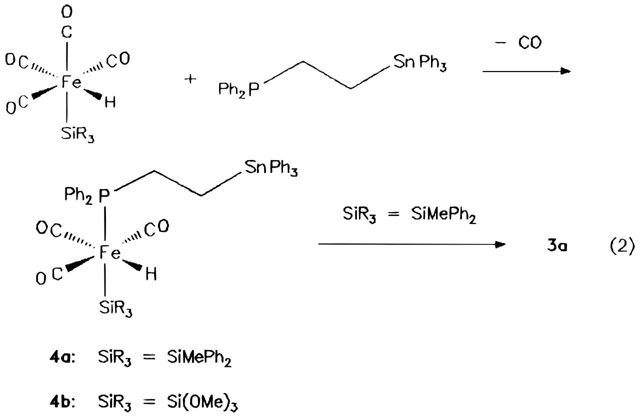
CO ligands. This requires the phenyl or methyl group *cis* to Sn (*trans* to P), as expected for oxidative addition products. Bonding of one phenyl (methyl) group to the iron atom in **3** results in a high-field shift of the corresponding ^{1}H NMR signals of about 0.5 (1.0) ppm relative to **1** or **2**. The ^{119}Sn signal is shifted from 4.0 ppm in $Ph_2PCH_2CH_2SnPh_3$ to 137.5 ppm in **3a** due to the metal coordination. Formation of the five-membered chelate ring results in a strong decrease of the $^3J_{SnCCP}$ coupling constant, from 253/248/230 Hz in **1a**−**c** to about 70−75 Hz in **3a**−**c**. The structure of **3a** was confirmed by an X-ray structure analysis which was earlier reported.[11] The structure of **3a** is static (separate signals for the equatorial and axial CO groups) up to 85 °C. The Sn−P coupling in the complexes **3a**,**d**,**e** shows the same trends (mixing of coupling "through the metal" and "through the backbone") as has been discussed for the P−P coupling in complexes with chelated diphosphinoalkane ligands.[14]

The chelate complex **3a** was also obtained in high yields, when $Ph_2PCH_2CH_2SnPh_3$ was thermally reacted with a toluene solution of the hydrido silyl complex *cis*-$(CO)_4Fe(H)SiMePh_2$ (eq 2). Mixing of both compounds at room temperature resulted in immediate CO evolution. Three signals were observed at 78.7 (strong signal), 72.3, and 58.7 ppm in the ^{31}P NMR spectrum of the solution. They are attributed to **3a**, **1a**, and the phosphane-substituted hydrido silyl complex **4a**. The latter value compares well with that of $(CO)_3(Ph_3P)Fe(H)SiMePh_2$ (60.9 ppm).[15] When the solution was heated to 70 °C, only the bands of **3a** were left in the IR spectrum.



For the better characterization of **4a** the reaction was also performed at −50 °C. At this temperature the subsequent reaction of **4a** to **3** was slowed down. Although this results in a higher **4a**/**3a** ratio, the complex **4a** could not be isolated analytically pure due to its high reactivity. Phosphane-substituted hydrido silyl complexes of the type *mer*-$(CO)_3(R'_3P)Fe(H)SiR_3$ have been prepared by photochemical reaction of $(CO)_4(R'_3P)Fe$ with $HSiR_3$[15−17] or by thermal reaction of *cis*-$(CO)_4Fe(H)SiR_3$ with PR'_3.[18,19] The latter reaction may be complicated by deprotonation reactions (with basic phosphanes) or silane elimination.

Oxidative addition of the Sn−Ph bond of **4a** to the iron center requires reductive elimination of the silane. The ready formation of **3a** shows that readdition of the silane to the vacant coordination site is less favorable than addition of the Sn−C bonds. The oxidative addition of Si−H bonds usually is much more favored than that of Sn−C bonds. In the present case the situation is obviously reversed by the chelate assistance of the Sn−C addition.

It is known that reductive elimination of silanes is rendered more difficult if the silicon atom is substituted by electronegative groups. When $(CO)_4Fe(H)Si(OMe)_3$ and $Ph_2PCH_2CH_2SnPh_3$ were reacted under the same conditions as the $SiMePh_2$ derivative, the ready formation of the phosphane-substituted complex **4b** was observed, but there was no indication for the subsequent formation of **3a** (eq 2). Compared with the $SiMePh_2$ derivative **4a**, the situation is reversed; i.e., oxidative addition of $HSi(OMe)_3$ is preferred to that of Sn−Ph (despite chelate assistance), or there is a high barrier for the reductive elimination of $HSi(OMe)_3$ which prevents vacation of the coordination site. Complex **4b** is stable and was fully characterized. The spectra are similar to those of **4a** and typical for a complex of the type *mer*-$(CO)_3(R'_3P)Fe(H)SiR_3$, with the hydrogen atom *cis* to both the SiR_3 and the PR_3 ligand.[15]

To probe the possibility of a double oxidative addition (as has been observed for Pt and Pd complexes[10]), a toluene solution of **2a** was also irradiated by UV light. The IR and ^{31}P NMR spectra showed no signals of **2a** after 2 h but instead those of **3a**, a new complex **5**, and uncoordinated $Ph_2PCH_2CH_2SnPh_3$. The portion of **5** was considerably increased when $Fe_2(CO)_9$ was first thermally reacted with a 4-fold excess of $Ph_2PCH_2CH_2SnPh_3$ and then irradiated with UV light (as previously discussed for the preparation of **3a** except for the different $Fe_2(CO)_9$:ligand ratio). After 7 h of irradiation, the IR bands of **1a** and **2a** were no longer observed, and the main product was **3a**, besides a small amount of **5**. Irradiation for an additional 12 h resulted in the nearly complete conversion of **3a** into **5**. This observation is an additional indication that formation of **5** from **2a** does proceed via elimination of one phosphane ligand (as discussed before), formation of **3a**, and readdition of the phosphane ligand (eq 3). The proposed formation of **5** from **3a** was confirmed by another experiment, in which isolated **3a** was irradiated with an equimolar amount of $Ph_2PCH_2CH_2SnPh_3$. Only **5** was formed. As in the case of **3a**, the "direct" synthesis of **5** (without isolation of **2a** or **3a**) is more convenient and results in a better yield.

Complex **5** was obtained as a yellow solid, soluble in common organic solvents, except saturated hydrocarbons. There is only one ν(CO) band in the IR spectrum of **5**, which is consistent with a complex of the type *trans*-$(CO)_2FeL_4$. There are *two* AB spin systems with about equal intensity in the ^{31}P NMR spectrum, each of them accompanied by tin satellites. The AB system with $\delta(P^1) = 74.8$ ppm and $\delta(P^2) = 62.7$ ppm is assigned to **5a**, because the $^2J_{PFeP}$ coupling constant of 57 Hz is typical to *trans* phosphane ligands (for example, 79 Hz

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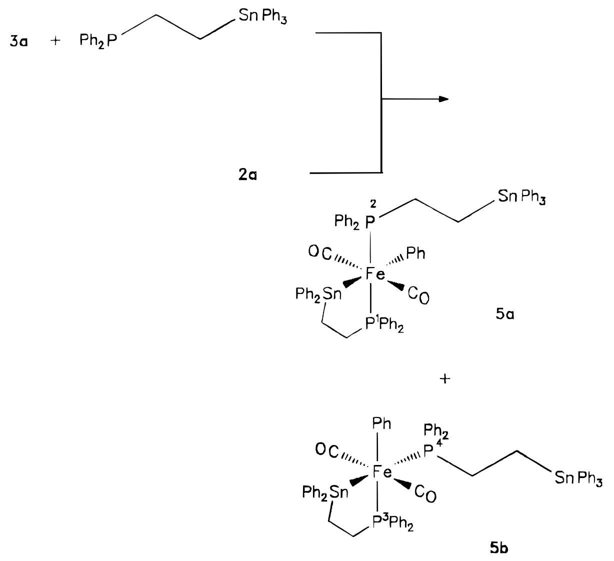

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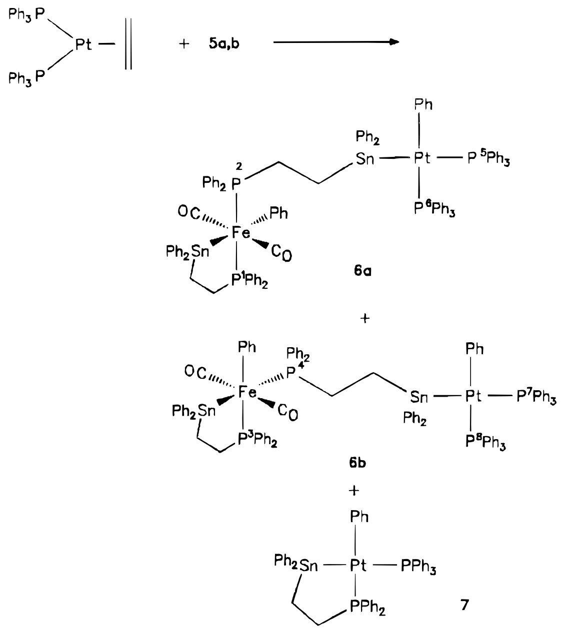

(4)

were found for $(CO)_2[P(OPh)_3]_2Fe(H)SnPh_3$^{20}). The second AB system [$\delta(P^3) = 68.7$ and $\delta(P^4) = 57.5$ ppm] shows a distinctly lower J_{PFeF} coupling of 13 Hz, which is assigned to the *cis* arrangement of the phosphane ligands in **5b**. The same value was found in $(CO)_2(dppe)Fe[Si(OEt)_3]SnMe_3$.[20] This assignment is confirmed by the analysis of the $^2J_{\mathrm{SnFeP}}$ and $^3J_{\mathrm{SnCCP}}$ coupling constants.

The original *cis* arrangement of Sn and the phenyl group is retained in **5b**. Formation of **5a** from **3a** requires a rearrangement, which is possible in the five-coordinate intermediate formed by CO abstraction from **3a**. There is no thermal isomerization up to 85 °C once **5a,b** are formed.

While the iron center in **5** was unreactive toward a second intramolecular oxidative addition, a Sn−Ph group of the dangling $SnPh_3$ group is readily added to the more reactive $(Ph_3P)_2Pt$ fragment. When a toluene solution of **5** was reacted with $(Ph_3P)_2Pt(C_2H_4)$ at room temperature, the AB systems of **5** in the ^{1}H NMR spectrum slowly decreased in intensity, while two new AB systems grew in. They were assigned to the two isomers of **6**. After 4 days, the signals of **5** had disappeared. Analysis of the reaction mixture was complicated by the formation of the platinum complex **7** (eq 4), which was previously prepared by reaction of $(Ph_3P)_2Pt(C_2H_4)$ with $Ph_2PCH_2CH_2SnPh_3$.[10]

When $Pd(PPh_3)_4$ was reacted with **5** at room temperature, the phosphane transfer reaction prevailed, and only the known complex $Pd(PPh_2CH_2CH_2SnPh_2)_2$ was obtained, which was previously prepared by reaction of $Pd(PPh_3)_4$ with $Ph_2PCH_2CH_2SnPh_3$.[10]

Attempts to separate the products from the reaction of **5** with $(Ph_3P)_2Pt(C_2H_4)$ by column chromatography or by crystallization failed. However, the identity and constitution of **6** was unequivocally established by ^{31}P NMR and ^{31}P/^{31}P COSY 45 measurements. In the ^{31}P NMR spectrum, there are four groups of signals for **6a** and **6b** each. The chemical shifts and the coupling of the phosphorus atoms coordinated to the iron center are very similar to those of **5**. However, there is an additional splitting of the signals of the nuclei P^2 and P^4 by coupling with the platinum-bonded phosphorus atoms P^5 and P^7, respectively. The COSY experiment proved that the additional splitting is indeed due to the unusual $^5J_{\mathrm{PCCSnPtP}}$ coupling. There is a chemical shift difference of 0.2 and 1.1 ppm between the corresponding phosphorus atoms at platinum in **6a,b**. This shows that the different geometry at the iron center is transmitted to the platinum center. The ^{31}P chemical shifts and the coupling constants $^2J_{\mathrm{PPtP}}$, $^2S_{\mathrm{nPtP}}$, and $^1J_{\mathrm{PtP}}$ of P^5−P^8 allow an unequivocal assignment of the geometry at the platinum center. The magnitude of $^2J_{\mathrm{PPtP}}$ is typical for a *cis*-$(Ph_3P)_2Pt$ arrangement. The nuclei P^5 and P^7 are split to a doublet of doublets by coupling with P^2 and P^4. The $^2J_{\mathrm{SnPtP}}$ coupling constants of P^5 and P^7 (1753 Hz) are more than 10 times larger than those of P^6 and P^8 (133/171 Hz). Therefore, P^5 and P^7 are *trans* to Sn. Similar coupling constants were found for *cis*-$(Ph_3P)_2Pt(Ph)SnPh_3$ and *cis*-$(Ph_3P)(Ph)PtPPh_2CH_2CH_2SnPh_2$.[10,21] The observed couplings are schematically summarized in Scheme 1 for **6a**.

Analogous to the oxidative addition of the dangling $SnPh_3$ group in **5** to a platinum center, a binuclear complex (**8**) was also obtained by the reaction of **4b** with $(Ph_3P)_2Pt(C_2H_4)$ (eq 5). The known complex **7** was again formed as a byproduct. There was no formation of a Fe−Pt bond by elimination of benzene or $PhSi(OMe)_3$ from **8**. Interestingly, the oxidative addition of the Sn−Ph bond to the platinum center is preferred to that of the Fe−H bond. By comparison, reaction of $(CO)_3[Si(OMe)_3]Fe(H)PPh_2CH_2PPh_2$ with $(Ph_3P)_2Pt(C_2H_4)$ resulted in the formation of $(CO)_3[Si(OMe)_3]Fe(\mu$-dppm)-$Pt(H)PPh_3$.[23]

The coordination geometry at the iron center was changed from *meridional* in **4b** to *facial* in **8**. This phenomenon was previously observed when binuclear complexes with the $(CO)_3(R'_3P)FeSiR_3$ fragment were prepared via the anionic complexes $[(CO)_3(R'_3P)FeSiR_3]^-$.[19] The complex **8** was only spectroscopically

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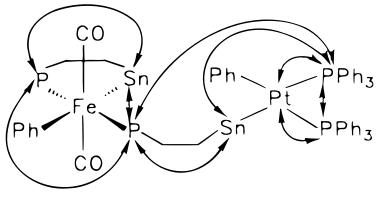
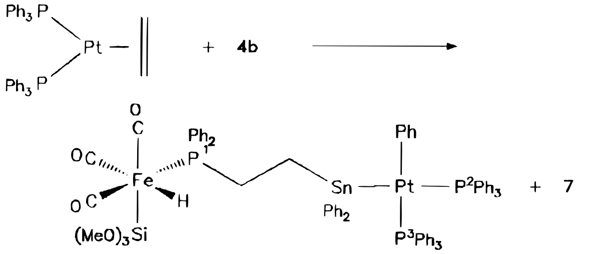
Scheme 1



characterized because of its thermal instability. However, the spectroscopic data are fully consistent with the proposed constitution and the geometry at the two metal centers.



(5)

8

Conclusions

Iron carbonyl fragments are inert toward the oxidative addition of nonactivated Sn−C bonds. However, chelate assistance promotes the addition of such bonds, and the chelated complexes **3** are readily formed from **1** by intramolecular oxidative addition of the Sn−Ph or Sn−Me groups of the $Ph_2P(CH_2)_nSnR_2R'$ ligands. Sn−Ph bonds are more readily added than Sn−Me bonds, and the formation of five- or six-membered metallacycles is more favorable than that of four-membered rings, as expected. The vacant coordination site at the iron atom necessary for the oxidative addition can be created by photochemical CO abstraction from the tetracarbonyl complexes **1**. Surprisingly, oxidative addition of the Sn−Ph bond is also initiated by thermal elimination of $HSiMePh_2$ from **4a**. The oxidative addition of Si−H bonds is much more favored than that of nonactivated Sn−C bonds, if the steric and electronic situation at the tin or silicon atom is comparable. The formation of **3a** from **4a** shows that chelate assistance promotes the (intramolecular) oxidative addition of the Sn−C bond to a point where it can compete with the readdition of $HSiMePh_2$. The observation that intramolecular oxidative addition is possible starting from the $SiMePh_2$ derivative **4a** but not from the $Si(OMe)_3$ derivative **4b**, in which reductive elimination of the silane is less facile, gives another qualitative estimate on the magnitude of the chelate effect. In an earlier work we have shown for the oxidative addition of Si−H bonds (to tungsten carbonyl complexes) that stabilization of the oxidative addition product by chelatation is slightly larger than by the electronic effects caused by either substituting a CO ligand for PR_3 or by replacing SiR_3 (R = alkyl, aryl) for $SiCl_3$ in nonchelated complexes.[22]

Experimental Section

All operations were performed in an atmosphere of dry and oxygen-free nitrogen, using dried and argon-saturated solvents. For UV irradiation, a water-cooled mercury high-pressure lamp TQ 150 (180 W, Heraeus) and Pyrex glassware were used. Instrumentation: Melting points, DuPont Thermal Analyzer 990; ^{1}H NMR spectra, Bruker AMX 400 (400.1 MHz); ^{13}C NMR spectra, Bruker AC 200 (50.3 MHz) or Bruker AMX 400 (100.6 MHz); ^{31}P NMR and ^{119}Sn NMR spectra, Jeol FX 90Q (36.3 MHz/33.4 MHz) or Bruker AMX 400 (161.9 MHz/149.2 MHz). If not otherwise stated, only the coupling constants to ^{119}Sn are given.

Preparation of $(CO)_4FePPh_2CH_2CH_2SnPh_3$ (1a) and $(CO)_3Fe(PPh_2CH_2CH_2SnPh_3)_2$ (2a). A 1.26 g (2.24 mmol) amount of $Ph_2PCH_2CH_2SnPh_3$ and 1.63 g (4.47 mmol) of $Fe_2(CO)_9$ were suspended in 20 mL of toluene. Most of the $Fe_2(CO)_9$ dissolved within 15 min on heating to 60 °C, while the color of the solution turned to dark brown and gas evolution occurred. The solution was stirred at 60 °C for additional 30 min to complete the reaction. After separation of the excess $Fe_2(CO)_9$ and removal of all volatile compounds (including $Fe(CO)_5$) *in vacuo*, a brown oil was obtained, which contained the complexes **1a**, **2a**, and (a little) **3a**, according to the IR and ^{31}P NMR spectra. The mixture was chromatographed on silica (column 50 × 1 cm; solvent, 1:1 petroleum ether/toluene). The first, light yellow zone contained **1a** and **3a**, the second, yellow zone only **1a**, and the third, orange zone **2a**. After removal of the solvents from the second and the third fraction, the complexes **1a** and **2a** are obtained as yellow (**1a**) or beige (**2a**) powders on recrystallization at −25 °C from 5 mL of petroleum ether (**1a**) or 10 mL of toluene/petroleum ether (1:4) (**2a**).

1a. Yield: 0.85 g (26%). Mp: 74 °C. IR (toluene, cm^{-1}): ν(CO) = 2043 (s), 1971 (m) 1938 (vs). ^{1}H NMR (d_6-acetone): δ 7.61−7.35 (m, 25 H, Ph), 2.92 (m, 2 H, PCH_2), 1.72 (m, 2 H, SnCH_2). ^{31}P{^{1}H} NMR (36.2 MHz, C_6D_6): δ 72.2 (s, $^3J_{SnCCP}$ = 253 Hz). Anal. Calc for $C_{36}H_{29}FeO_4PSn$: C, 59.14; H, 4.00. Found: C, 59.21; H, 4.10.

2a. Yield: 1.17 g (21%). Mp: 114 °C. IR (toluene, cm^{-1}): ν(CO) = 1940 (w), 1882 (s) 1876 (s). ^{1}H NMR (C_6D_6): δ 7.75−6.90 (m, 25 H, Ph), 3.15 (m, 4 H, PCH_2), 2.10 (m, 4 H, SnCH_2). ^{31}P{^{1}H} NMR (36.2 MHz, C_6D_6): δ 80.5 (s, A_2 portion), $^2J_{PFeP}$ = 31 Hz from the ABX portion. Anal. Calc for $C_{67}H_{58}FeO_3P_2Sn_2$: C, 63.55; H, 4.62. Found: C, 63.31; H, 4.80.

Preparation of $(CO)_3(Ph)\overline{FePPh_2CH_2CH_2Sn}Ph_2$ (3a). (a) From 1a. A 0.64 g (0.88 mmol) amount of **1a** was dissolved in 20 mL of toluene and irradiated for 2 h at −20 °C, during which gas was evolved and the yellow color of the solution intensified. After filtration and removal of the solvent, **3a** was crystallized at −25 °C from 5 mL of toluene/petroleum ether (1:2) and then washed three times with 2 mL of petroleum ether each. Yield: 0.43 g (79% from **1a**).

(b) Direct Synthesis from $Fe_2(CO)_9$. A 727 mg (2.00 mmol) amount of $Fe_2(CO)_9$ and 563 mg (1.00 mmol) of $Ph_2PCH_2CH_2SnPh_3$ were reacted as described above. After removal of excess $Fe_2(CO)_9$ by filtration, the brown solution was diluted with toluene to 100 mL and then irradiated for 20 h at −10 °C. The IR bands of **2a** disappeared within a few hours during the photolysis. The reaction was finished when the mono(phosphane) complex **1a** was no longer observed in the IR spectrum. Isolation of **3a** was the same as for method a. Yield: 0.49 g (71% from $Ph_2PCH_2CH_2SnPh_3$) of yellow powder. Mp: 178 °C. IR (toluene, cm^{-1}): ν(CO) = 2028 (w), 1983 (m, sh), 1964 (vs). ^{1}H NMR (d_6-acetone): δ 7.59−7.04 (m, 20 H, PPh and SnPh), 6.81−6.79 (m, 5 H, FePh), 2.75 (m, 2 H, PCH_2), 1.59 (m, 2 H, SnCH_2). ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): δ 78.7 (s, J_{SnP} = 75 Hz). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ 213.1 (d, CO_{ax}, $^2J_{PFeC}$ = 14.5 Hz), 212.7 (d, CO_{eq}, $^2J_{PFeC}$ = 11.8 Hz), 146.3−123.9 (C_6H_5), 33.0 (d, PCH_2, $^1J_{PC}$ = 32.4 Hz), 10.1 (d, SnCH_2, $^2J_{PCC}$ = 19.4 Hz). ^{119}Sn NMR (33.4 MHz, C_6D_6): δ 137.5 (d, J_{SnP} = 75 Hz). Anal. Calc for $C_{35}H_{29}FeO_3PSn$: C, 59.79; H, 4.16. Found: C, 59.52; H, 4.45.

(c) From $(CO)_4Fe(H)SiMePh_2$. To a solution of 549 mg (1.50 mmol) of $(CO)_4Fe(H)(SiMePh_2)$ in 20 mL of toluene was added 845 mg (1.50 mmol) of $Ph_2PCH_2CH_2SnPh_3$. The solution was stirred for 18 h at room temperature and then at 70 °C for 4 h. The reaction was monitored by IR and ^{31}P NMR spectroscopy. There was a violent formation of gas, and the solution turned brown. After the gas evolution ceased, the IR spectrum only showed the CO bands of **3a**. The solution was filtered, the solvent removed *in vacuo*, and **3a** crystallized from toluene/petroleum ether (1:1) at −25 °C. The crystals were washed several times with 10 mL of petroleum ether each, until the solution was colorless. Additional fractions of **3a** were obtained from the combined washing solutions. Yield: 875 mg (83%).

Preparation of $(CO)_3(Ph)\overline{FePPh_2CH_2CH_2Sn}MePh$ (3b). A solution of 0.78 g (1.49 mmol) of $Ph_2PCH_2CH_2SnMePh_2$ in 10 mL of toluene was added to a suspension of 1.09 g (3.00 mmol) of $Fe_2(CO)_9$ in 20 mL of toluene. The reaction mixture was warmed to 40 °C until most of the $Fe_2(CO)_9$ had dissolved by reaction, during which the color of the solution turned brown and gas was evolved. After cooling, excess $Fe_2(CO)_9$ was filtrated off. The IR and ^{31}P NMR spectra showed the presence of the compounds **1**−**3b**. After removal of all volatiles *in vacuo*, the obtained brown, viscous oil was submitted to column chromatography at −5 °C (column 40 × 0.5 cm, silica gel). Four fractions were obtained. The first three were eluted with petroleum ether/toluene (1:1), and the fourth was eluted with toluene. Only the bis(phosphane) complex **2b** (IR (toluene cm^{-1}): $\nu(CO) = 1939$ (m), 1885 (s), 1875 (s, sh)) was separated (4th zone) by this procedure.

Zones 1−3 were combined, dissolved in 100 mL of toluene, and irradiated with UV light at −20 °C for 5 h. After separation of the insoluble parts and the removal of the solvent *in vacuo*, a brown oil was obtained, which was dissolved in 0.5 mL of toluene. Upon addition of 10 mL of pentane the ochre complex **3b** was precipitated, which was washed three times with 5 mL of pentane each. Yield: 392 mg (41%). Mp: 44 °C (dec). IR (toluene, cm^{-1}): $\nu(CO) = 2023$ (s), 1978 (s, sh) 1956 (vs). ^1H NMR (C_6D_6): δ 7.83−6.93 (m, 20 H, Ph), 2.25 (m, 2 H, PCH_2), 1.26 (m, 2 H, $SnCH_2$), 0.73 (s, 3 H, $SnCH_3$, $^2J_{SnCH} = 46$ Hz). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6): δ 79.3 (J_{SnP} = 69 Hz). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): δ 213.9 (d, CO_{ax}, $^2J_{PFeC} = 14$ Hz), 213.1 (d, CO_{eq}, $^2J_{PFeC} = 9.8$ Hz), 145.8−125.6 (Ph), 33.2 (d, PCH_2, $^1J_{PC} = 32.3$ Hz), 9.8 (d, $SnCH_2$, $^2J_{PCC}$ = 19.7 Hz), −6.1 (s, $SnCH_3$, $^1J_{SnC} = 329$ Hz). ^{119}Sn NMR (33.4 MHz, C_6D_6): δ 169.0 (d, $J_{SnP} = 70$ Hz). Anal. Calc for $C_{30}H_{27}FeO_3PSn$: C, 56.16; H, 4.25. Found: C, 55.09; H, 4.03.

Preparation of $(CO)_3Fe(PPh_2CH_2CH_2SnMe_3)_2$ (2c) and $(CO)_3(Me)\overline{FePPh_2CH_2CH_2Sn}Me_2$ (3c). The suspension of 2.00 g (5.52 mmol) of $Fe_2(CO)_9$ and 1.04 g (2.76 mmol) of $Ph_2PCH_2CH_2SnMe_3$ in 30 mL of toluene was stirred for 2 h at room temperature, during which a violent formation of gas was observed. After filtration of the excess $Fe_2(CO)_9$ and removal of all volatile components *in vacuo*, an orange colored oil was obtained. The IR and ^{31}P NMR spectra showed the presence of the compounds **1**−**3c**, the compound **3c** only in traces. The mixture was submitted to column chromatography (column 25 × 1 cm, petroleum ether, silica gel). The first yellow zone contained a mixture of **1c** and **3c**. The second, orange colored fraction contained **2c**. The compound **2c** was obtained as a yellow powder after removal of the solvent from the second zone and crystallization from 5 mL of petroleum ether at −25 °C. Yield: 0.44 g (18%). Mp: 138 °C. IR (toluene, cm^{-1}): $\nu(CO) = 2043$ (w), 1884 (s), 1872 (s, sh). ^1H NMR (C_6D_6): δ 7.42−6.97 (m, 20 H, Ph), 2.88 (m, 4 H, PCH_2), 1.29 (m, 4 H, $SnCH_2$), −0.02 (s, 18H, $SnCH_3$, $^2J_{SnCH} = 53$ Hz). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6): δ 80.6 (s with ABX subspectra). Anal. Calc for $C_{37}H_{46}FeO_3P_2Sn_2$: C, 49.71; H, 5.19. Found: C, 50.03; H, 5.06.

The first zone of the chromatography was dissolved in 70 mL of toluene and irradiated at −20 °C for 45 min. After filtration and removal of the solvent a yellow oil was obtained. The product was recrystallized from 2 mL of petroleum ether at −78 °C. The yellow crystals of **3c** already contained some brown decomposition products. IR (toluene, cm^{-1}): $\nu(CO)$ = 2013 (w), 1964 (s, sh), 1944 (s). ^1H NMR (C_6D_6): δ 1.67 (m, 2 H, PCH_2), 0.70 (m, 2 H, $SnCH_2$), 0.52 (s, 3H, $SnCH_3$, $^2J_{SnCH}$ = 37 Hz), −0.45 (d, 3 H, $FeCH_3$, $^3J_{PFeCH} = 9$ Hz). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6): δ 83.2 ($J_{SnP} = 76$ Hz). A byproduct with δ 88.2 ($J_{SnP} = 222$ Hz) was additionally observed.

Preparation of $(CO)_3(H)(Ph_2MeSi)FePPh_2CH_2CH_2SnPh_3$ (4a). A solution of $(CO)_4Fe(H)(SiMePh_2)$ in d_8-toluene was transferred to a NMR tube. When a 1.5-fold excess of $Ph_2PCH_2CH_2SnPh_3$ was added at −50 °C, violent gas evolution occurred. The sample was held at −50 to −30 °C, until the reaction was finished. ^1H NMR (d_8-toluene, −40 °C): δ 7.9−6.8 (m, 35 H, Ph), 2.71 (m, 2 H, PCH_2), 1.55 (m, 2 H, $SnCH_2$), 1.24 (s, 3 H, $SiCH_3$), −9.04 (d, 1 H, FeH, $^2J_{PFeH} = 27.7$ Hz). $^{31}P\{^1H\}$ NMR (161.9 MHz, d_8-toluene, −40 °C): δ 59.1 ($^3J_{SnCCP}$ = 252 Hz).

Preparation of $(CO)_3(H)[(MeO)_3Si]FePPh_2CH_2CH_2SnPh_3$ (4b). The solution of 845 mg (1.50 mmol) of $Ph_2PCH_2CH_2SnPh_3$ in 35 mL of toluene was added to a freshly prepared solution of 1.50 mmol of $(CO)_4Fe(H)Si(OMe)_3$ in 35 mL of petroleum ether. The solution was stirred for 6 h at −30 °C until gas formation was finished. The yellow solution was quickly filtered, and the solvents were removed *in vacuo*. The yellow raw product was washed several times at 0 °C with 20 mL of petroleum ether each, until the solution stayed colorless. Yield: 0.60 g (48%). Mp: 44 °C (dec), light-yellow powder. IR (toluene, cm^{-1}): $\nu(CO) = 2043$ (w), 1985 (s, sh) 1974 (vs). ^1H NMR (C_6D_6): δ 7.9−6.9 (m, 25 H, Ph), 3.75 (s, 9 H, OCH_3), 2.80 (m, 2 H, PCH_2), 1.61 (m, 2 H, $SnCH_2$), −9.19 (d, 1 H, FeH, $^2J_{PFeH} = 26.0$ Hz). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6): δ 57.5 ($^3J_{SnCCP} = 239$ Hz). $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6): δ 210.8 (d, CO, $^2J_{PFeC} = 12.1$ Hz), 137.7−127.5 (C_6H_5), 50.6 (s, OCH_3), 30.5 (d, PCH_2, $J_{PC} = 20.0$ Hz), 3.5 (d, $SnCH_2$, $^2J_{PCC} = 3.6$ Hz). Anal. Calc for $C_{38}H_{39}FeO_6PSiSn$: C, 55.30; H, 4.76. Found: C, 54.92; H, 4.72.

Preparation of $(CO)_2(Ph)\overline{Fe(PPh_2CH_2CH_2Sn}Ph_2)PPh_2CH_2CH_2SnPh_3$ (5). (a) From 2. A solution of 0.99 g (0.78 mmol) of **2** in 20 mL of toluene was irradiated for 7 h at −20 °C. The progress of the reaction was monitored by IR and ^{31}P NMR spectroscopy. After irradiation for 2 h, the starting compound had completely disappeared in the IR spectrum. New CO bands were observed at 2030 (w), 1980 (w), 1964 (m), and 1906 cm^{-1}, and in the ^{31}P NMR spectrum the signals of **5** and resonances at 78.7, 30.3, and −9.49 ppm were observed. After an additional 5 h of irradiation, the IR spectrum of the yellow solution showed only one CO band at 1905 cm^{-1}. In the ^{31}P NMR spectrum, the four doublets of **5a,b** and additional weak signals at 30.3−9.49 ppm were observed. After removal of the solvent and crystallization from 1:1 petroleum ether/toluene at −25 °C, complex **5** was obtained as a yellow powder. Yield: 0.45 g (46% from **2**).

(b) Direct Synthesis from $Fe_2(CO)_9$. A 364 mg (1.00 mmol) amount of $Fe_2(CO)_9$ and 2.25 g (4.00 mmol) of $Ph_2PCH_2CH_2SnPh_3$ were reacted in 20 mL of toluene at 60 °C as described above. After filtration and dilution to 100 mL, the solution was irradiated for 19 h at −10 °C. After 7 h the CO bands of **1a** and **2a** had disappeared, and the band of **5** at 1906 cm^{-1} was already observed besides that of **3a**. The reaction was finished, when the CO bands of **3a** no longer decreased in intensity. After the separation of a small amount of an unsoluble compound, the solvent was removed *in vacuo* from the brown solution. The product precipitated when the obtained brown oil was stirred for 1 h with 20 mL of toluene/petroleum ether (1:1). The yellow solid was washed three times with 10 mL of petroleum ether each. From the combined solutions additional fractions of the product were obtained by crystallization of the concentrated solutions at −25 °C. Yield: 0.97 g (78%). Mp: 115 °C (dec). IR (toluene, cm^{-1}): $\nu(CO) = 1906$ (s). ^1H NMR (C_6D_6, numbering of the P atoms shown in eq 2): δ 7.73−6.72 (m, 50 H, Ph), 2.70 (m, 2 H, P^1CH_2), 2.58 (m, 2 H, P^3CH_2), 2.37 (m, 4 H, $P^{4/2}CH_2$), 1.40 (m, 2 H, $SnCH_2$), 1.34 (m, 2 H, $SnCH_2$), 1.17 (m, 4 H, $SnCH_2$). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6): Isomer **5a**, δ 74.8 (P^1, d,

$^2J_{\mathrm{PFeP_{trans}}} = 57$ Hz, $J_{^{117/119}\mathrm{SnP}} = 52$ Hz), 62.7 (P^2, d, $^2J_{\mathrm{SncisFeP}} = 114$ Hz; $^3J_{\mathrm{SnCCP}} = 200$ Hz); isomer **5b**, δ 68.7 (P^3, d, $^2J_{\mathrm{PFeP_{cis}}} = 13$ Hz, $J_{\mathrm{SnP}} = 57$ Hz), 57.5 (P^4, d, $J_{\mathrm{SnP}} = 169$ Hz). Anal. Calc for $C_{66}H_{58}FeO_2P_2Sn_2$: C, 64.01; H, 4.72. Found: C, 65.88; H, 5.02.

(c) By Photochemical Reaction of 3a with $Ph_2PCH_2CH_2SnPh_3$. A 608 mg (0.87 mmol) amount of **3a** was dissolved in 50 mL of toluene and cooled to −10 °C. A solution of 487 mg (0.87 mmol) of $Ph_2PCH_2CH_2SnPh_3$ in 20 mL of toluene was then added. The solution was irradiated at −10 °C, during which it turned intensively yellow, and a gas was formed. The reaction was monitored by IR spectroscopy. After 11 h the CO bands of **3a** had nearly disappeared. Spectroscopic analysis (^{1}H NMR, ^{31}P{^{1}H} NMR) of the product after filtration and removal of the solvent showed that **5a,b** were formed in a 1:1 ratio.

Preparation of $(CO)_2(Ph)\overline{Fe(PPh_2CH_2CH_2Sn}Ph_2)PPh_2CH_2CH_2SnPh_2Pt(Ph)(PPh_3)_2$ (6). A solution of 169 mg (0.20 mmol) of $(Ph_3P)_2Pt(C_2H_4)$ was added in several portions at room temperature during 30 min to a solution of 204 mg (0.17 mmol) of **5** in 5 mL of toluene. While the color changed from yellow to red, an immediate formation of gas was observed. The solution was stirred in the dark for 4 days. After 4 h, 2 days, and 4 days the solution was analyzed by ^{31}P NMR spectroscopy. Two microspatulas of $(Ph_3P)_2Pt(C_2H_4)$ were added after 4 h and 2 d, because unreacted **5** was observed but no $(Ph_3P)_2Pt(C_2H_4)$. Complex **5** was completely consumed after 4 days. To remove excess $(Ph_3P)_2Pt(C_2H_4)$ (by thermal decomposition), the solution was heated to 40 °C for 2 h. Attempts to separate the product complexes by crystallization from toluene/petroleum ether or toluene/methylene chloride mixtures or by column chromatography failed.

6. IR (toluene, cm^{-1}): ν(CO) = 1904 (s). ^{31}P{^{1}H} NMR (161.9 MHz, d_8-toluene, numbering of the phosphorus atoms shown in eq 4): Isomer **6a**, δ 74.6 (P^1, d, $^2J_{\mathrm{PFeP_{trans}}} = 55$ Hz, $J_{\mathrm{SnP}} = 54$ Hz), 61.8 (P^2, dd, $^2J_{\mathrm{PFeP_{trans}}} = 55$ Hz, $^5J_{\mathrm{PCCSnPtP^5}} = 10$ Hz, $J_{\mathrm{SnP}} = 171$ Hz), 26.8 (P^5, dd, $^2J_{\mathrm{PPtP_{cis}}} = 14$ Hz, $^2J_{\mathrm{SntransPtP}} = 1753$ Hz, $^1J_{\mathrm{PtP}} = 2245$ Hz), 23.1 (P^6, d, $^2J_{\mathrm{SncisPtP}} = 171$ Hz, $^1J_{\mathrm{PtP}} = 2060$ Hz); isomer **6b**, δ 69.6 (P^3, d, $^2J_{\mathrm{PFeP_{cis}}} = 13$ Hz, $J_{\mathrm{SnP}} = 57$ Hz), 58.2 (P^4, dd, $^5J_{\mathrm{PCCSnPtP^7}} = 7$ Hz, $J_{\mathrm{SnP}} = 231$ Hz), 26.6 (P^7, dd, $^2J_{\mathrm{PPtP_{cis}}} = 14$ Hz, $^2J_{\mathrm{SntransPtP}} = 1753$ Hz, $^1J_{\mathrm{PtP}} = 2233$ Hz), 22.0 (P^8, d, $^2J_{\mathrm{SncisPtP}} = 171$ Hz, $^1J_{\mathrm{PtP}} = 2046$ Hz). ^{119}Sn NMR (149.2 MHz, C_6D_6): Isomer **6a**, δ 112.9 (dd, $^2J_{\mathrm{SnFeP^1}} = 53$ Hz, $^2J_{\mathrm{SnFeP^2}} = 107$ Hz); isomer **6b**, δ 131.4 (dd, $^2J_{\mathrm{SnFeP^3}} = 60$ Hz, $^2J_{\mathrm{SnFeP^4}} = 168$ Hz).

Preparation of $(CO)_3(H)[(MeO)_3Si]Fe(PPh_2CH_2CH_2SnPh_2)Pt(Ph)(PPh_3)_2$ (8). The solution of 316 mg (0.38 mmol) of $(Ph_3P)_2Pt(C_2H_4)$ in 10 mL of toluene was added to the solution of 310 mg (0.38 mmol) of **4b** in 10 mL of toluene at 0 °C. The solution was stirred for 1 h, during which a weak formation of gas was observed. The evolved CO was occasionally removed *in vacuo*. After filtration and removal of the solvent *in vacuo*, the yellow solid was washed three times with 5−10 mL of pentane each. The spectroscopic data showed that **7** was additionally formed. Complex **8** was only spectroscopically characterized. IR (toluene, cm^{-1}): ν(CO) = 2035 (w), 1970 (s) 1915 (s). ^{1}H NMR (C_6D_6): δ 7.6−6.5 (m, 40 H, Ph), 3.80 (s, 9 H, $SiOCH_3$), 2.39 (m, 2 H, PCH_2), 1.20 (m, 2 H, $SnCH_2$), −9.45 (d, 1 H, FeH, $^2J_{\mathrm{PFeH}} = 25.2$ Hz). ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6, numbering of the P atoms shown in eq 5: δ 56.0 (P^1, d, $^3J_{\mathrm{SnCCP}} = 68$ Hz, $^5J_{\mathrm{PCCSnPtP^2}} = 12$ Hz), 26.5 (P^2, t, $^2J_{\mathrm{PPtP_{cis}}}/^5J_{\mathrm{PCCSnPtP^1}} = 13$ Hz, $^2J_{\mathrm{PPtSn_{trans}}} = 1793$ Hz, $^1J_{\mathrm{PtP}} = 2311$ Hz), 21.5 (P^3, d, $^2J_{\mathrm{PPtP_{cis}}} = 14$ Hz, $^2J_{\mathrm{SncisPtP}} = 171$ Hz, $^1J_{\mathrm{PtP}} = 2050$ Hz).

Preparation of $Ph_2PCH_2SnPh_3$. A solution of 2.29 (11.1 mmol) of $LiCH_2PPh_2$ in 40 mL of THF was added dropwise to a solution of 4.50 g (11.7 mmol) of Ph_3SnCl in 40 mL of THF at −50 °C. The mixture was then warmed to room temperature and stirred for 24 h. The yellow oil obtained by removal of the solvent *in vacuo* was dissolved in 50 mL of toluene and filtered. After removal of the solvent *in vacuo*, the solid was 4-times washed with 20 mL of petroleum ether each. Yield: 3.8 g (62%). Mp: 85 °C, colorless solid. ^{1}H NMR ($CDCl_3$): δ 7.25 (m, 25 H, Ph), 2.01 (d, 2 H, CH_2, $^2J_{\mathrm{PCH}} = 2$ Hz, $^2J_{\mathrm{SnCH}} = 61$ Hz). ^{13}C NMR ($CDCl_3$): δ 134.6 (m, Ph), 8.7 (d, CH_2, $^1J_{\mathrm{PC}} = 34$ Hz). ^{31}P{^{1}H} NMR (161.9 MHz, d_6-acetone): δ −19.9 ($^2J_{\mathrm{SnCP}} = 109$ Hz). ^{119}Sn NMR (33.4 MHz, d_6-acetone): δ −109.2 (d). Anal. Calc for $C_{31}H_{27}PSn$: C, 67.79; H, 4.95; Sn, 21.6. Found: C, 67.81; H, 4.96; Sn, 20.8.

Preparation of $(CO)_4FePPh_2(CH_2)_nSnPh_3$ (1d, *n* = 1; 1e, *n* = 3). The preparation was performed analogous to that of **1a**, starting from 2.00 mmol of $Ph_2P(CH_2)_nSnPh_3$. In the reaction of $Ph_2PCH_2SnPh_3$, only the mono(phosphane) complex **1d** was formed, while in the reaction of $Ph_2P(CH_2)_3SnPh_3$ the bis(phosphane) complex **2e** (IR ν(CO) = 1885 cm^{-1}; ^{31}P NMR δ 73.0) and the oxidative addition product **3e** were obtained as minor byproducts. These compounds were separated by column chromatography as described for **1a**. The compounds **1d,e** were obtained as yellow solids by recrystallization from toluene/petroleum ether (5:1) at −25 °C.

1d. Yield: 889 mg (62%). Mp: 69 °C (dec). IR (toluene, cm^{-1}): ν(CO) = 2043 (w), 1972 (m) 1938 (vs). ^{1}H NMR (C_6D_6): δ 7.70−7.05 (m, 25 H, Ph), 2.63 (d, 2 H, CH_2, $^2J_{\mathrm{PCH}} = 11$ Hz, $^2J_{\mathrm{SnCH}} = 64$ Hz). ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): δ 64.6 ($^2J_{\mathrm{SnCP}} = 70$ Hz). ^{119}Sn NMR (33.4 MHz, C_6D_6): δ −112.6 (d). Anal. Calc for $C_{35}H_{27}FeO_4PSn$: C, 58.62; H, 3.80. Found: C, 58.44; H, 3.71.

1e. Yield: 628 mg (43%). Mp: 76 °C (dec). IR (toluene, cm^{-1}): ν(CO) = 2040 (s), 1974 (m) 1937 (vs). ^{1}H NMR (C_6D_6): δ 7.51−7.12 (m, 25 H, Ph), 2.40 (m, 2 H, PCH_2), 2.00 (m, 2 H, $CH_2CH_2CH_2$), 1.26 (m, 2 H, $SnCH_2$). ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): δ 64.0 ($^4J_{\mathrm{SnCCCP}} = 14$ Hz). ^{119}Sn NMR (33.4 MHz, C_6D_6): δ −104.0 (d). Anal. Calc for $C_{37}H_{31}FeO_4PSn$: C, 59.65; H, 4.19. Found: C, 59.12; H, 3.98.

Preparation of $(CO)_3(Ph)\overline{FePPh_2(CH_2)_nSn}Ph_2$ (3d, *n* = 1; 3e, *n* = 3). The preparation was performed analogous to that of **3a** starting from 500 mg (0.69 mmol) of **1d** and 318 mg (0.43 mmol) of **1e** (irradiation in toluene for 7 h and 3 h at −20 °C).

When the irradiation of **1d** was monitored by ^{31}P NMR spectroscopy, the dominating signal was that of **3d**. However, several byproducts were formed, with ^{31}P NMR signals between 73 and 10 ppm. The complete separation of the side products was possible neither by crystallization nor by column chromatography. The column chromatography (column 30 × 0.5 cm, 1:1 toluene/petroleum ether) at 0 °C resulted in five fractions. The second, yellow fraction only contained **1d** and **3d**. Crystallization at −25 °C from toluene/petroleum ether (5:1) only resulted in an enrichment of **3d** but not in a complete separation from **1d**.

Compound **3e** was obtained by crystallization from 15 mL of toluene/petroleum ether (10:1) at −25 °C as a beige solid.

3d. IR (toluene, cm^{-1}): ν(CO) = 2025 (w), 1985 (m, sh), 1965 (vs). ^{1}H NMR (C_6D_6): δ 7.74−6.73 (m, 25 H, Ph), 2.68 (d, 2 H, PCH_2, $^2J_{\mathrm{PCH}} = 12$ Hz, $^2J_{\mathrm{SnCH}} = 45$ Hz). ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): δ 7.1 ($J_{\mathrm{SnP}} = 9$ Hz).

3e. Yield: 207 mg (67%). Mp: 66 °C (dec). IR (toluene, cm^{-1}): ν(CO) = 2023 (m), 1979 (s, sh), 1955 (vs). ^{1}H NMR (C_6D_6): δ 7.58−6.81 (m, 25 H, Ph), 1.76 (m, 4 H, PCH_2CH_2), 1.19 (m, 2 H, $SnCH_2$). ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): δ 42.9 (s, $J_{\mathrm{SnP}} = 134$ Hz). ^{119}Sn NMR (33.4 MHz, C_6D_6): δ 12.9 (d, $J_{\mathrm{SnP}} = 137$ Hz). Anal. Calc for $C_{36}H_{31}FeO_3PSn$: C, 60.29; H, 4.36. Found: C, 58.68; H, 4.23.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft (Bonn) and the Fonds zur Förderung der wissenschaftlichen Forschung (Vienna).

OM960424V