consists of a butterfly arrangement of metal atoms or, alternatively, a square-pyramidal Ru_4P arrangement, the phosphorus acting as a basal skeletal atom. If we assume the latter structural description, the diyne is μ_3-η^2-bonded to Ru(1)Ru(3)P(1) in a fashion commonly encountered for alkynes at a trimetal center with a C(14)–C(15) bond length of 1.394 (5) Å. The longest Ru–Ru bond (Ru(3)–Ru(4) = 2.915 (1) Å) is the hinge to wingtip vector void of any bridging ligands. Of particular interest is the bonding mode of the acetylene. Atoms Ru(3) and P(1) are σ-bound to the acetylenic carbons C(14) and C(15) (Ru(3)–C(14) = 2.188 (4) Å, P(1)–C(15) = 1.827 (4) Å), and Ru(1) is involved in a π-interaction with the same fragment (Ru(1)–C(14) = 2.282 (4) Å, Ru(1)–C(15) = 2.309 (4) Å). While the overall Ru_4PC_2 skeleton of **3** is nido with Ru(1) capping a distorted-pentagonal Ru(2)–Ru(3)–P(1)–C(14)–C(15) face as observed in the trimetal cluster $Fe_3(CO)_9[P(p\text{-}CH_3O\text{-}C_6H_4)C(Ph)C(Ph)]$,[6a,f] the original square Ru(1)–Ru(3)–Ru(4)–P(1) face of **1** is retained, with the four-coordinate P(1) atom in **1** becoming five-coordinate in **3**. The diphenylbutadiyne in **3** is coordinated in a manner similar to that found in $Ru_5(CO)_{12}(\mu_3\text{-}\eta^2\text{-}PhC{\equiv}CC{\equiv}CPh)(\mu\text{-}PPh_2)$[19] with a pendant acetylenic fragment (C(16)–C(17) = 1.187 (6) Å). Ten of the twelve carbonyl ligands in **3** are terminally bound to the ruthenium atoms, the remaining two, C(12)O(12) and C(11)O(11), bridging Ru(2)–Ru(4) and Ru(1)–Ru(2), respectively (Ru(1)–C(11) = 1.997 (4) Å, Ru(2)–C(11) = 2.173 (5) Å and Ru(4)–Ru(12) = 2.144 (4) Å, Ru(2)–C(12) = 2.086 Å).

Addition of 2,4-hexadiyne to an *n*-hexane solution of either **3** (at 60 °C) or **4** (at 35 °C) results in the formation (60%) of the cluster $Ru_4(CO)_8(\mu_4\text{-}PPh)(PhC{\equiv}CC{\equiv}CPh)(MeC{\equiv}CC{\equiv}CMe)_2$ (**5**; Scheme I). Compound **5** exhibited IR and ^{31}P NMR spectroscopic properties similar to those of **2**.[17] The formation of **5** from **3** identifies the source of the η^2 interaction to Ru(14) as originating from the μ_3-η^2-bound acetylene in the intermediate. The two uncoordinated acetylenic fragments in **2** therefore result from the additional diyne units added to **3**, the original μ_3-η^2-Ru_2P bound diyne interacting with all four ruthenium atoms in **2**. Overall, the unsaturated hydrocarbon ligand donates 12 electrons and in terms of cluster electron counting compound **2** is a 64-electron cluster, consistent with its square-planar arrangement of ruthenium atoms. The formation of clusters **2** and **5** proceeds with remarkable regiospecificity, a single isomeric form being observed for both compounds. In each case there are four potential isomers, differing in their regiochemistry of addition during the formation of the metallacyclopentadiene and cyclobutadiene rings. We found no spectroscopic evidence supporting the formation of other possible isomers.

The generation of **5** from **3** or **4** and 2,4-hexadiyne suggests a strategy for the designed synthesis of unsymmetrically substituted hydrocarbon fragments via cooligomerization of variously functionalized diynes and monoynes. Moreover, in **3** both the pendant triple bond and the μ_3-η^2-alkyne are sites of unsaturation. Accordingly, reaction of **3** (1 equiv) with PhC≡CPh (2 equiv) affords $Ru_4(CO)_8(\mu_4\text{-}PPh)[\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}(Ph)CC(Ph)C(Ph)C\text{-}\eta^4\text{-}CC(Ph)C(Ph)C(Ph)]$ (**6**), which is spectroscopically similar to **2**[18] but lacks two uncoordinated –C≡CPh moieties.

These studies suggest that mixed transition-metal–main-group clusters may direct new and unusual oligomerization reactions. We are currently exploring the potential of ruthenium–phosphinidene clusters to effect novel coupling sequences.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support of this work and to the Government of Ontario for a scholarship (to J.F.C.).

Supplementary Material Available: For complexes **2** and **3**, details of the structure determination (Tables S1 and S8), atomic positional parameters (Tables S2 and S9), bond distances (Tables S3 and S10), bond angles (Tables S4 and S11), anisotropic thermal parameters (Tables S5 and S12), and hydrogen atom positions (Tables S6 and S13) (27 pages). Ordering information is given on any current masthead page. Observed and calculated structure factors are available from the authors upon request.

OM9202534

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Transition Metal Stannyl Complexes. 6.[1] Chelate-Assisted Oxidative Addition of Sn–C Bonds to an Iron Center

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Summary: The phenyl stannyl complex $(CO)_3(Ph)FePPh_2CH_2CH_2SnPh_2$ (**3**) is prepared by oxidative addition of a Sn–Ph group of $Ph_2PCH_2CH_2SnPh_3$ (**1**) by two different routes: reaction of $Fe_2(CO)_9$ with **1** via $(CO)_4FePPh_2CH_2CH_2SnPh_3$ or reaction of $(CO)_4Fe(H)SiMePh_2$ with **1** via $(CO)_3(H)(MePh_2Si)FePPh_2CH_2CH_2SnPh_3$.

While oxidative addition of E–H bonds (E = C, Si, Sn) to transition metal centers is well understood, there are hardly any systematic investigations on the oxidative addition (reductive elimination) of Si–Si, Sn–Sn, Si–C, or Sn–C bonds. A better understanding on how these bonds can be activated by transition metals is necessary to develop catalytic processes involving these bonds.

We recently reported that reaction of $(Ph_3P)_4Pd$ with $Ph_2PCH_2CH_2SnR_3$ (R = Ph, Me) readily gave *trans*-$Pd(PPh_2CH_2CH_2SnR_2)_2$ by oxidative addition of two Sn–R groups and elimination of R–R. Products corresponding to earlier steps of the reaction, $(Ph_3P)(Ph)PtPPh_2(CH_2)_nSnPh_2$ (*n* = 2, 3) and *cis,cis,cis*-$(Me)_2Pt(PPh_2CH_2CH_2SnMe_2)_2$, were obtained by reaction of

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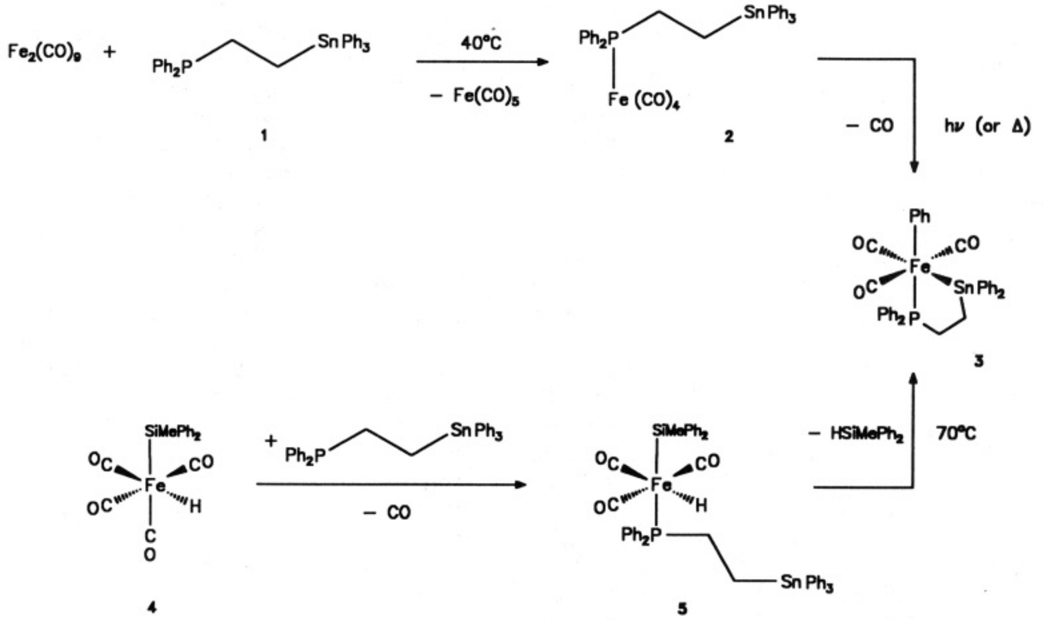
[1] Part 5: Schubert, U.; Schubert, J. *J. Organomet. Chem.*, in press.

Scheme I



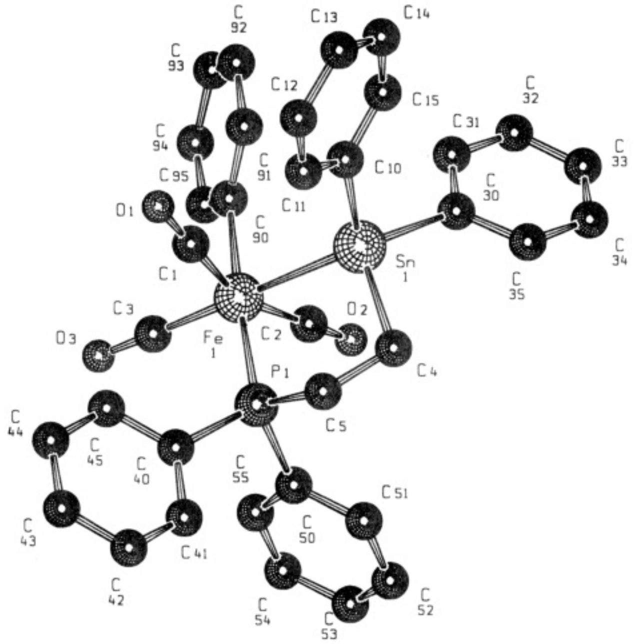


Figure 1. Molecular structure of $(CO)_3(Ph)FePPh_2CH_2CH_2SnPh_2$ (**3**). Bond lengths (pm): Fe–Sn = 259.9 (2), Fe–P = 226.5 (4), Fe–C(90) = 209 (1), Sn–C(4) = 216 (2), Sn–C(10) = 218 (1), Sn–C(30) = 216 (2), P–C(5) = 184 (1). Bond angles (deg): Sn–Fe–C(90) = 92.2 (4), Sn–Fe–P = 85.3 (1), Sn–Fe–C(1) = 83.0 (4), Sn–Fe–C(2) = 81.3 (4), Sn–Fe–C(3) = 178.1 (5), C(90)–Fe–P = 176.5 (3), C(90)–Fe–C(1) = 85.6 (5), C(90)–Fe–C(2) = 82.9 (5), C(90)–Fe–C(3) = 89.1 (6), C(1)–Fe–C(2) = 160.1 (5), C(1)–Fe–C(3) = 95.7 (6), C(2)–Fe–C(3) = 100.3 (5).

$(Ph_3P)_2Pt(C_2H_4)$ with $Ph_2P(CH_2)_nSnR_3$.[2]

Oxidative addition of Sn–C bonds to platinum centers is also possible if nonchelating stannanes are employed.[3] However, with other metal centers oxidative addition of Sn–C bonds is less straightforeward. In these cases the reaction might be facilitated by incorporation of the Sn–C bond into a chelate system. For example, thermal reaction of $Fe(CO)_5$ with Bu_2SnPh_2 or $Bu_2Sn(CH{=}CH_2)_2$ afforded $[(CO)_4Fe(\mu\text{-}SnBu_2)]_2$, whereas no isolable products were obtained with a variety of other tetraorganotin compounds.[4] On the other hand, $Fe(CO)_4$ generated from $Fe_2(CO)_9$ inserted into one Sn–C bond of dimethylstannacyclopentane to yield the metallacycle $(CO)_4FeCH_2CH_2CH_2SnMe_2$.[5]

We found that $Ph_2P(CH_2)_2SnPh_3$ (**1**) reacts with an equimolar amount of $Fe_2(CO)_9$ in toluene at 40 °C to give an approximate 1:1 mixture of $(CO)_4FePPh_2(CH_2)_2SnPh_3$ (**2**) and $(CO)_3Fe[PPh_2(CH_2)_2SnPh_3]_2$, which were separated by column chromatography.[6] UV irradiation of **2** resulted in the oxidative addition of one Sn–Ph bond to the iron center and formation of the stable phenyl stannyl complex **3** in high yield (Scheme I).[7] Inspection of the spectra of

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(6) A suspension of **1** (2.52 g, 4.47 mmol) and $Fe_2(CO)_9$ (0.88 g, 4.47 mmol) in 50 mL of toluene is stirred at 40 °C for 6 h, during which CO is evolved. Filtration and removal of all volatiles in vacuo affords a brown oil, which is redissolved in 20 mL of toluene. A solution of MeI (0.19 mL, 3.0 mmol) in 10 mL of toluene is added to convert unreacted **1** to its phosphonium salt. The mixture is refluxed for 1 h. Then all volatiles are removed in vacuo, and 10 mL of diethyl ether is added. After 10 min at room temperature the phosphonium salt is filtered off. The concentrated yellow solution is chromatographed on silica at 0 °C with 1:1 hexane/toluene. The first zone contains a mixture of **2** and **3**, the second zone **2**, and the third zone $(CO)_3Fe[PPh_2(CH_2)_2SnPh_3]_2$. Complex **2** is recrystallized from hexane (0.85 g, 26%): yellow powder, mp 74 °C dec. IR (toluene): $\nu_{CO} = 2043$ (s), 1971 (m), 1938 (vs) cm^{-1}. ^{31}P NMR (C_6D_6): δ 72.2 ($^3J_{^{119}SnCCP} = 253$ Hz). ^1H NMR (acetone-d_6): δ 7.61–7.35 (m, 25 H, Ph), 2.92 (m, 2 H, PCH_2), 1.72 (m, 2 H, $SnCH_2$). Anal. Calc for $C_{36}H_{29}FeO_4PSn$ (**1**): C, 59.14; H, 4.00. Found: C, 59.21; H, 4.10. $(CO)_3Fe[PPh_2(CH_2)_2SnPh_3]_2$ is recrystallized from toluene/hexane (1:4) (1.17 g, 21%): pale yellow powder, mp 114 °C dec. IR (toluene): $\nu_{CO} =$ 1884 (vs) cm^{-1}. ^{31}P NMR (C_6D_6): δ 80.5 ($^2J_{PFeP} = 31$ Hz). ^1H NMR (C_6D_6): δ 7.75–6.90 (m, 50 H, Ph), 3.15 (m, 4 H, PCH_2), 2.10 (m, 4 H, $SnCH_2$). Anal. Calc for $C_{67}H_{58}FeO_3P_2Sn_2$: C, 63.55; H, 4.62. Found: C, 63.31; H, 4.80.

(7) A solution of **2** (0.64 g, 0.88 mmol) in 20 mL of toluene is irradiated with a high-pressure mercury lamp at −20 °C for 2 h. During the reaction CO is evolved and the yellow solution darkens. The solvent is removed in vacuo, and the residue is redissolved in 5 mL of toluene/hexane (1:2). At −25 °C **3** precipitates as a yellow powder, which is washed three times with 2 mL of hexane each: yield 0.49 g (79%); mp 85 °C dec. IR (toluene): $\nu_{CO} = 2028$ (w), 1983 (sh), 1964 (s) cm^{-1}. ^{31}P NMR (C_6D_6): δ 78.7 ($J_{SnP} = 75$ Hz). ^{119}Sn NMR (C_6D_6): δ 137.5 ($J_{SnP} = 75$ Hz). ^1H NMR (C_6D_6): δ 7.59–7.04 (m, 20 H, Ph), 6.81–6.79 (m, 5 H, Fe–*Ph*), 2.75 (m, 2 H, PCH_2), 1.59 (m, 2 H, $SnCH_2$). ^{13}C NMR (C_6D_6): δ 213.1 (d, 2 CO_{ax}, $^2J_{PFeC} = 14.5$ Hz), 212.7 (d, CO_{equ}, $^2J_{PFeC} = 11.8$ 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). Anal. Calc for $C_{35}H_{29}FeO_3PSn$: C, 59.79; H, 4.16. Found: C, 59.52; H, 4.45.

the reaction mixture of 1 and $Fe_2(CO)_9$ showed that small quantities of 3 were already formed during the preparation of 2. Irradiation is therefore only necessary to accelerate the overall reaction.

The oxidative addition product 3 was obtained in higher yield (71%) by a modification of the preparation procedure, by which workup after the first step is unnecessary: To avoid the presence of unreacted 1, which has to be separated, a 2-fold excess of $Fe_2(CO)_9$ was used. A toluene solution of 1 and $Fe_2(CO)_9$ was heated to 60 °C for 15 min and then irradiated at −10 °C for 24 h without isolation of 2. Although $(CO)_3Fe[PPh_2(CH_2)_2SnPh_3]_2$ was also present after the thermal reaction step, only 3 (and some unreacted 2) was isolated after irradiation. Obviously $(CO)_3Fe[PPh_2(CH_2)_2SnPh_3]_2$ was also converted to 3 by loss of a phosphine ligand.

The ν_{CO} pattern in the IR spectra of 3 is consistent with a meridional $Fe(CO)_3$ moiety. In the ^{1}H-NMR spectrum one phenyl group shows a high-field shift relative to 2. The ^{119}Sn NMR signal is shifted from 4.0 ppm in 1 to 137.5 ppm in 3, and the SnP coupling constant decreases from 172 Hz in 1 to 75 Hz in 3 (due to the mixing of $^2J_{SnFeP}$ and $^3J_{SnCCP}$). In the ^{13}C NMR spectrum two signals are observed for the chemically nonequivalent CO ligands; therefore, the molecule is rigid at room temperature. While the spectra clearly prove the occurrence of a Fe–Sn bond and a Fe–Ph group in 3, the spectra give no unequivocal information on the stereochemical outcome of the oxidative addition reaction. The X-ray structure analysis of 3[8] (Figure 1) shows that the phenyl group is cis to the tin atom and therefore trans to the phosphorus atom. In toluene solution there is no isomerization up to 85 °C according to high-temperature ^{31}P NMR spectra. The octahedral coordination of the iron atom is slightly distorted, the biggest deviation being the bending of two CO ligands toward the tin atom (C(1)–Fe–C(2) = 160.1 (5)°, Sn–Fe–C(1) = 83.0 (4)°, Sn–Fe–C(2) = 81.3 (4)°).

Octahedral hydrido stannyl complexes of iron, $(CO)_2(dppe)Fe(H)SnR_3$ or *mer*-$(CO)_3(PPh_3)Fe(H)SnR_3$ (R = Me, Ph), were previously prepared by us by reacting the silyl complexes $(CO)_3(PPh_3)Fe(H)SiMe_3$ or $(CO)_2(dppe)Fe(H)SiMe_3$ with $HSnR_3$.[9] The driving force for this reaction is both the higher stability of Fe–Sn bonds and the volatility of $HSiMe_3$, which prevents readdition of the silane. We used a similar approach to develop an alternative method for the preparation of 3 (Scheme I). The hydrido silyl complex $(CO)_4Fe(H)SiMePh_2$ (4) in toluene was reacted with 1 at room temperature (18 h) and then at 70 °C (4 h). Complex 3 was obtained by this procedure 3 in 83% yield. As an intermediate, the phosphine-substituted hydrido silyl complex 5 was spectroscopically identified. When the reaction was carried out at −50 to −30 °C, complex 5 was the sole product,[10] which was then converted to 3 at higher temperatures by silane elimination. The alternate mechanistic possibility, replacement of H–$SiMePh_2$ by R_3Sn–Ph and subsequent addition of the phosphorus atom to the metal, was not observed.

Although complexes of the type $(CO)_3(PR'_3)Fe(H)SiR_3$ were prepared by thermal CO/PR'_3 exchange,[11] it is rather surprising that reaction of 4 with 1 proceeds at such low temperatures. Formation of 3 from 5 shows that addition of the Sn–C bond is favored over the readdition of $HSiMePh_2$. This is probably due to both the chelate effect and the higher strength of the Fe–Sn compared with Fe–Si bond.

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Supplementary Material Available: Tables of the positional parameters, anisotropic thermal parameters, and all bond distances and angles for 3 (11 pages). Ordering information is given on any current masthead page.

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(8) Crystals were obtained from toluene/hexane (1:1). Crystallographic data for 3: orthorhombic, space group $P2_12_12_1$; a = 1353.8 (3), b = 1391.7 (5), c = 1653.7 (4) pm; V = 3116 (3) pm^3; Z = 4; d_{calcd} = 1.49 g cm^{-3}. A total of 3818 reflections were measured at 293 K ($2° \le 2\theta \le 54°$, Mo Kα radiation, λ = 71.069 pm) on an Enraf-Nonius CAD4 diffractometer. The structure was solved by direct methods (SHELXS) using 2619 decay and absorption corrected reflections ($I \ge \sigma(I)$); R = 0.061, R_w = 0.063.

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(10) Spectroscopic data for 5 (−40 °C): ^{31}P NMR ($C_6D_5CD_3$) δ 59.1 ($^3J_{SnP}$ = 251 Hz); ^{1}H NMR ($C_6D_5CD_3$) δ 2.71 (m, 2 H, PCH_2), 1.55 (m, 2 H, SnCH_2), 1.24 (s, 3 H, Si*Me*), −9.04 (d, 1 H, Fe*H*, $^2J_{PFeH}$ = 27.7 Hz).

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β-Hydrogen Abstraction by Thiyl Radicals

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Summary: **Alkanethiyl radicals, typified by $C_2H_5S^\bullet$, react rapidly in aqueous solution with $C_2H_5ML(H_2O)^{2+}$, where ML = Co([14]aneN$_4$), k = 1.15 × 10^8 L mol^{-1} s^{-1}, and Cr([15]aneN$_4$), k = 5.9 × 10^7 L mol^{-1} s^{-1}. The use of $C_2D_5ML(H_2O)^{2+}$ leads to k_H/k_D = 2.6 (Co) and 3.3 (Cr), consistent with β-hydrogen abstraction and formation of ethylene. The methylcobalt complex forms $C_2H_5SCH_3$, with k = 2.4 × 10^7 L mol^{-1} s^{-1} and k_H/k_D ~ 1.**

Since C–H bonds are in general stronger than S–H bonds, the position of equilibrium lies to the left in reactions such as

$$RS^\bullet + R'H \rightleftarrows RSH + R'^\bullet \qquad (1)$$

Indeed, alkanethiyl radicals can be prepared by the reverse of (1), as we have done in this study. Alkyl radicals were generated by photohomolysis[1] of $R'Co([14]aneN_4)H_2O^{2+}$ (R′ = CH_3, C_2H_5) in aqueous solution in the presence of a thiol such as cysteine or ethanethiol, thus yielding $RS^\bullet$.[2]

What is new and unexpected, however, is the observation of a reaction between $C_2H_5S^\bullet$ and organometallic com-

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