neous decolorization of the yellow solution and disappearance of the ^{29}Si NMR signal at +76.68 ppm, which was replaced by a signal at −7.42 ppm. The resonance at −7.05 ppm remained unchanged throughout. Ethoxysilane **5**, which has a ^{29}Si NMR signal at −7.42 ppm, was isolated from the reaction mixture by preparative TLC (Scheme I).

These results appear to indicate photochemical formation of the yellow silene 1,1-dimesityl-2,2-diphenylsilene (**7**), which is thermally stable at room temperature and has $\delta(^{29}Si) = +76.68$ ppm. The yield of **7** was estimated as 33% from the mesityl methyl proton signals in the ^1H NMR spectrum, but isolation of **7** has so far been unsuccessful. One of the other products of the photolysis is believed to be a derivative of dimesitylsilanethione (**8**). In the presence of ethanol, **8** was trapped to produce **6**. When no trapping agent is present, however, unstable **8** may dimerize or trimerize to give the compound with $\delta = -7.05$ ppm.

As a proof of structure, **5** was synthesized independently by reaction of sodium ethoxide with chlorodimesityl(diphenylmethyl)silane; the latter compound was prepared from dichlorodimesitylsilane and (diphenylmethyl)lithium.[11]

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Supplementary Material Available: Tables of crystallographic data, atomic coordinates and anisotropic thermal parameters, and bond lengths and angles and diagrams for **3** (13 pages); a listing of observed and calculated structure factor amplitudes for **3** (24 pages). Ordering information is given on any current masthead page.

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[11] Experimental procedure for **5**: Dichlorodimesitylsilane (1.70 g, 5.03 mmol) was reacted with (diphenylmethyl)lithium tetramethylethylenediamine complex (1.46 g, 5.03 mmol) in benzene at room temperature for 20 h. The formation of chlorodimesityl(diphenylmethyl)silane was followed by ^1H NMR spectroscopy, and the pure sample was separated from the reaction mixture by preparative GC. ^1H NMR (C_6D_6, δ): 2.03 (s, 6 H, p-CH_3), 2.21 (s, 12 H, o-CH_3), 4.46 (s, 1 H, Ph_2CH), 6.61 (s, 4 H, Mes H), 6.9–7.1 (m, 6 H, Ph H), 7.3–7.4 (m, 4 H, Ph H). Exact mass (m/e): calcd for $^{12}C_{31}{}^1H_{33}{}^{28}Si$ (product − Cl) 433.2351, found 433.2322. The benzene solvent in the reaction mixture was replaced by toluene, and an ethanol solution of sodium ethoxide (1.02 g, 15.0 mmol) was added to the mixture, which was then heated to 110 °C for 60 h. Compound **5** was isolated in 34% yield by column chromatography (SiO_2; hexane–ethyl acetate).

Synthesis and Structure of Bimetallic Allyl, Alkoxysilyl Complexes $[Fe\{Si(OMe)_3\}(CO)_3(\mu\text{-dppm})M(\eta^3\text{-}2\text{-}RC_3H_4)]$ (M = Pd, Pt; R = H, Me) and of $[Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(CO)_3(\mu\text{-dppm})Pd(SnPh_3)]$, a Sn–Pd–Fe–Si Chain Complex with a μ_2-η^2-SiO Bridge

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Summary: The bimetallic allyl, alkoxysilyl complexes $[Fe\{Si(OMe)_3\}(CO)_3(\mu\text{-dppm})M(\eta^3\text{-}2\text{-}RC_3H_4)]$ (M = Pd, R = Me, **2a**; M = Pd, R = H, **2b**; M = Pt, R = H, **3**) have been prepared from the iron metalate $[Fe\{Si(OMe)_3\}(CO)_3(\eta^1\text{-dppm})]^-$, in which the dppm ligand helps in assembling and stabilizing the dinuclear unit. The crystal structure of **2a** was determined by X-ray diffraction (Fe–Pd = 269.94 (7) pm). Reaction of **2a** with $HSnPh_3$ afforded $[Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(CO)_3(\mu\text{-dppm})Pd(SnPh_3)]$ (**4a**), the first Sn–Pd–Fe–Si chain complex, in which the presence of an unusual μ_2-η^2-SiO bridge between the Fe and Pd atoms was established by X-ray diffraction (Fe–Pd = 266.55 (5), Sn–Pd = 259.50 (4), Pd–O(4) = 216.5 (2) pm). The lability of the O→Pd bond accounts for the dynamic behavior of the alkoxysilyl ligand, evidenced by variable-temperature ^1H NMR spectroscopy, which renders the methoxy protons equivalent above 313 K ($\Delta G^{\ddagger} \approx 65 \pm 2$ kJ/mol).

Despite numerous studies on the chemistry of silicon-containing transition-metal compounds,[1] there is only one example in the literature where μ_2-η^2-SiO (side-on) coordination for an alkoxysilyl ligand has been established by an X-ray diffraction study.[2] The resulting PdFeSiO four-membered ring in $[Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(CO)_3(\mu\text{-dppm})PdCl]$ (dppm = $Ph_2PCH_2PPh_2$) was found to be kinetically labile (^1H NMR evidence) but thermodynamically stable, as typical donor ligands such as CO or PPh_3 would not displace the O→Pd bond under mild conditions. The novel features associated with this μ_2-η^2-SiO bonding, as well as its possible relevance to the stabilization of (i) coordinatively unsaturated, reactive metal complexes or surface species, (ii) silylene complexes,[3] and (iii) metal

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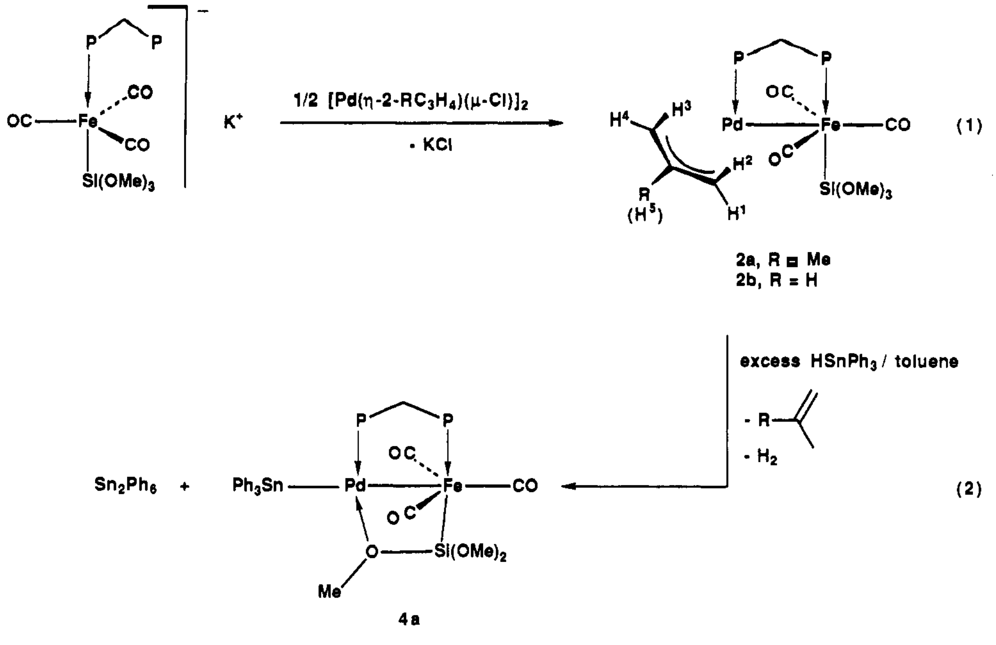
Scheme I



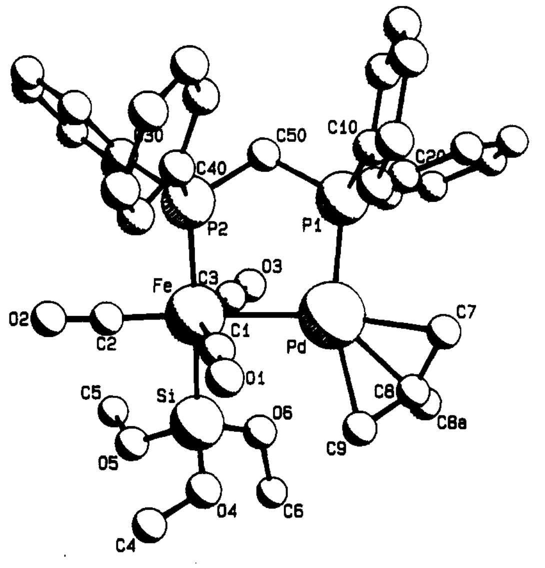


Figure 1. Structure of **2a**. Selected bond lengths (pm) and angles (deg) are as follows: Pd–Fe, 269.94 (7); Fe–P(2), 222.5 (1); Fe–Si, 230.3 (1); Pd–P (1), 225.1 (1); Pd–C(7), 217.1 (5); Pd–C(8), 216.1 (4); Pd–C(9), 223.2 (5); Pd–Fe–Si, 93.38 (4); Pd–Fe–P(2), 90.58 (3); P(2)–Fe–Si, 173.50 (6); Pd–Fe–C(1), 64.7 (1); Pd–Fe–C(3), 78.0 (2); Fe–Pd–P(1), 94.81 (3); Fe–Si–O(4), 117.5 (2); Fe–Si–O(5), 115.8 (2); Fe–Si–O(6), 111.5 (1).

colloids that catalyze hydrosilylation reactions,[4] prompted further studies. The dinuclear unit required for the occurrence of this unprecedented μ_2-η^2-SiO bonding mode may be conveniently generated and stabilized through the assistance of the dppm ligand. We now report the synthesis of the bimetallic allyl complexes [Fe{Si(OMe)$_3$}(CO)$_3$(μ-dppm)Pd(η^3-2-RC$_3$H$_4$)] (R = Me, **2a**; R = H, **2b**) and of [Fe{μ-Si(OMe)$_2$(OMe)}(CO)$_3$(μ-dppm)Pd(SnR'$_3$)] (R' = Ph, **4a**; R' = Bu, **4b**), the first Sn–Pd–Fe–Si chain complexes, in which the presence of a μ_2-η^2-SiO bridge was

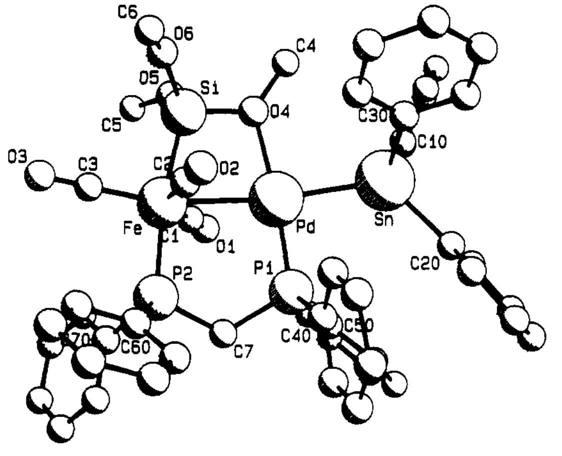
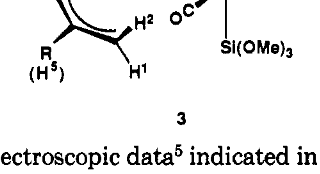


Figure 2. Structure of **4a**. Selected bond lengths (pm) and angles (deg) are as follows: Pd–Fe, 266.55 (5); Fe–P(2), 220.7 (1); Fe–Si, 225.8 (1); Pd–P(1), 218.78 (9); Pd–Sn, 259.50 (4); Pd–O(4), 216.5 (2); Si–O(4), 166.3 (3); Si–O(5), 160.0 (3); Si–O(6), 158.1 (3); Sn–Pd–Fe, 169.34 (2); Sn–Pd–O(4), 94.91 (6); Sn–Pd–P(1), 90.20 (3); P(1)–Pd–O(4), 174.79 (7); Pd–Fe–Si, 75.00 (3); Pd–Fe–P(2), 95.82 (3); P(2)–Fe–Si, 170.75 (6); Pd–Fe–C(1), 66.3 (1); Pd–Fe–C(2), 74.1 (1); Fe–Si–O(4), 102.89 (9); Si–O(4)–Pd, 103.2 (1).

established by an X-ray diffraction study on **4a**. All reactions were carried out under purified nitrogen, but the products are air-stable in the solid state.

Treatment of [Pd(η^3-2-MeC$_3$H$_4$)(μ-Cl)]$_2$ with 2 equiv of K[Fe{Si(OMe)$_3$}(CO)$_3$(η^1-dppm)] in tetrahydrofuran (THF) afforded **2a** in 84% yield (eq 1 Scheme I). The chloride bridges of the tetrameric compound [PtCl(η^3-C$_3$H$_5$)]$_4$ were cleaved by the iron metalate in an analogous manner, yielding [Fe{Si(OMe)$_3$}(CO)$_3$(μ-dppm)Pt(η^3-C$_3$H$_5$)] (**3**) in



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71% yield. Spectroscopic data[5] indicated in both cases the

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formation of a dppm bridge and the equivalence of all methoxy protons. This is reflected in the solid-state structure of **2a** (Figure 1).[8] It shows that the coordination geometry at the iron atom is more similar to the trigonal-bipyramidal geometry of the precursor than to the octahedral geometry found in the related complexes *mer*-$[Fe(SiR_3)(CO)_3(PR'_3)ML_n]$, with nonbridging ligands.[9] The geometry at the palladium atom is similar to that observed in other Pd–allyl complexes[10a] such as $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)(SnCl_3)L]$ (L = CO,[10b] $PhCH{=}CH_2$[10c]). Only the angle Fe–Pd–P is somewhat smaller, owing to the dppm bridge. The different nature of the trans ligand induces a longer Fe–Pd distance in **2a** (269.9 (1) pm) than in related **1** (258.2 (1) pm).[2] The dihedral angle between the C(7)–C(8)–C(9) plane of the allyl ligand (C(8a) deviates from this plane by 0.41 (1) Å) and the Fe–Pd–P(1) plane is 114.4 (8)°, whereas that between the Pd–C(7)–C(9) and Fe–Pd–P(1) planes is 5.9°. Assignments of the ^1H NMR resonances[5] result from comparison between the spectra of **2a** and **2b** and selective decoupling experiments and are consistent with literature data.[11] Variable-temperature ^1H NMR spectroscopy indicates a dynamic behavior for the allyl ligand, which results in protons H^3 and H^4 appearing as a broad singlet in **2b** or doublet in **2a** (owing to coupling with H^5) above the coalescence temperature (sequence in toluene (approximate temperatures): **2a** (283 K) < **2b** (298 K) < **3** (coalescence not yet reached at 335 K)). The protons H^1 and H^2 remained almost unaffected in the temperature range investigated (273–333 K, limited by product stability). An $\eta^3 \rightarrow \eta^1$ (through C(7)) $\rightarrow \eta^3$ rearrangement exchanging the protons H^3 and H^4 is most likely taking place (note that it might be assisted through stabilization of a 14e Pd center by a MeO→Pd interaction; see below). This would also be consistent with Pd–C(9) being longer than Pd–C(7).

Whereas **2b** did not react even with an excess of $HSiMePh_2$ or of the more reactive H_2SiPh_2 over a prolonged period of time, it reacted with excess $HSnPh_3$ under mild conditions (toluene, 20 °C, 1 h) to give **4a** in good yields and Sn_2Ph_6 (eq 2; Scheme I).[12] This reaction represents an extension to tin[13] of the propene elimination method known for $HSiR_3$.[14] With $HSnBu_3$, only ca. 50% of **2b** was converted to **4b** despite the use of a 10-fold excess of reagent. Addition of several portions resulted first in an immediate color change from yellow to red, accompanied

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(5) (a) Synthesis of $[Fe\{Si(OMe)_3\}(CO)_3(\mu\text{-dppm})Pd(\eta^3\text{-}2\text{-}MeC_3H_4)$ (**2a**): A solution of $K[Fe\{Si(OMe)_3\}(CO)_3(\eta^1\text{-dppm})]$ ([K]1;[2] 0.685 g, 1 mmol) in THF (25 mL) was added at −25 °C to a slurry of $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)(\mu\text{-}Cl)]_2$[6] (0.197 g, 0.5 mmol) in THF (5 mL). After completion of the reaction (10 min, IR monitoring of the disappearance of the ν(CO) bands at 1928 w, 1847 vs, 1826 s, sh cm^{-1} due to [K]1), the yellow solution was filtered and evaporated to dryness. The residue was extracted with ca. 35 mL of warm Et_2O. After addition of 10 mL of hexane to the filtered solution and slow concentration in vacuo, yellow **2a** precipitated. Yellow crystals slowly formed at −15 °C, which were collected by filtration and dried in vacuo. Concentration of the mother liquor afforded a further crop of the air-stable product: overall isolated yield 0.730 g, 84%; mp 162 °C dec. Anal. Calc for $C_{35}H_{38}FeO_6P_2PdSi$ (M_r = 807.02): C, 52.09; H, 4.75. Found: C, 51.84; H, 4.75. IR (THF, ν(CO)): 1956 m, 1887 s, 1860 vs cm^{-1}. ^1H NMR (200 MHz, C_6D_6, 333 K): δ 1.71 (s, 3 H, allyl–CH_3), 2.89 (s, br, 2 H, allyl $H^{3,4}$), 3.47 (t, 2 H, PCH_2P, ^2J(P–H) = 10.3 Hz), 3.86 (d, 1 H, ^3J(P–H) = 11.4 Hz, allyl H^2), 3.96 (s, 9 H, OCH_3), 5.39 (d, 1 H, ^3J(P–H) = 7.9 Hz, allyl H^1), 6.95–7.50 (m, 20 H, C_6H_5). ^1H NMR (200 MHz, $CDCl_3$, 253 K): δ 1.82 (s, 3 H, allyl–CH_3), 2.52 (s, 1 H, allyl H^3), 3.45–3.67 (13 H, OCH_3 + PCH_2P, +2 allyl H), 4.82 (d, 1 H, ^3J(P–H) = 6.4 Hz, allyl H^1), 7.03–7.57 (m, 20 H, C_6H_5) (coalescence of the signals for $H^{3,4}$ occurs around 313 K). $^{31}P\{^1H\}$ NMR (81.02 MHz, acetone-d_6/CH_2Cl_2, referenced to external H_3PO_4): δ 29.7 (d, P(Pd), ^{2+3}J(P–P) = 110 Hz), 67.7 (d, P(Fe), ^{2+3}J(P–P) = 110 Hz). $^{29}Si\{^1H\}$ NMR (39.76 MHz, C_6D_6, 293 K, referenced to external $SiMe_4$): δ 12.9 (d, ^2J(P–Si) = 33.5 Hz). (b) Synthesis of $[Fe\{Si(OMe)_3\}(CO)_3(\mu\text{-dppm})Pd(\eta^3\text{-}C_3H_5)$ (**2b**): This complex was prepared in a manner similar to **2a** by using $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$:[6] yield 0.651 g, 82%; mp 156 °C, dec. Anal. Calcd for $C_{34}H_{36}FeO_6P_2PdSi$ (M_r = 792.96): C, 51.50; H, 4.58. Found: C, 51.99; H, 4.53. IR (THF, ν(CO)): 1956 s, 1889 m, 1861 vs cm^{-1}. ^1H NMR (200 MHz, C_6D_6, 323 K): δ 2.93 (d, 2 H, ^3J(H–H^5) = 9.4 Hz, allyl $H^{3,4}$), 3.43 (t, 2 H, PCH_2P, ^2J(P–H) = 10.1 Hz), 3.82 (t, br, 1 H, ^3J(H–H^5) ≈ ^3J(P–H) = 12.9 Hz, allyl H^2), 3.98 (s, 9 H, OCH_3), 5.15 (m, 1 H, allyl H^5), 5.51 (t, 1 H, ^3J(H–H^5) ≈ ^3J(P–H) = 7.6 Hz, allyl H^1), 6.95–7.71 (m, 20 H, C_6H_5). ^1H NMR (200 MHz, $CDCl_3$, 323 K): 3.25 (d, 2 H, ^3J(H–H^5) = 9.2 Hz, allyl $H^{3,4}$), 3.43–3.77 (overlapping signals, 12 H, OCH_3, PCH_2P, allyl H^4), 5.13 (t, 1 H, ^3J(H–H^5) ≈ ^3J(P–H) = 7.6 Hz, allyl H^1), 5.39 (m, 1 H, allyl H^2), 7.17–7.45 (m, 20 H, C_6H_5). $^{31}P\{^1H\}$ NMR (81.02 MHz, acetone-d_6/CH_2Cl_2, referenced to external H_3PO_4): δ 27.7 (d, P(Pd), ^{2+3}J(P–P) = 106 Hz), 67.1 (d, P(Fe), ^{2+3}J(P–P) = 106 Hz). (c) Synthesis of $[Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(CO)_3(\mu\text{-dppm})Pt(\eta^3\text{-}C_3H_5)$ (**3**): This complex was prepared similarly to **2a** by using $[Pt(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_4$.[7] Because of its lower solubility, the residue was extracted with CH_2Cl_2. Layering the concentrated solution with hexane afforded long yellow needles of **3**: yield 0.621 g, 71%. Anal. Calcd for $C_{34}H_{36}FeO_6P_2PtSi$ (M_r = 881.61): C, 46.32; H, 4.12. Found: C, 46.28; H, 4.11. IR (THF, ν(CO)): 1963 s, 1898 s, 1868 s cm^{-1}. ^1H NMR (200 MHz, C_6D_6, 333 K): δ 2.55 (m, br, 2 H, allyl), 3.21 (t, br, 1 H, ^3J(H–H^5) ≈ ^3J(P–H) = 11.5 Hz, allyl), 3.60 (t, 2 H, PCH_2P, ^2J(P–H) = 10.1 Hz, ^3J(Pt–H) = 48.9 Hz), 3.91 (s, 9 H, OCH_3), 4.55 (m, 1 H, allyl H^5), 5.18 (t, br, 1 H, ^3J(H–H^5) ≈ ^3J(P–H) = 5.6 Hz, allyl), 6.95–7.70 (m, 20 H, C_6H_5). $^{31}P\{^1H\}$ NMR (81.02 MHz, acetone-d_6/CH_2Cl_2): δ 22.8 (d, P(Pt), ^{2+3}J(P–P) = 101 Hz, ^1J(Pt–P) = 4146 Hz), 68.2 (d, P(Fe), ^{2+3}J(P–P) = 101 Hz, ^2J(Pt–P) = 99 Hz).

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(8) Crystal data for **2a**: space group $P2_1/c$, a = 1154 (2) pm, b = 1681 (2) pm, c = 1855 (2) pm, β = 92.39 (6)°, V = 3595 × 10^6 pm^3, Z = 4, D_{calc} = 1.49 g cm^{-3}. An empirical absorption correction was applied to 5620 unique reflections. The structure was solved by the Patterson method and refined (4504 reflections, $F_o \geq 2\sigma(F_o)$) to R = 0.057 and R_w = 0.058. Crystal data for **4a**·0.7(toluene): space group $P2_1/c$, a = 1529 (2) pm, b = 2843 (6) pm, c = 1385 (3) pm, β = 116.19 (7)°, V = 5401 × 10^6 pm^3, Z = 4, D_{calc} = 1.43 g cm^{-3}. An empirical absorption correction was applied to 8676 unique reflections. The structure was solved by the Patterson method and refined (6576 reflections, $F_o \geq 2\sigma(F_o)$) to R = 0.038 and R_w = 0.040. All non-hydrogen atoms were treated anisotropically.

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(12) Synthesis of $[Fe\{Si(OMe)_2(OMe)\}(CO)_3(\mu\text{-dppm})Pd(SnPh_3)$ (**4a**): To a stirred solution of **2a** (0.807 g, 1 mmol) in toluene (20 mL) was added $HSnPh_3$ (0.877 g, 2.5 mmol) in several portions within 1 h. An immediate color change from yellow to red occurred, and each addition was accomplished by vigorous gas evolution. Layering the concentrated solution with hexane afforded white crystals of Sn_2Ph_6 as a minor product (ca. 10%, satisfactory elemental analysis) and deep red, air-stable crystals of **4**: yield 0.804 g, 73%; mp 162 °C dec. Anal. Calcd for $C_{49}H_{46}FeO_6P_2PdSiSn$ (M_r = 1101.91): C, 53.41; H, 4.21; Si, 2.55; Pd, 9.66. Found: C, 52.28; H, 4.07; Si, 2.73; Pd, 9.30. IR (THF, ν(CO)): 1959 vs, 1900 m, 1872 s cm^{-1}. ^1H NMR (200 MHz, toluene-d_8, 243 K): δ 3.42 (t, 2 H, PCH_2P, ^2J(P–H) = 10.1 Hz), 3.57 (s, 3 H, PdOMe), 3.93 (s, 6 H, $SiOCH_3$), 6.65–7.71 (m, 35 H, C_6H_5). $^{31}P\{^1H\}$ NMR (81.02 MHz, acetone-d_6/CH_2Cl_2): δ 36.1 (d, P(Pd), ^{2+3}J(P–P) = 48 Hz, ^2J(Sn–P) = 34 Hz), 57.9 (d, P(Fe), ^{2+3}J(P–P) = 48 Hz, ^3J(Sn–P) = 48 Hz; the J(Sn–P) coupling constants represent average values for coupling with $^{117/119}Sn$ (not resolved)). $^{119}Sn\{^1H\}$ NMR (89.55 MHz, C_6D_6, 298 K, referenced to external $SnMe_4$): δ 295.7 (dd, ^2J(^{119}Sn–P) = 39 Hz, ^3J(^{119}Sn–P) = 50 Hz). $^{29}Si\{^1H\}$ NMR (59.60 MHz, CH_2Cl_2/C_6D_6, 300 K, referenced to external $SiMe_4$): δ 15.1 (dd, ^2J(P–Si) = 30.4 Hz, ^3J(P–Si) = 5.6 Hz). Selected data for $[Fe\{Si(OMe)_2(OMe)\}(CO)_3(\mu\text{-dppm})Pd(SnBu_3)$ (**4b**): $^{31}P\{^1H\}$ NMR (81.02 MHz, acetone-d_6/THF) δ 37.3 (d, P(Pd), ^{2+3}J(P–P) = 49 Hz), 60.8 (d, P(Fe), ^{2+3}J(P–P) = 49 Hz).

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each time by vigorous gas evolution. $^{31}P\{^1H\}$ NMR monitoring of the reaction mixture only showed the resonances due to **2b** and **4b**. Therefore, the bimetallic allyl precursor appears to catalyze the formation of distannanes. The structure of **4a** was definitely established by X-ray diffraction (Figure 2).[8] The Fe–Pd–Sn chain makes an angle of 169.34 (2)°, and the Fe–Pd bond is bridged by an unusual μ_2-η^2-alkoxysilyl ligand. The Pd–O bond distance of 216.5 (2) pm, similar to other $Pd^{II} \leftarrow O$ dative bonds,[15] is slightly longer than in in $[\overline{Fe\{\mu\text{-}Si(OMe)_2(\underline{OMe})\}(CO)_3(\mu\text{-dppm})Pd}Cl]$ (210.0 (4) pm), perhaps due to the presence of the bulky $-SnPh_3$ group cis to that bond. The Si–O(4) bond (166.3 (3) pm) is significantly longer than the other two Si–O bonds in this molecule (160.0 (3) and 158.1 (3) pm), consistent with a bimetallic "activation" of this bond. The Pd–Sn distance is in the expected range,[13] and the Fe–Pd distance is shorter than in $[\overline{Fe\{\mu\text{-}Si(OMe)_2(\underline{OMe})\}(CO)_3(\mu\text{-dppm})Pd}Cl]$, as a combined result of the change in trans ligand and of the bridging mode of the SiOMe group. The latter also causes the geometry at the iron atom to be much more distorted than in **2a**. Thus, while the $Si(OMe)_3$ group is slightly bent away from the Pd atom in **2a**, the Pd–Fe–Si angle decreases to 75.00 (3)° in **4a**. The C(3)–Fe–Si angle (90.3 (1)°) remains about the same as in **2a** (C(2)–Fe–Si = 86.4 (2)°), but the C(3)–Fe–P angle opens by about 8.5°; i.e., the tilt of the $Si(OMe)_3$ group is accompanied by a tilting of the CO ligand trans to the Pd–Fe bond. The ^1H NMR spectroscopic data for **4a** indicate a dynamic behavior for the $-Si(OMe)_3$ group. The high-temperature spectrum (toluene, 363 K) reveals the presence of nine identical protons for the $-Si(OMe)_3$ group, as evidenced by the singlet at δ 3.78. Progressive cooling of the toluene solution broadens this signal until coalescence is reached at ca. 313 K ($\Delta G^{\ddagger} \approx 65 \pm 2$ kJ/mol). A rigid four-membered FePdSiO ring structure with a μ_2-η^2-SiO bridge exists at 243 K, as shown by the prescence of two well-separated singlets for the methoxy protons at δ 3.93 and 3.57 in a 2:1 ratio, respectively, and a further triplet at δ 3.42 for the dppm protons. Although the magnitude of the Sn–P couplings in the ^{31}P and ^{119}Sn NMR spectra is consistent with the molecular structure,[13] it is not clear why ^2J(P–Sn) is smaller than ^3J(P–Sn). With a value of 15.1 ppm, the $^{29}Si\{^1H\}$ NMR chemical shift for **4a**[12] is very similar to that for **2a** (12.9 ppm) and related molecules containing a $-Si(OMe)_3$ group and is consistent with our bonding description, where no silylene-type contribution needs to be invoked.[3]

The reactivity of heterobimetallic allyl complexes[16] such as **2** will be further investigated. Replacement of the allyl group with a ligand occupying only one coordination site on a metal center adjacent to a $M-Si(OR)_3$ moiety may represent a general access to μ_2-η^2-SiO bonding. The interaction between the hard oxygen donor atom and the soft palladium ion is the most remarkable feature of **4**. Studies are in progress to delineate the electronic and steric factors that favor the formation of such four-membered rings. That this entropically favored intramolecular μ_2-η^2-SiO bridge formation is associated with a hemilabile behavior of the $-Si(OR)_3$ ligand is particularly interesting with respect to the stabilization of unsaturated, reactive polymetallic molecular or surface species.

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Registry No. [K]1, 123674-03-3; **2a**, 132408-39-0; **2b**, 132374-55-1; **3**, 132374-56-2; **4a**, 132374-57-3; **4a**·0.7(toluene), 132486-31-8; **4b**, 132374-58-4; $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)(\mu\text{-}Cl)]_2$, 12081-18-4; $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$, 12012-95-2; $[Pt(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_4$, 123756-28-5; Sn_2Ph_6, 1064-10-4.

Supplementary Material Available: Tables of experimental crystallographic details, final atomic coordinates, thermal parameters, bond lengths, bond angles, and torsional angles for **2a** and **4a** and Figures S-1 and S-2, showing the structures of **2a** and **4a** with the complete labeling scheme (33 pages); listings of observed and calculated structure factor amplitudes for **2a** and **4a** (49 pages). Ordering information is given on any current masthead page.

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[15] For a coordinated water molecule, Pd–O = 220 (1) pm; see: Deeming, A. J.; Rothwell, I. P.; Hursthouse, M. B.; New, L. *J. Chem. Soc., Dalton Trans.* **1978**, 1490. For a coordinated ketone, Pd–O = 216.3 (3) pm; see: Russel, D. R.; Tucker, P. A. *Ibid.* **1975**, 1743.

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Chemospecific, Biphasic Reduction of α,β-Unsaturated Aldehydes and Ketones Catalyzed by $(Cy_3P)_2Rh(H)Cl_2$

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Summary: The rhodium(III) complex $(Cy_3P)_2Rh(H)Cl_2$ is an effective catalyst precursor for the hydrogenation of the double bond of α,β-unsaturated aldehydes or ketones under mild conditions.

The selective homogeneous catalytic hydrogenation of carbon–carbon double bonds in unsaturated carbonyl compounds, especially aldehydes, has been the object of a number of investigations.[1,2] The highly effective olefin hydrogenation catalyst $[(Ph_3P)_3RuCl_2]$ was shown to be completely inactive in the hydrogenation of unsaturated

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