Supporting Information A

Content

Experimental

General information.

All manipulations were carried out under argon (99.999 %) atmosphere using standard Schlenk techniques or an MBraun Glovebox. The argon for Schlenk techniques is additionally dried through SICAPENT®. All solvents (protonated and deuterated) were degassed via "freeze-pump-thaw" method and dried with diverse methods. Benzene and *o*-DFB were dried over activated aluminium oxide, before this benzene-d_6 is additionally distilled from Na/K. Diethyl ether and tetrahydrofuran were obtained from an MBRAUN solvent purification system (SPS) and distilled from Na/K. Toluene, obtained from an MBRAUN SPS, and toluene-d_8 are distilled from Na/K. *n*-hexane and *n*-pentane were obtained from an MBRAUN SPS. 1-bromo-4-(*tert*-butyl)-2,6-bis[bis(trimethylsilyl)methyl]benzene (TbbBr)[1-2], $[TbbGeBr]_2$[3], $[TbbSnBr_2][Li(thf)_2]$[4], $TbbSnH_3$[4], $[Ar^*PbH]_2$[5-6], Tris(triethylphosphine)iridiumchloride ($(Et_3P)_3IrCl$),[7] Tetrakis(trimethylphosphine)iridiumchloride ($(Me_3P)_4IrCl$)[8], sodium tetrakis[3,5-bis(trifluormethyl)phenyl]borate ($Na[BAr^F_4]$)[9] and *Brookhart's* acid[10] were synthesized following the respective literature. The commercially purchased chemicals (*sigma aldrich*, *abcr* and *apollo scientific*) were used as received. All air and moisture sensitive chemicals were stored under argon atmosphere.

NMR spectroscopy.

The NMR spectra were recorded with either a *Bruker* Avance III HD 300 NanoBay NMR spectrometer equipped with a 5 mm BBFO probe head operating at 300.13 (^{1}H), 96.29 (^{11}B), 75.48 (^{13}C) 282.40 (^{19}F), 59.62 (^{29}Si) and 111.92 MHz (^{119}Sn), a *Bruker* Avance II+ 400 NMR spectrometer equipped with a 5 mm QNP (quad nucleus probe) head operating at 400.11 (^{1}H), 100.62 (^{13}C), 376.43 MHz (^{19}F), 161.97 MHz (^{31}P), a *Bruker* AV II+ 500 NMR spectrometer with a variable temperature set up and with a 5 mm ATM probe head or a 5 mm TBO probe head operating at 500.13 (^{1}H), 160.46 (^{11}B) 125.76 (^{13}C), 99.36 (^{29}Si), 202.46 (^{31}P), 186.55 MHz (^{119}Sn) or a *Bruker* Avance III HDX 600 spectrometer with a variable temperature set up and a 5 mm Prodigy BBO Cryo probe head operating at 600.13 (^{1}H), 192.55 (^{11}B), 150.92 (^{13}C) 564.63 (^{19}F), 119.23 (^{29}Si) and 223.79 MHz (^{119}Sn). The chemical shifts are reported as δ in ppm relative to the following external standards: tetramethylsilane (^{1}H, ^{13}C and ^{29}Si), lithium chloride (^{7}Li), boron trifluoride diethyl etherate (^{11}B), trichlorofluoromethane (^{19}F), 85% phosphoric acid (^{31}P) and tetramethyltin (^{119}Sn).[11] The chemical shifts were referenced using the chemical shift of the solvent ^{2}H resonance frequency as follows: Ξ = 32.08397 % for ^{11}B, Ξ = 25.145020 % for ^{13}C, Ξ = 94.094011 % for ^{19}F, Ξ = 19.867187 % for ^{29}Si, Ξ = 40.480742 for ^{31}P and Ξ = 37.290632 % for ^{119}Sn.[11] The multiplicity of the signals is abbreviated as s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet and m = multiplet or br. = broad/unresolved. The proton and carbon signals were assigned via detailed analysis of ^{1}H, ^{13}C{^{1}H}(-UDEFT), ^{13}C{^{1}H}-DEPT135, ^{1}H-^{1}H-COSY, ^{1}H-^{13}C-HSQC and ^{1}H-^{13}C-HMBC NMR spectra. Selected 1D-NMR spectra of the compounds can be found in the Supporting Information. Variable temperature NMR spectra were equilibrated for 10 min prior to acquisition, the actual temperature was determined by using the method of van Geet.[12-13] Spectra were analyzed using gNMR 5.0,[14] and analysis of exchange rates was performed with ACTPAR,[15] a nonlinear least-squares program that considers errors in both dimensions. The 112.01 MHz ^{119}Sn MAS solid-state NMR spectrum of **4** was obtained for a powdered sample packed into a 4 mm o.d. zirconia rotor using a Bruker Avance III HD spectrometer with a 300 MHz wide-bore magnet. Because cross-polarization was unsuccessful, direct excitation with high-power proton decoupling was employed. Sample spinning rates of 10 and 11 kHz were used to identify the isotropic peak. Chemical shifts were referenced with respect to external $SnMe_4$ (Ξ = 37.290632%) by the substitution method: an external sample of $CHCl_3$ in acetone was spun at 2 kHz and the external magnetic field was adjusted such that the ^1H chemical shift of $CHCl_3$ matched a predetermined chemical shift wrt. external 1% TMS in $CHCl_3$.

IR spectroscopy.

The IR spectra were recorded as potassium bromide pellets, which were prepared in an MBraun glovebox and measured with a *Bruker* VERTEX 70 IR spectrometer.

Crystal structure determination.

X-ray data were collected with a *Bruker* Smart APEX II diffractometer with graphite monochromated Mo-K_α radiation. The used programs were Bruker APEX2 v2011.8-0 including SADABS for absorption correction, SAINT for data reduction, SHELXS for structure solution and SHELXLE or WinGX suite of programs v1.70.01 including SHELXL for structure refinement.[16-22] All details of the structure refinement and solution can be found in the Supporting Information.

Syntheses

Synthesis of $(Me_3P)_4IrH$. The synthesis was carried out based on a literature procedure but is nevertheless described here due to other or additional observations.[23] $(Me_3P)_4IrCl$ (974 mg, 1.83 mmol, 1.0 equiv) is suspended in tetrahydrofuran (50.0 mL). Dihydrogen is bubbled through the orange suspension under stirring till the solid is completely colorless to yield quantitatively $(Me_3P)_4IrClH_2$ (approximately 30 to 45 minutes – it may be necessary to refill the evaporated solvent). To the resulting suspension of $(Me_3P)_4IrClH_2$ (977 mg, 1.83 mmol, 1.0 equiv) in tetrahydrofuran potassium *tert*-butoxide (324 mg, 2.74 mmol, 1.5 equiv) is added. The colorless suspension clears and turns pale yellow. After 45 minutes at room temperature the solvent is removed under reduced pressure and the resulting solid is extracted with *n*-pentane (10.0, 10.0, 7.00 mL) and filtered through a syringe filter. The solvent is removed under reduced pressure to yield 811 mg of $(Me_3P)_4IrH$ (1.63 mmol, 89 %) as a pale-yellow solid. The purity is sufficient for our reactions. *Analytical data.* **^{1}H** [400.11 MHz, 299.20 K, benzene-d_6]: δ (ppm) −13.80 (quint, 1H, Ir*H*, $^2J_{31P\text{-}H}$ = 5.9 Hz), 1.49 (m, 36H, PMe_3-*H*). **^{31}P{^{1}H}** [161.97 MHz, 299.20 K, benzene-d_6]: δ (ppm) −57.8 (s, PMe_3).

Synthesis of $TbbGe(Br){=}IrH(PMe_3)_3$ (**1**). [$(TbbGeBr)_2$] (150 mg, 125 µmol, 1.0 equiv) and $(Me_3P)_4IrH$) (124 mg, 249 µmol, 2.0 equiv) are weighed in and mixed up. Subsequently benzene (5.00 mL) is added and the resulting orange solution is stirred for 24 hours at room temperature. The reaction mixture is dried under reduced pressure and the orange solid is extracted three times with *n*-pentane (4.00, 4.00 and 2.00 mL) and filtered through a syringe filter. The solvent is removed under reduced pressure to yield 244 mg (238 µmol, 96 %) orange solid of $TbbGe(Br){=}IrH(PMe_3)_3$ (**1**). Suitable crystals for X-ray diffraction could be obtained out of a slowly evaporated *n*-pentane solution at −38 °C. *Analytical data.* **^{1}H** [400.11 MHz, 299.20 K, benzene-d_6]: δ (ppm) −11.82 (q, 1H, Ir*H*, $^2J_{31P\text{-}H}$ = 20.8 Hz), 0.34 (s, 18H, $Si(CH_3)_3$), 0.43 (s, 18H, $Si(CH_3)_3$), 1.37 (s, 9H, ^{t}Bu-*H*), 1.49 (m, 27H, PMe_3-*H*), 3.09 (s, 2H, C*H*$(SiMe_3)_2$), 6.85 (s, 2H, *m*-Tbb*H*). **^{13}C{^{1}H}** [100.62 MHz, 299.20 K, benzene-d_6]: δ (ppm) 1.2 (s, $Si(CH_3)_3$), 1.7 (s, $Si(CH_3)_3$), 26.8 (m, $P(CH_3)_3$), 28.0 (s, *C*H$(SiMe_3)_2$), 31.1 (s, ^{t}Bu-CH_3), 34.0 (s, ^{t}Bu-*C*Me$_3$), 121.8 (s, *m*-C_{Tbb}), 144.5 (s, *o*-C_{Tbb}), 149.3 (s, *p*-C_{Tbb}), 157.9 (m, *i*-C_{Tbb}–Ge). **^{29}Si** [59.63 MHz, 299.20 K, benzene-d_6]: δ (ppm) 2.7 (m, *Si*Me$_3$), 3.4 (m, *Si*Me$_3$). **^{31}P{^{1}H}** [161.97 MHz, 299.20 K, benzene-d_6]: δ (ppm) −45.6 (s, PMe_3). **IR** [KBr, cm^{-1}] ν(Ir–H) 2008. **Elemental analysis** calculated for $TbbGe(Br){=}IrH(PMe_3)_3$ ($C_{33}H_{77}BrGeIrP_3Si_4$): C 38.71, H 7.58. Found: C 38.81, H 7.63.

Synthesis of $TbbSn(Br)=IrH(PMe_3)_3$ (**2**). $[TbbSnBr_2][Li(thf)_2]$ (200 mg, 227 µmol, 1.0 equiv) and $(Me_3P)_4IrH$ (113 mg, 227 µmol, 1.0 equiv) are weighed in and mixed up. Subsequently benzene (4.00 mL) is added and the resulting red suspension is stirred for one hour at room temperature. The reaction mixture is dried under reduced pressure and the orange-red solid is co-evaporated with *n*-pentane (2.00 mL) and then extracted three times with *n*-pentane (4.00, 4.00 and 2.00 mL) and filtered through a syringe filter. The solvent is removed under reduced pressure to yield 232 mg (217 µmol, 95 %) orange solid of $TbbSn(Br)=IrH(PMe_3)_3$ (**2**). The purity is sufficient for our reactions. For higher purity the compound can be crystallized out of a concentrated *n*-pentane or toluene solution at −38 °C. The crystals were always twinned, which is why no X-ray molecule structure could be obtained. *Analytical data.* **^{1}H** [400.11 MHz, 299.20 K, benzene-d_6]: δ (ppm) −12.65 (q + sat., 1H, Ir*H*, $^{2}J_{119Sn\text{-}H}$ = 219 Hz, $^{2}J_{31P\text{-}H}$ = 18.6 Hz), 0.37 (s, 36H, $Si(CH_3)_3$), 1.36 (s, 9H, ^{t}Bu-*H*), 1.51 (m, 27H, PMe_3-*H*), 2.75 (s, 2H, C*H*$(SiMe_3)_2$), 6.94 (s, 2H, *m*-Tbb*H*). **^{13}C{^{1}H}** [100.62 MHz, 299.20 K, benzene-d_6]: δ (ppm) 1.2 (s, Si(*C*$H_3)_3$), 28.3 (m, P(*C*$H_3)_3$), 30.5 (s, *C*H$(SiMe_3)_2$), 31.1 (s, ^{t}Bu-*C*H_3), 34.2 (s, ^{t}Bu-*C*Me$_3$), 122.2 (s, *m*-C_{Tbb}), 146.6 (s, *o*-C_{Tbb}), 149.7 (s, *p*-C_{Tbb}), 167.0 (m, *i*-C_{Tbb}–Sn). **^{29}Si** [59.63 MHz, 299.20 K, benzene-d_6]: δ (ppm) 2.5 (m, *Si*Me$_3$). **^{31}P{^{1}H}** [161.97 MHz, 299.20 K, benzene-d_6]: δ (ppm) −43.7 (s + sat., *P*Me$_3$, $^{2}J_{119Sn\text{-}31P}$ = 598 Hz). **^{119}Sn** [111.92 MHz, 299.20 K, benzene-d_6]: δ (ppm) 566 ("dq", Tbb*Sn*(Br)Ir, $^{2}J_{119Sn\text{-}31P}$ = 603 Hz, $^{2}J_{119Sn\text{-}1H}$ = 218 Hz). **^{119}Sn{^{1}H}** [111.92 MHz, 299.20 K, benzene-d_6]: δ (ppm) 566 ("q", Tbb*Sn*(Br)Ir, $^{2}J_{119Sn\text{-}31P}$ = 599 Hz). **IR** [KBr, cm^{-1}] ν(Ir–H) 2010. **Elemental analysis** calculated for $TbbSn(Br)=IrH(PMe_3)_3$ ($C_{33}H_{77}BrIrP_3Si_4Sn$): C 37.04, H 7.25. Found: C 37.17, H 7.25.

Synthesis of $[TbbGeIrH(PMe_3)_3][BAr^{F}_4]$ (**3**). $TbbGe(Br)=IrH(PMe_3)_3$ (**1**) (100 mg, 97.7 µmol, 1.0 equiv) and $Na[BAr^{F}_4]$ (82.2 mg, 92.8 µmol, 0.95 equiv) are weighed in and mixed up. Subsequently *o*-DFB (1.00 mL) and benzene (1.00 mL) is added, and the resulting dark red suspension is stirred for five minutes at room temperature. The reaction mixture is filtered through a syringe filter, then the filter is washed with benzene (1.00 mL) and the dark red solution is dried under reduced pressure. The resulting solid is washed three times with *n*-pentane (2.00 mL each time) and dried under reduced pressure to yield 149 mg (82.4 µmol, 89 %) red solid of $[TbbGeIrH(PMe_3)_3][BAr^{F}_4]$ (**3**). *Analytical data.* **^{1}H** [400.11 MHz, 299.20 K, benzene-d_6 + *o*-DFB]: δ (ppm) −11.87 (q, 1H, Ir*H*, $^{2}J_{31P\text{-}H}$ = 8.8 Hz), 0.07 (s, 36H, $Si(CH_3)_3$), 1.17 (s, 9H, ^{t}Bu-*H*), 1.37 (m, 27H, PMe_3-*H*), 2.34 (s, 2H, C*H*$(SiMe_3)_2$), 6.73 (s, 2H, *m*-Tbb*H*, covered by *o*-DFB), 7.62 (br. s, 4H, *p*-BAr^{F}-*H*), 8.31 (br. m, 8H, *o*-BAr^{F}-*H*). **^{11}B** [96.29 MHz, 299.20 K, benzene-d_6 + *o*-DFB]: δ (ppm) −6.0 (s, *B*Ar$^{F}_4$). **^{13}C{^{1}H}** [100.62 MHz, 299.20 K, benzene-d_6 + *o*-DFB]: δ (ppm) −0.1 (s, Si(*C*$H_3)_3$), 27.0 (m, P(*C*$H_3)_3$), 30.2 (s, ^{t}Bu-*C*H_3), 30.6 (s, *C*H$(SiMe_3)_2$), 34.8 (s, ^{t}Bu-*C*Me$_3$), 117.5 (m, *p*-BAr^{F}-*C*), 122.3 (s, *m*-C_{Tbb}), 124.9 (q, *C*F$_3$, $^{1}J_{19F\text{-}13C}$ = 272 Hz), 129.5 (br. q, *m*-BAr^{F}-*C*, $^{2}J_{19F\text{-}13C}$ = 31.9 Hz), 135.0 (s, *o*-BAr^{F}-*C*), 146.3 (s, *o*-C_{Tbb}), 156.0 (s, *p*-C_{Tbb}), 159.1 (m, *i*-C_{Tbb}–Ge), 162.4 (q, *i*-BAr^{F}-*C*, $^{1}J_{13C\text{-}11B}$ = 49.8 Hz). **^{19}F{^{1}H}** [376.48 MHz, 299.20 K, benzene-d_6 + *o*-DFB]: δ (ppm) −62.3 (s, C*F*$_3$). **^{29}Si** [59.63 MHz, 299.20 K, benzene-d_6 + *o*-DFB]: δ (ppm) 3.3 (m, *Si*Me$_3$). **^{31}P{^{1}H}** [161.97 MHz, 299.20 K, benzene-d_6 + *o*-DFB]: δ (ppm) −43.9 (br. s, PMe$_3$). **Elemental analysis** calculated for $[TbbGeIrH(PMe_3)_3][BAr^{F}_4]$ ($C_{65}H_{89}BF_{24}GeIrP_3Si_4$): C 43.20, H 4.96. Found: C 42.93, H 5.25.

Synthesis of $[Ar^{*}GeIrH(PMe_3)_3][BAr^{F}_4]$ (**3'**). *Step 1:* To a mixture of $[Ar^{*}GeCl]_2$ (29.6 mg, 25.1 µmol, 1.0 equiv) and $(Me_3P)_4IrH$ (25.0 mg, 50.2 µmol, 2.0 equiv) benzene (2.00 mL) is added directly. The orange-colored reaction mixture is stirred at room temperature for 24 hours. The solvent is removed under reduced pressure, and it is co-evaporated with *n*-pentane (2.00 mL). The orange solid is extracted with *n*-pentane (2×2.00 mL) and filtered through a syringe filter. The solvent is removed under reduced pressure to yield 47.5 mg (47.0 µmol, 94 %) of the iridium germylene $Ar^{*}GeCl=IrH(PMe_3)_3$ as an orange solid. The iridium germylene was not characterized and the crude product was reacted in the next step as follows: *Step 2:* To a mixture of $Ar^{*}GeClIrH(PMe_3)_3$ (47.5 mg, 47.0 µmol, 1.0 equiv) and $Na[BAr^{F}_4]$ (39.5 mg, 44.6 µmol, 0.95 equiv) *o*-DFB (0.50 mL) and benzene (0.50 mL) is added. The resulting deep red to orange-brown suspension is stirred for five minutes at room temperature. It is then filtered through a syringe filter. The filter is washed again with benzene (0.50 mL). The solvent is removed under reduced pressure and the resulting gel-like solid is washed three times with *n*-pentane (1.00 mL) to yield 64.2 mg (34.9 µmol, 83 %) red to orange-brown solid of [Ar*GeIrH(PMe$_3$)$_3$][BAr$^F{}_4$] (**3’**) as product. Suitable single crystals could be obtained by overlaying a concentrated *o*-DFB solution with n-pentane at –38 °C. *Analytical data.* **^{1}H** [600.13 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −12.84 (q, 1H, Ir*H*, $^2J_{31P\text{-}H}$ = 10.3 Hz), 1.04 (d, 12H, *o*-^{i}Pr-C*H*$_3$, $^3J_{H\text{-}H}$ = 6.9 Hz), 1.13 (m, 27H, PMe$_3$-*H*), 1.23 (d, 12H, *o*-^{i}Pr-C*H*$_3$, $^3J_{H\text{-}H}$ = 6.9 Hz), 1.24 (d, 12H, *p*-^{i}Pr-C*H*$_3$, $^3J_{H\text{-}H}$ = 6.9 Hz), 2.75 (sept, 4H, *o*-^{i}Pr-C*H*, $^3J_{H\text{-}H}$ = 6.9 Hz), 2.81 (sept, 2H, *p*-^{i}Pr-C*H*, $^3J_{H\text{-}H}$ = 6.9 Hz), 6.90 and 7.21 (m [d + t], 3H, *m*-C$_6$*H*$_3$ und *p*-C$_6$*H*$_3$, $^3J_{H\text{-}H}$ = 7.7 Hz), 7.10 (s, 4H, *m*-*H*$_{Trip}$), 7.62 (br. s, 4H, *p*-BAr$^F{}_4$-*H*), 8.30 (br. m, 8H, *o*-BAr$^F{}_4$-*H*). **^{11}B{^{1}H}** [192.55 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −6.0 (s, *B*Ar$^F{}_4$). **^{13}C{^{1}H}** [150.90 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) 23.6 (s, *o*-^{i}Pr-*C*H$_3$), 23.8 (s, *p*-^{i}Pr-*C*H$_3$), 24.3 (s, *o*-^{i}Pr-*C*H$_3$), 26.4 (m, P(*C*H$_3$)$_3$), 30.9 (s, *o*-^{i}Pr-*C*H), 34.2 (s, *p*-^{i}Pr-*C*H), 117.5 (br. m, *p*-BAr$^F{}_4$-*C*), 121.6 (s, *m*-C$_{Trip}$), 124.9 (q, *C*F$_3$, $^1J_{19F\text{-}13C}$ = 272 Hz), 129.5 (br. q, *m*-BAr$^F{}_4$-*C*, $^2J_{19F\text{-}13C}$ = 31.5 Hz), 130.0 (s, *m*-*C*$_6$H$_3$), 130.7 (s, *p*-*C*$_6$H$_3$), 132.2 (s, *i*-C$_{Trip}$), 135.0 (s, *o*-BAr$^F{}_4$-*C*), 142.2 (s, *o*-*C*$_6$H$_3$), 147.9 (s, *o*-C$_{Trip}$), 150.5 (s, *p*-*C*$_{Trip}$), 162.4 (q, *i*-BAr$^F{}_4$-*C*, $^1J_{13C\text{-}11B}$ = 49.8 Hz), 162.7 (m, *i*-*C*$_6$H$_3$−Ge). **^{19}F{^{1}H}** [564.69 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −62.4 (s, C*F*$_3$). **^{31}P{^{1}H}** [161.97 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −43.2 (br. s, *P*Me$_3$).

Synthesis of [TbbSnIrH(PMe$_3$)$_3$][BAr$^F{}_4$] (**4**). TbbSn(Br)=IrH(PMe$_3$)$_3$ (**2**) (167 mg, 156 µmol, 1.0 equiv) and Na[BAr$^F{}_4$] (131 mg, 148 µmol, 0.95 equiv) are weighed in and mixed up. Subsequently *o*-DFB (1.00 mL) and benzene (1.00 mL) is added, and the resulting dark brown suspension is stirred for five minutes at room temperature. The reaction mixture is filtered through a syringe filter, then the filter is washed with benzene (1.00 mL) and the dark brown solution is dried under reduced pressure. The resulting solid is co-evaporated with *n*-pentane (2.00 mL), washed four times with *n*-pentane (2.00 mL each time) and dried under reduced pressure to yield 243 mg (131 µmol, 88 %) brown solid of [TbbSnIrH(PMe$_3$)$_3$][BAr^{F}4] (**4**). Crystals for X-ray diffraction could be obtained out of a concentrated *o*-DFB solution layered with *n*-pentane at −38 °C. *Analytical data.* **^{1}H** [400.11 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −11.32 (q + sat., 1H, Ir*H*, $^2J_{31P\text{-}H}$ = 10.3 Hz, $^2J_{119Sn\text{-}H}$ = 119 Hz), 0.08 (s, 36H, Si(C*H*$_3$)$_3$), 1.19 (s, 9H, ^{t}Bu-*H*), 1.40 (br. m, 27H, PMe$_3$-*H*), 1.75 (s, 2H, C*H*(SiMe$_3$)$_2$), 6.81 (s, 2H, *m*-Tbb*H*), 7.63 (br. s, 4H, *p*-BAr^F-*H*), 8.31 (br. m, 8H, *o*-BAr^F-*H*). **^{11}B** [96.29 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −6.0 (s, *B*Ar$^F{}_4$). **^{13}C{^{1}H}** [100.62 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) 0.0 (s, Si(*C*H$_3$)$_3$), 27.8 (m, P(*C*H$_3$)$_3$), 30.3 (s, ^{t}Bu-*C*H$_3$), 31.8 (s, *C*H(SiMe$_3$)$_2$), 34.7 (s, ^{t}Bu-*C*Me$_3$), 117.5 (m, *p*-BAr^F-*C*), 123.5 (s, *m*-*C*$_{Tbb}$), 124.9 (q, *C*F$_3$, $^1J_{19F\text{-}13C}$ = 272 Hz), 129.5 (br. q, *m*-BAr^F-*C*, $^2J_{19F\text{-}13C}$ = 30.5 Hz), 135.0 (s, *o*-BAr^F-*C*), 145.7 (s, *o*-*C*$_{Tbb}$), 153.9 (s, *p*-*C*$_{Tbb}$), 162.4 (q, *i*-BAr^F-*C*, $^1J_{13C\text{-}11B}$ = 49.8 Hz), 177.5 (m, *i*-*C*$_{Tbb}$−Sn). **^{19}F{^{1}H}** [282.38 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −62.3 (s, C*F*$_3$). **^{29}Si** [59.63 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) 2.6 (m, *Si*Me$_3$). **^{31}P{^{1}H}** [161.97 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −38.5 (br. s + sat., *P*Me$_3$, $^2J_{119Sn\text{-}31P}$ = 347 Hz). **^{119}Sn** [111.92 MHz, 299.20 K, benzene-d$_6$]: δ (ppm) 1424 (br. q, Tbb*Sn*Ir, $^2J_{119Sn\text{-}31P}$ = 349 Hz). **^{119}Sn{^{1}H}** [111.92 MHz, 299.20 K, benzene-d$_6$]: δ (ppm) 1424 (br. q, Tbb*Sn*Ir, $^2J_{119Sn\text{-}31P}$ = 347 Hz). **Elemental analysis** calculated for [TbbSnIrH(PMe$_3$)$_3$][BAr$^F{}_4$] ($C_{65}H_{89}BF_{24}SnIrP_3Si_4$): C 42.12, H 4.84. Found: C 41.67, H 5.17.

Synthesis of [Ar*SnIrH(PMe$_3$)$_3$][BAr$^F{}_4$] (**4’**). *Method A – Step 1:* To a mixture of [Ar*SnCl]$_2$ (20.0 mg, 15.7 µmol, 1.0 equiv.) and (Me$_3$P)$_4$IrH (15.6 mg, 31.4 µmol, 2.0 equiv.) benzene (0.50 mL) is added directly. The immediately red colored reaction mixture is stirred at room temperature for two hours. The solvent is removed under reduced pressure and it is co-evaporated with *n*-pentane (1.00 mL) to yield 31.3 mg (29.6 µmol, 94 %) of the iridium stannylene Ar*SnClIrH(PMe$_3$)$_3$ as an red solid. The iridium stannylene was not characterized and the crude product was reacted in the next step as follows: *Method A – Step 2:* To a mixture of Ar*SnClIrH(PMe$_3$)$_3$ (31.3 mg, 29.6 µmol, 1.0 equiv.) and Na[BAr$^F{}_4$] (23.6 mg, 26.6 µmol, 0.90 equiv.) benzene (0.30 mL) and *o*-DFB (0.10 mL) is added. The resulting deep red to orange-brown suspension is stirred for five minutes at room temperature. It is then filtered through a syringe filter. The filter is washed again with benzene (0.20 mL). The solvent is removed under reduced pressure and the resulting gel-like solid is washed three times with *n*-pentane (1.00 mL). The crude product is dissolved in *o*-DFB (0.20 mL), layered with *n*-pentane (2.00 mL) and stored at –38 °C to yield 32.8 mg (17.4 µmol, 65 %) red to orange-brown crystals of $[Ar^{*}SnIrH(PMe_3)_3][BAr^F_4]$ (**4'**) as product overnight. The obtained crystals were not suitable for X-ray diffraction.

Method B: To a mixture of $[Ar^{*}SnH]_2$ (22.5 mg, 18.7 µmol, 0.95 equiv.) and $[Ph_3C][BAr^F_4]$ (41.4 mg, 37.4 µmol, 1.9 equiv.) *o*-DFB (1.00 mL) is added directly. The reaction mixture is stirred at room temperature for five minutes till an orange clear solution is obtained. Subsequently the formed cation [Ar*Sn(*o*-DFB)]$[BAr^F_4]$ is added directly to $(Me_3P)_4IrH$ (19.6 mg, 39.4 µmol, 2.0 equiv). The solvent of the resulting deep brown solution is removed under reduced pressure. The resulting oil is washed with *n*-pentane (3×1.00 mL) to yield 61.9 mg (32.8 µmol, 88 %) deep brown solid of $[Ar^{*}SnIrH(PMe_3)_3][BAr^F_4]$ (**4'**) was obtained as product. For crystallization the solid is dissolved in *o*-DFB (0.30 mL), layered with *n*-pentane (2.00 mL) and stored at –38 °C. 39.2 mg (20.8 µmol, 56 %) of deep brown crystals of $[Ar^{*}SnIrH(PMe_3)_3][BAr^F_4]$ (**4'**) were obtained as product. These crystals were not suitable for X-ray diffraction. Via both methods A and B, small amounts of two or three minor products were observed, which could not be identified. Neither washing nor crystallization led to a purification. *Analytical data.* ^{1}**H** [600.13 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −13.61 (q + sat., 1H, Ir*H*, $^{2}J_{Sn\text{-}H}$ = 127 Hz, $^{2}J_{31P\text{-}H}$ = 11.4 Hz), 1.04 (d, 12H, *o*-^{i}Pr-C*H*$_3$, $^{3}J_{H\text{-}H}$ = 6.8 Hz), 1.18 (m, 27H, PMe$_3$-*H*), 1.23 (d, 12H, *o*-^{i}Pr-C*H*$_3$, $^{3}J_{H\text{-}H}$ = 6.8 Hz), 1.24 (d, 12H, *p*-^{i}Pr-C*H*$_3$, $^{3}J_{H\text{-}H}$ = 6.8 Hz), 2.80 (sept, 4H, *o*-^{i}Pr-C*H*, $^{3}J_{H\text{-}H}$ = 6.8 Hz), 2.81 (sept, 2H, *p*-^{i}Pr-C*H*, $^{3}J_{H\text{-}H}$ = 6.8 Hz), 7.07 and 7.27 (m [d + t], 3H, *m*-C$_6$*H*$_3$ und *p*-C$_6$*H*$_3$, $^{3}J_{H\text{-}H}$ = 7.7 Hz), 7.13 (s, 4H, *m*-*H*$_{Trip}$), 7.63 (br. s, 4H, *p*-BAr$^F_4$-*H*), 8.32 (br. m, 8H, *o*-BAr$^F_4$-*H*). ^{11}**B{^{1}H}** [192.55 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −6.0 (s, *B*Ar$^F_4$). ^{13}**C{^{1}H}** [150.90 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) 23.6 (s, *p*-^{i}Pr-*C*H$_3$), 23.8 (s, *o*-^{i}Pr-*C*H$_3$), 24.4 (s, *o*-^{i}Pr-*C*H$_3$), 27.9 (m, P(*C*H$_3$)$_3$), 30.7 (s, *o*-^{i}Pr-*C*H), 34.1 (s, *p*-^{i}Pr-*C*H), 117.5 (br. m, *p*-BAr$^F_4$-*C*), 121.9 (s, *m*-C$_{Trip}$), 124.9 (q, *C*F$_3$, $^{1}J_{19F\text{-}13C}$ = 272 Hz), 129.5 (br. q, *m*-BAr$^F_4$-*C*, $^{2}J_{19F\text{-}13C}$ = 31.5 Hz), 129.9 (s, *p*-*C*$_6$H$_3$), 130.4 (s, *m*-C$_6$H$_3$), 132.8 (s, *i*-C$_{Trip}$), 135.0 (s, *o*-BAr$^F_4$-*C*), 142.4 (s, *o*-*C*$_6$H$_3$), 148.0 (s, *o*-*C*$_{Trip}$), 150.7 (s, *p*-*C*$_{Trip}$), 162.4 (q, *i*-BAr$^F_4$-*C*, $^{1}J_{13C\text{-}11B}$ = 49.8 Hz), 179.0 (m, *i*-*C*$_6$H$_3$–Sn). ^{19}**F{^{1}H}** [564.69 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −62.3 (s, C*F*$_3$). ^{31}**P{^{1}H}** [161.97 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −39.2 (br., *P*Me$_3$). ^{119}**Sn{^{1}H}** [223.79 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) 1076 (q, Ar**Sn*Ir, $^{2}J_{119Sn\text{-}31P}$ = 491 Hz).

Synthesis of $[TbbGe(NH_2)IrH_2(PMe_3)_3][BAr^F_4]$ (**5**). $[TbbGeIrH(PMe_3)_3][BAr^F_4]$ (**1**) (30.0 mg, 16.6 µmol, 1.0 equiv) is dissolved in benzene(-d$_6$) (0.30 mL) and *o*-DFB (0.05 mL) and the dark red solution is transferred into a *J. Young* NMR tube. The solution is degassed with one "freeze-pump-thaw" cycle and the atmosphere is changed with ammonia, whereby the solution becomes colorless immediately. The compound is characterized via NMR spectroscopy, where a quantitative reaction can be observed. For crystallization the solvent is removed under reduced pressure and the resulting colorless solid is dissolved in *o*-DFB. Subsequently the concentrated solution is layered with *n*-pentane at −38 °C to yield 24.3 mg (13.5 µmol, 81 %) colorless crystals of $[TbbGe(NH_2)IrH_2(PMe_3)_3][BAr^F_4]$ (**5**) overnight, which were suitable for X-ray diffraction. *Analytical data.* ^{1}**H** [400.11 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −12.80 (m, 2H, Ir*H*), 0.06 (s, 18H, Si(C*H*$_3$)$_3$), 0.11 (s, 18H, Si(C*H*$_3$)$_3$), 1.23 (s, 9H, ^{t}Bu-*H*), 1.25 (m, 9H, PMe$_3$-*H*), 1.27 (m, 18H, PMe$_3$-*H*), 1.29 (s, 2H, C*H*(SiMe$_3$)$_2$), 4.56 (br., 2H, N*H*$_2$), 6.78 (s, 2H, *m*-Tbb*H*), 7.63 (br. s, 4H, *p*-BAr^F-*H*), 8.32 (br. m, 8H, *o*-BAr^F-*H*). ^{11}**B** [96.29 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −6.0 (s, *B*Ar$^F_4$). ^{13}**C{^{1}H}** [100.62 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) 0.4 (s, Si(*C*H$_3$)$_3$), 0.6 (s, Si(*C*H$_3$)$_3$), 23.5 (m, P(*C*H$_3$)$_3$), 23.8 (m, P(*C*H$_3$)$_3$), 30.6 (s, ^{t}Bu-*C*H$_3$), 31.6 (s, *C*H(SiMe$_3$)$_2$), 34.2 (s, ^{t}Bu-*C*Me$_3$), 117.5 (br. m, *p*-BAr^F-*C*), 121.8 (s, *m*-*C*$_{Tbb}$), 124.9 (q, *C*F$_3$, $^{1}J_{19F\text{-}13C}$ = 273 Hz), 129.5 (br. q, *m*-BAr^F-*C*, $^{2}J_{19F\text{-}13C}$ = 31.5 Hz), 135.0 (s, *o*-BAr^F-*C*), 143.2 (s, *i*-*C*$_{Tbb}$–Ge), 145.6 (s, *o*-*C*$_{Tbb}$), 153.1 (s, *p*-*C*$_{Tbb}$), 162.4 (q, *i*-BAr^F-*C*, $^{1}J_{13C\text{-}11B}$ = 49.8 Hz). ^{19}**F{^{1}H}** [376.48 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −62.3 (s, C*F*$_3$). ^{29}**Si** [59.63 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) 3.5 (m, *Si*Me$_3$), 4.2 (m, *Si*Me$_3$). ^{31}**P{^{1}H}** [161.97 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −62.3 (d, 2x *P*Me$_3$, $^{2}J_{31P\text{-}31P}$ = 20.7 Hz), −53.8 (t, 1x *P*Me$_3$,

$^{2}J_{\text{31P-31P}}$ = 20.7 Hz). **Elemental analysis** calculated for [TbbGe(NH$_2$)IrH$_2$(PMe$_3$)$_3$][BAr$^{F}_{4}$] (C$_{65}$H$_{92}$BF$_{24}$GeIrNP$_3$Si$_4$): C 42.79, H 5.08, N 0.77. Found: C 43.16, H 4.64, N 0.52.

Reaction of **4** with an excess NH$_3$ (**6***). [TbbSnIrH(PMe$_3$)$_3$][BAr$^{F}_{4}$] (**4**) (31.1 mg, 16.8 µmol, 1.0 equiv) is dissolved in benzene(-d$_6$) (0.30 mL) and *o*-DFB (0.05 mL) and the dark brown solution is transferred into a *J. Young* NMR tube. The solution is degassed with one "freeze-pump-thaw" cycle and the atmosphere is changed with ammonia, whereby the solution becomes orange immediately. After 30 minutes a red oil precipitates and the solution becomes yellow. The compound is characterized via NMR spectroscopy, where a quantitative reaction can be observed. *Analytical data.* **^{1}H** [400.11 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −13.67 (m + sat., 2H, Ir*H*, $^{2}J_{\text{Sn-H}}$ = 242 Hz), 0.08 (br. s, 18H, Si(C*H*$_3$)$_3$), 0.10 (br. s, 18H, Si(C*H*$_3$)$_3$), 1.25 (s, 9H, ^{t}Bu-*H*), 1.28 (br., 2H, possibly N*H*$_2$, under PMe$_3$), 1.29 (m, 18H, PMe$_3$-*H*), 1.32 (m, 9H, PMe$_3$-*H*), 1.99 (s, 2H, C*H*(SiMe$_3$)$_2$), 6.77 (br. s, 2H, *m*-Tbb*H*, under *o*-DFB), 7.62 (br. s, 4H, *p*-BAr^{F}-*H*), 8.28 (br. m, 8H, *o*-BAr^{F}-*H*). **^{11}B** [96.29 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −6.0 (s, *B*Ar$^{F}_{4}$). **^{13}C{^{1}H}** [100.62 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −0.1 (s, Si(*C*H$_3$)$_3$), 0.8 (s, Si(*C*H$_3$)$_3$), 24.8 (m, P(*C*H$_3$)$_3$), 24.9 (m, P(*C*H$_3$)$_3$), 30.6 (s, ^{t}Bu-*C*H$_3$), 31.1 (s, *C*H(SiMe$_3$)$_2$), 33.9 (s, ^{t}Bu-*C*Me$_3$), 117.5 (br. m, *p*-BAr^{F}-*C*), 122.5 (s, *m*-*C*$_{\text{Tbb}}$), 124.9 (q, *C*F$_3$, $^{1}J_{\text{19F-13C}}$ = 272 Hz), 129.5 (br. q, *m*-BAr^{F}-*C*, $^{2}J_{\text{19F-13C}}$ = 31.3 Hz), 135.0 (s, *o*-BAr^{F}-*C*), 144.5 (br. s, *i*-*C*$_{\text{Tbb}}$–Sn), 149.2 (*o*-*C*$_{\text{Tbb}}$, under *o*-DFB), 150.9 (s, *p*-*C*$_{\text{Tbb}}$), 162.3 (q, *i*-BAr^{F}-*C*, $^{1}J_{\text{13C-11B}}$ = 49.8 Hz). **^{19}F{^{1}H}** [376.48 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −62.3 (s, C*F*$_3$). **^{29}Si** [59.63 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) 1.4 (m, *Si*Me$_3$), 2.2 (m, *Si*Me$_3$). **^{31}P{^{1}H}** [161.97 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −60.9 (d + sat., 2x *P*Me$_3$, $^{2}J_{\text{119Sn-31P}}$ = 135 Hz, $^{2}J_{\text{31P-31P}}$ = 16.6 Hz), −50.1 (t + sat., 1x *P*Me$_3$, $^{2}J_{\text{119Sn-31P}}$ = 1827 Hz, $^{2}J_{\text{31P-31P}}$ = 16.6 Hz). **^{119}Sn** [111.92 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −11 (br. d, Tbb*Sn*(NH$_2$)Ir, $^{2}J_{\text{119Sn-31P}}$ = 1831 Hz). **^{119}Sn{^{1}H}** [111.92 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −11 (br. d, $^{2}J_{\text{119Sn-31P}}$ = 1827 Hz). **Elemental analysis** calculated for [TbbSn(NH$_2$)NH$_3$IrH$_2$(PMe$_3$)$_3$][BAr$^{F}_{4}$] (C$_{65}$H$_{95}$BF$_{24}$SnIrN$_2$P$_3$Si$_4$): C 41.36, H 5.07, N 1.48. Found: C 41.29, H 4.60, N 0.66.

Synthesis of [TbbGe(NHNH$_2$)IrH$_2$(PMe$_3$)$_3$][BAr$^{F}_{4}$] (**7**). [TbbGeIrH(PMe$_3$)$_3$][BAr$^{F}_{4}$] (**1**) (32.4 mg, 17.9 µmol, 1.0 equiv) is dissolved in benzene (0.30 mL) and *o*-DFB (0.30 mL). Subsequently N$_2$H$_4$ solution (17.9 µL, 1 M in thf, 17.9 µmol, 1.0 equiv) is added and the dark red suspension discolors immediately. The pale yellow solution is dried under reduced pressure. The resulting solid is co-evaporated with *n*-pentane (1.00 mL) and then washed with *n*-pentane (1.00 mL) to yield 30.9 mg colorless solid of [TbbGe(NHNH$_2$)IrH$_2$(PMe$_3$)$_3$][BAr$^{F}_{4}$] (**7**) (16.8 µmol, 94 %). Crystals for X-ray diffraction could be obtained out of a concentrated *o*-DFB solution layered with *n*-pentane at −38 °C. *Analytical data.* **^{1}H** [400.11 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −13.03 (m, 2H, Ir*H*), 0.05 (s, 18H, Si(C*H*$_3$)$_3$), 0.10 (s, 18H, Si(C*H*$_3$)$_3$), 1.23 (s, 9H, ^{t}Bu-*H*), 1.27 (m, 9H, PMe$_3$-*H*), 1.28 (s, 2H, C*H*(SiMe$_3$)$_2$), 1.35 (m, 18H, PMe$_3$-*H*), 2.95 (br. s, 2H, N*H*$_2$), 6.44 (br. m, 1H, N*H*), 6.78 (s, 2H, *m*-Tbb*H*), 7.64 (br. s, 4H, *p*-BAr^{F}-*H*), 8.33 (br. m, 8H, *o*-BAr^{F}-*H*). **^{11}B** [96.29 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −6.0 (s, *B*Ar$^{F}_{4}$). **^{13}C{^{1}H}** [100.62 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) 0.5 (s, Si(*C*H$_3$)$_3$), 0.7 (s, Si(*C*H$_3$)$_3$), 24.0 (m, P(*C*H$_3$)$_3$), 24.3 (m, P(*C*H$_3$)$_3$), 30.6 (s, ^{t}Bu-*C*H$_3$), 31.3 (s, *C*H(SiMe$_3$)$_2$), 34.1 (s, ^{t}Bu-*C*Me$_3$), 117.6 (br. m, *p*-BAr^{F}-*C*), 121.8 (s, *m*-*C*$_{\text{Tbb}}$), 124.8 (q, *C*F$_3$, $^{1}J_{\text{19F-13C}}$ = 272 Hz), 129.5 (br. q, *m*-BAr^{F}-*C*, $^{2}J_{\text{19F-13C}}$ = 31.3 Hz), 135.0 (s, *o*-BAr^{F}-*C*), 141.8 (s, *i*-*C*$_{\text{Tbb}}$–Ge), 146.1 (s, *o*-*C*$_{\text{Tbb}}$), 152.9 (s, *p*-*C*$_{\text{Tbb}}$), 162.4 (q, *i*-BAr^{F}-*C*, $^{1}J_{\text{13C-11B}}$ = 49.8 Hz). **^{19}F{^{1}H}** [376.48 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −62.3 (s, C*F*$_3$). **^{29}Si** [59.63 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) 2.5 (m, *Si*Me$_3$), 3.4 (m, *Si*Me$_3$). **^{31}P{^{1}H}** [161.97 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −62.3 (d, 2x *P*Me$_3$, $^{2}J_{\text{31P-31P}}$ = 20.0 Hz), −53.7 (t, 1x *P*Me$_3$, $^{2}J_{\text{31P-31P}}$ = 20.0 Hz). **IR** [KBr, cm^{-1}] ν(Ir–H) 2036, ν(N–H) 3332. **Elemental analysis** calculated for [TbbGe(NHNH$_2$)IrH$_2$(PMe$_3$)$_3$][BAr$^{F}_{4}$] (C$_{65}$H$_{93}$BF$_{24}$GeIrN$_2$P$_3$Si$_4$): C 42.45, H 5.10, N 1.52. Found: C 42.55, H 4.83, N 1.25.

Synthesis of [TbbSn(NHNH$_2$)IrH$_2$(PMe$_3$)$_3$][BAr$^{F}_{4}$] (**8**). [TbbSnIrH(PMe$_3$)$_3$][BAr$^{F}_{4}$] (**2**) (33.2 mg, 17.9 µmol, 1.0 equiv) is dissolved in benzene (0.30 mL) and *o*-DFB (0.30 mL). Subsequently N$_2$H$_4$ solution (17.9 µL, 1 M in thf, 17.9 µmol, 1.0 equiv) is added and the dark brown suspension discolors over ten minutes to a pale yellow. After another ten minutes the pale yellow solution is dried under reduced pressure. The resulting solid is washed with *n*-pentane (2 x 1.00 mL) to yield 30.5 mg colorless solid of [TbbSn(NHNH$_2$)IrH$_2$(PMe$_3$)$_3$][BAr$^{\mathrm{F}}_4$] (**8**) (16.2 µmol, 90 %). *Analytical data.* **^{1}H** [400.11 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −13.47 (m + sat., 2H, Ir*H*, $^2J_{\mathrm{Sn\text{-}H}}$ = 251 Hz), 0.09 (s, 36H, Si(C*H*$_3$)$_3$), 0.97 (s, 2H, C*H*(SiMe$_3$)$_2$), 1.23 (s, 9H, ^{t}Bu-*H*), 1.28 (m, 9H, PMe$_3$-*H*), 1.37 (m, 18H, PMe$_3$-*H*), 3.11 (br., 2H, N*H*$_2$), 3.52 (very br., 1H, possibly N*H*), 6.83 (s, 2H, *m*-Tbb*H*), 7.64 (br. s, 4H, *p*-BAr$^{\mathrm{F}}$-*H*), 8.34 (br. m, 8H, *o*-BAr$^{\mathrm{F}}$-*H*). **^{11}B** [96.29 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −6.0 (s, *B*Ar$^{\mathrm{F}}_4$). **^{13}C{^{1}H}** [100.62 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) 0.4 (s, Si(*C*H$_3$)$_3$), 24.7 (m, P(*C*H$_3$)$_3$), 25.2 (m, P(*C*H$_3$)$_3$), 30.6 (s, ^{t}Bu-*C*H$_3$), 34.2 (s, ^{t}Bu-*C*Me$_3$), 34.9 (s, *C*H(SiMe$_3$)$_2$), 117.6 (br. m, *p*-BAr$^{\mathrm{F}}$-*C*), 122.1 (s, *m*-*C*$_{\mathrm{Tbb}}$), 124.9 (q, *C*F$_3$, $^1J_{\mathrm{19F\text{-}13C}}$ = 273 Hz), 129.5 (br. q, *m*-BAr$^{\mathrm{F}}$-*C*, $^2J_{\mathrm{19F\text{-}13C}}$ = 32.1 Hz), 135.0 (s, *o*-BAr$^{\mathrm{F}}$-*C*), 147.5 (s, *o*-*C*$_{\mathrm{Tbb}}$), 149.8 (m, *i*-*C*$_{\mathrm{Tbb}}$–Sn), 153.1 (s, *p*-*C*$_{\mathrm{Tbb}}$), 162.4 (q, *i*-BAr$^{\mathrm{F}}$-*C*, $^1J_{\mathrm{13C\text{-}11B}}$ = 49.8 Hz). **^{19}F{^{1}H}** [376.48 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −62.2 (s, C*F*$_3$). **^{29}Si** [59.63 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) 2.9 (m, *Si*Me$_3$). **^{31}P{^{1}H}** [121.49 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −60.1 (d + sat., 2x *P*Me$_3$, $^2J_{\mathrm{31P\text{-}31P}}$ = 15.9 Hz, $^2J_{\mathrm{119Sn\text{-}31P}}$ = 126 Hz), −45.5 (t + sat., 1x *P*Me$_3$, $^2J_{\mathrm{31P\text{-}31P}}$ = 15.9 Hz, $^2J_{\mathrm{117Sn\text{-}31P}}$ = 1604 Hz, $^2J_{\mathrm{119Sn\text{-}31P}}$ = 1678 Hz). **^{119}Sn** [111.92 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) 604 (br. d, Tbb*Sn*(NHNH$_2$)Ir, $^2J_{\mathrm{119Sn\text{-}31P}}$ = 1682 Hz). **^{119}Sn{^{1}H}** [111.92 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) 604 (dt, Tbb*Sn*(NHNH$_2$)Ir, $^2J_{\mathrm{119Sn\text{-}31P}}$ = 1682 Hz, $^2J_{\mathrm{119Sn\text{-}31P}}$ = 125 Hz). **IR** [KBr, cm^{-1}] ν(Ir–H) 2017, ν(N–H) 3335. **Elemental analysis** calculated for [TbbSn(NHNH$_2$)IrH$_2$(PMe$_3$)$_3$][BAr$^{\mathrm{F}}_4$] ($C_{65}H_{93}BF_{24}SnIrN_2P_3Si_4$): C 41.41, H 4.97, N 1.49. Found: C 41.55, H 4.75, N 0.85.

Synthesis of [TbbGe(OH)IrH$_2$(PMe$_3$)$_3$][BAr$^{\mathrm{F}}_4$] (**9**). [TbbGeIrH(PMe$_3$)$_3$][BAr$^{\mathrm{F}}_4$] (**1**) (29.2 mg, 16.2 µmol, 1.0 equiv) and BaCl$_2$·H$_2$O (7.31 mg, 32.3 µmol, 2.0 equiv) are weighed in and mixed up. Subsequently *o*-DFB (1.00 mL) is added, and the dark red suspension is stirred at ambient temperature for one hour. The suspension becomes colorless and cloudy. The reaction mixture is filtered through a syringe filter and the solvent is removed under reduced pressure. The resulting solid is co-evaporated with *n*-pentane to yield 28.1 mg colorless solid of [TbbGe(OH)IrH$_2$(PMe$_3$)$_3$][BArF$_4$] (**9**) (15.4 µmol, 95 %). Crystals for X-ray diffraction could be obtained out of a concentrated *o*-DFB solution layered with *n*-pentane at −38 °C. *Analytical data.* **^{1}H** [400.11 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −12.69 (m, 2H, Ir*H*), 0.07 (s, 36H, Si(C*H*$_3$)$_3$), 1.19 (s, 9H, ^{t}Bu-*H*), 1.25 (m, 9H, PMe$_3$-*H*), 1.34 (m, 18H, PMe$_3$-*H*), 1.36 (s, 2H, C*H*(SiMe$_3$)$_2$), 5.29 (d, 1H, O*H*, $^4J_{\mathrm{31P\text{-}1H}}$ = 3.8 Hz), 6.79 (s, 2H, *m*-Tbb*H*), 7.62 (br. s, 4H, *p*-BAr$^{\mathrm{F}}$-*H*), 8.32 (br. m, 8H, *o*-BAr$^{\mathrm{F}}$-*H*). **^{11}B** [96.29 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −6.0 (s, *B*Ar$^{\mathrm{F}}_4$). **^{13}C{^{1}H}** [100.62 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) 0.2 (s, Si(*C*H$_3$)$_3$), 23.4 (m, P(*C*H$_3$)$_3$), 23.8 (m, P(*C*H$_3$)$_3$), 30.5 (s, ^{t}Bu-*C*H$_3$), 32.0 (s, *C*H(SiMe$_3$)$_2$), 34.3 (s, ^{t}Bu-*C*Me$_3$), 117.6 (m, *p*-BAr$^{\mathrm{F}}$-*C*), 122.1 (s, *m*-*C*$_{\mathrm{Tbb}}$), 124.9 (q, *C*F$_3$, $^1J_{\mathrm{19F\text{-}13C}}$ = 272 Hz), 129.5 (br. q, *m*-BAr$^{\mathrm{F}}$-*C*, $^2J_{\mathrm{19F\text{-}13C}}$ = 31.4 Hz), 135.0 (s, *o*-BAr$^{\mathrm{F}}$-*C*), 145.0 (s, *o*-*C*$_{\mathrm{Tbb}}$), 147.1 (s, *i*-*C*$_{\mathrm{Tbb}}$–Ge), 154.4 (s, *p*-*C*$_{\mathrm{Tbb}}$), 162.4 (q, *i*-BAr$^{\mathrm{F}}$-*C*, $^1J_{\mathrm{13C\text{-}11B}}$ = 49.8 Hz). **^{19}F{^{1}H}** [376.48 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −62.3 (s, C*F*$_3$). **^{29}Si** [59.63 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) 3.6 (m, *Si*Me$_3$). **^{31}P{^{1}H}** [161.97 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −58.7 (d, 2x *P*Me$_3$, $^2J_{\mathrm{31P\text{-}31P}}$ = 20.6 Hz), −51.9 (t, 1x *P*Me$_3$, $^2J_{\mathrm{31P\text{-}31P}}$ = 20.6 Hz). **IR** [KBr, cm^{-1}] ν(Ir–H) 2051, ν(O–H) 3593. **Elemental analysis** calculated for [TbbGe(OH)IrH$_2$(PMe$_3$)$_3$][BArF$_4$] ($C_{65}H_{91}BF_{24}GeIrOP_3Si_4$): C 42.77, H 5.03. Found: C 42.79, H 4.75.

Synthesis of [TbbSn(OH)IrH$_2$(PMe$_3$)$_3$][BAr$^{\mathrm{F}}_4$] (**10**). [TbbSnIrH(PMe$_3$)$_3$][BAr$^{\mathrm{F}}_4$] (**2**) (40.0 mg, 21.6 µmol, 1.0 equiv) and BaCl$_2$·H$_2$O (9.77 mg, 43.2 µmol, 2.0 equiv) are weighed in and mixed up. Subsequently *o*-DFB (1.00 mL) is added and the dark red suspension is stirred at ambient temperature for two hours. The suspension becomes pale yellow and cloudy. The reaction mixture is filtered through a syringe filter and the solvent is removed under reduced pressure. The resulting solid is co-evaporated with *n*-pentane to yield 39.1 mg pale yellow solid of [TbbSn(OH)IrH$_2$(PMe$_3$)$_3$][BAr$^{\mathrm{F}}_4$] (**10**) (20.9 µmol, 97 %).

Crystals for X-ray diffraction could be obtained out of a concentrated *o*-DFB solution layered with *n*-pentane at −38 °C. *Analytical data.* **^{1}H** [400.11 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −13.29 (m, 2H, Ir*H*), 0.07 (s, 36H, Si(C*H*$_3$)$_3$), 1.04 (s, 2H, C*H*(SiMe$_3$)$_2$), 1.20 (s, 9H, ^{t}Bu-*H*), 1.26 (m, 9H, PMe$_3$-*H*), 1.37 (m, 18H, PMe$_3$-*H*), 4.11 (br. s, 1H, O*H*), 6.86 (s, 2H, *m*-Tbb*H*), 7.63 (br. s, 4H, *p*-BAr^F-*H*), 8.32 (br. m, 8H, *o*-BAr^F-*H*). **^{11}B** [96.29 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −6.0 (s, *B*Ar$^F_4$). **^{13}C{^{1}H}** [100.62 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) 0.0 (s, Si(*C*H$_3$)$_3$), 24.4 (m, P(*C*H$_3$)$_3$), 24.8 (m, P(*C*H$_3$)$_3$), 30.5 (s, ^{t}Bu-*C*H$_3$), 34.4 (s, ^{t}Bu-*C*Me$_3$), 35.2 (s, *C*H(SiMe$_3$)$_2$), 117.6 (m, *p*-BAr^F-*C*), 122.6 (s, *m*-*C*$_{\text{Tbb}}$), 124.9 (q, *C*F$_3$, $^1J_{\text{19F-13C}}$ = 272 Hz), 129.5 (br. q, *m*-BAr^F-*C*, $^2J_{\text{19F-13C}}$ = 31.6 Hz), 135.0 (s, *o*-BAr^F-*C*), 146.5 (s, *o*-*C*$_{\text{Tbb}}$), 154.3 (s, *p*-*C*$_{\text{Tbb}}$), 155.4 (s, *i*-*C*$_{\text{Tbb}}$–Sn), 162.4 (q, *i*-BAr^F-*C*, $^1J_{\text{13C-11B}}$ = 49.8 Hz). **^{19}F{^{1}H}** [376.48 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −62.3 (s, C*F*$_3$). **^{29}Si** [59.63 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) 2.9 (m, *Si*Me$_3$). **^{31}P{^{1}H}** [161.97 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −56.3 (d + sat., 2x *P*Me$_3$, $^2J_{\text{31P-31P}}$ = 15.7 Hz, $^2J_{\text{119Sn-31P}}$ = 124 Hz), −43.8 (t, 1x *P*Me$_3$, $^2J_{\text{31P-31P}}$ = 15.7 Hz, $^2J_{\text{119Sn-31P}}$ = 1714 Hz). **^{119}Sn** [111.92 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) 648 (br. m, Tbb*Sn*(OH)Ir). **^{119}Sn{^{1}H}** [111.92 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) 648 (dt, Tbb*Sn*(OH)Ir, $^2J_{\text{119Sn-31P}}$ = 1730 Hz, $^2J_{\text{119Sn-31P}}$ = 128 Hz). **IR** [KBr, cm^{-1}] ν(Ir−H) 2024, ν(O−H) 3614. **Elemental analysis** calculated for [TbbSn(OH)IrH$_2$(PMe$_3$)$_3$][BAr$^F_4$] (C$_{65}$H$_{91}$BF$_{24}$SnIrOP$_3$Si$_4$): C 41.72, H 4.90. Found: C 41.45, H 4.84.

Synthesis of [TbbGe(X)IrH$_2$(PMe$_3$)$_3$][BAr$^F_4$] (**11a**, **11b**). **11a, X = Cl**: [TbbGeIrH(PMe$_3$)$_3$][BAr$^F_4$] (**3**) (30.0 mg, 16.6 µmol, 1.0 equiv) is dissolved in *o*-DFB (0.20 mL). Subsequently HCl·OEt$_2$ (8.30 µL, 2 M in diethyl ether, 16.6 µmol, 1.0 equiv) is added and the dark red suspension turns yellow immediately. After five minutes at ambient temperature the yellow solution is dried under reduced pressure. The resulting solid is washed with *n*-pentane (2 x 1.00 mL) to yield 28.6 mg pale yellow solid of [TbbGeClIrH$_2$(PMe$_3$)$_3$][BAr$^F_4$] (**11a**) (15.5 µmol, 93 %). Suitable crystals for X-ray diffraction could be obtained out of a concentrated *o*-DFB solution layered with *n*-pentane at −38 °C. Unfortunately, the crystals were always twinned. **11b, X = Br**: TbbGeBrIrH(PMe$_3$)$_3$ (**1**) (23.6 mg, 23.1 µmol, 1.0 equiv) is dissolved in benzene(-d$_6$) (0.30 mL) and *o*-DFB (0.05 mL). The orange solution is directly added to *Brookharts* acid ([H(OEt$_2$)$_2$][BAr$^F_4$], 22.2 mg, 21.9 µmol, 0.95 equiv) whereby the solution turns yellow immediately. The solvent is removed under reduced pressure and the resulting solid is washed with *n*-pentane (2×1.00 mL) to yield 31.7 mg (16.8 µmol, 77 %) [TbbGe(Br)IrH$_2$(PMe$_3$)$_3$][BAr$^F_4$] (**11b**) as a pale yellow solid. Via NMR-spectroscopy a purity about 70 % can be determined which is why the synthesis route is not preferred. The following NMR characterization was carried out with the chloride derivative **11a**. *Analytical data.* **^{1}H** [400.11 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −12.21 (m, 2H, Ir*H*), 0.12 (s, 36H, Si(C*H*$_3$)$_3$), 1.21 (s, 9H, ^{t}Bu-*H*), 1.25 (s, 2H, C*H*(SiMe$_3$)$_2$ under PMe$_3$), 1.27 (m, 9H, PMe$_3$-*H*), 1.32 (m, 18H, PMe$_3$-*H*), 6.79 (s, 2H, *m*-Tbb*H*), 7.62 (br. s, 4H, *p*-BAr^F-*H*), 8.31 (br. m, 8H, *o*-BAr^F-*H*). **^{11}B** [96.29 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −6.0 (s, *B*Ar$^F_4$). **^{13}C{^{1}H}** [100.62 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) 0.5 (s, Si(*C*H$_3$)$_3$), 22.3 (m, P(*C*H$_3$)$_3$), 23.6 (m, P(*C*H$_3$)$_3$), 30.4 (s, ^{t}Bu-*C*H$_3$), 32.8 (s, *C*H(SiMe$_3$)$_2$), 34.3 (s, ^{t}Bu-*C*Me$_3$), 117.5 (m, *p*-BAr^F-*C*), 122.3 (s, *m*-*C*$_{\text{Tbb}}$), 124.9 (q, *C*F$_3$, $^1J_{\text{19F-13C}}$ = 272 Hz), 129.5 (qm, *m*-BAr^F-*C*, $^2J_{\text{19F-13C}}$ = 31.4 Hz), 135.0 (s, *o*-BAr^F-*C*), 144.6 (s, *o*-*C*$_{\text{Tbb}}$), 149.8 (s, *i*-*C*$_{\text{Tbb}}$–Ge), 154.7 (s, *p*-*C*$_{\text{Tbb}}$), 162.4 (q, *i*-BAr^F-*C*, $^1J_{\text{13C-11B}}$ = 49.8 Hz). **^{19}F{^{1}H}** [376.48 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −62.4 (s, C*F*$_3$). **^{29}Si** [59.63 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) 4.5 (m, *Si*Me$_3$). **^{31}P{^{1}H}** [161.97 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −57.5 (d, 2x *P*Me$_3$, $^2J_{\text{31P-31P}}$ = 20.0 Hz), −50.9 (t, 1x *P*Me$_3$, $^2J_{\text{31P-31P}}$ = 20.0 Hz). **IR** [KBr, cm^{-1}] ν(Ir−H) 2031, ν(Ir−H) 2055. **Elemental analysis** calculated for [TbbGeClIrH$_2$(PMe$_3$)$_3$][BAr$^F_4$] (C$_{65}$H$_{90}$BClF$_{24}$GeIrP$_3$Si$_4$): C 42.34, H 4.92. Found: C 42.56, H 4.73.

Synthesis of [TbbSn(X)IrH$_2$(PMe$_3$)$_3$][BAr$^F_4$] (**12a**, **12b**). **12a, X = Cl**: [TbbSnIrH(PMe$_3$)$_3$][BAr$^F_4$] (**4**) (30.0 mg, 16.2 µmol, 1.0 equiv) is dissolved in *o*-DFB (0.20 mL). Subsequently HCl·OEt$_2$ (8.09 µL, 2 M in diethyl ether, 16.2 µmol, 1.0 equiv) is added and the dark brown suspension turns yellow immediately. After five minutes at ambient temperature the yellow solution is dried under reduced pressure. The resulting solid is washed with *n*-pentane (2 x 1.00 mL) to yield 28.8 mg pale yellow solid of [TbbSn(Cl)IrH$_2$(PMe$_3$)$_3$][BAr$^F_4$] (**12a**) (15.2 µmol, 94 %). **12b, X = Br**: TbbSn(Br)IrH(PMe$_3$)$_3$ (**2**) (24.7 mg, 23.1 µmol, 1.0 equiv) is dissolved in benzene(-d$_6$) (0.30 mL) and *o*-DFB (0.05 mL). The red-orange solution is directly added to *Brookhart*s acid ([H(OEt$_2$)$_2$][BAr$^F_4$], 22.2 mg, 21.9 µmol, 0.95 equiv) whereby the solution turns yellow immediately. The solvent is removed under reduced pressure and the resulting solid is washed with *n*-pentane (2×2.00 mL). The solid is dissolved in *o*-DFB (0.20 mL), layered with *n*-pentane (2.00 mL) and stored at −38 °C for crystallization to yield 25.7 mg (13.3 µmol, 61 %) [TbbSnBrIrH$_2$(PMe$_3$)$_3$][BAr$^F_4$] (**12b**) as a yellow solid. The obtained crystals were suitable for X-ray diffraction. **Elemental analysis** calculated for [TbbSnBrIrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] ($C_{65}H_{90}BBrF_{24}SnIrP_3Si_4$): C 40.36, H 4.69. Found: C 40.72, H 4.49. The following NMR characterization was carried out with the chloride derivative. *Analytical data.* **^{1}H** [400.11 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −12.98 (m + sat., 2H, Ir*H*, $^{2}J_{\mathrm{119Sn-H}}$ = 255 Hz), 0.12 (s, 36H, Si(C*H*$_3$)$_3$), 0.95 (s, 2H, C*H*(SiMe$_3$)$_2$), 1.21 (s, 9H, ^{t}Bu-*H*), 1.27 (m, 9H, PMe$_3$-*H*), 1.32 (m, 18H, PMe$_3$-*H*), 6.89 (s, 2H, *m*-Tbb*H*), 7.63 (br. s, 4H, *p*-BAr^F-*H*), 8.31 (br. m, 8H, *o*-BAr^F-*H*). **^{11}B** [96.29 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −6.0 (s, *B*Ar$^F_4$). **^{13}C{^{1}H}** [100.62 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) 0.2 (s, Si(*C*H$_3$)$_3$), 23.8 (m, P(*C*H$_3$)$_3$), 24.1 (m, P(*C*H$_3$)$_3$), 30.5 (s, ^{t}Bu-*C*H$_3$), 34.5 (s, ^{t}Bu-*C*Me$_3$), 36.0 (s, *C*H(SiMe$_3$)$_2$), 117.6 (br. m, *p*-BAr^F-*C*), 123.0 (s, *m*-C_{Tbb}), 124.8 (q, *C*F$_3$, $^{1}J_{\mathrm{19F-13C}}$ = 272 Hz), 129.5 (qm, *m*-BAr^F-*C*, $^{2}J_{\mathrm{19F-13C}}$ = 31.5 Hz), 135.0 (s, *o*-BAr^F-*C*), 146.2 (s, *o*-C_{Tbb}), 154.7 (s, *p*-C_{Tbb}), 157.4 (s, *i*-C_{Tbb}–Sn), 162.4 (q, *i*-BAr^F-*C*, $^{1}J_{\mathrm{13C-11B}}$ = 49.8 Hz). **^{19}F{^{1}H}** [376.48 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −62.3 (s, C*F*$_3$). **^{29}Si** [59.63 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) 3.9 (m, *Si*Me$_3$). **^{31}P{^{1}H}** [121.49 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −55.4 (d + sat., 2x *P*Me$_3$, $^{2}J_{\mathrm{31P-31P}}$ = 14.7 Hz, $^{2}J_{\mathrm{Sn-31P}}$ = 132 Hz), −42.5 (t + sat., 1x *P*Me$_3$, $^{2}J_{\mathrm{31P-31P}}$ = 14.7 Hz, $^{2}J_{\mathrm{117Sn-31P}}$ = 1714 Hz, $^{2}J_{\mathrm{119Sn-31P}}$ = 1777 Hz). **^{119}Sn** [111.92 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) 772 (br. d, Tbb*Sn*ClIr, $^{2}J_{\mathrm{119Sn-31P}}$ = 1785 Hz). **^{119}Sn{^{1}H}** [111.92 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) 772 (dt, Tbb*Sn*ClIr, $^{2}J_{\mathrm{119Sn-31P}}$ = 1784 Hz, $^{2}J_{\mathrm{119Sn-31P}}$ = 126 Hz). **IR** [KBr, cm^{-1}] ν(Ir−H) 1970, ν(Ir−H) 2023. **Elemental analysis** calculated for [TbbSnClIrH$_2$(PMe$_3$)$_3$][BAr$^F_4$] ($C_{65}H_{90}BClF_{24}SnIrP_3Si_4$): C 41.31, H 4.80. Found: C 40.82, H 4.44.

Synthesis of [TbbGe(H)IrH$_2$(PMe$_3$)$_3$][BAr$^F_4$] (**13**). [TbbGeIrH(PMe$_3$)$_3$][BAr$^F_4$] (**3**) (20.7 mg, 11.5 µmol, 1.0 equiv) is dissolved in benzene(-d$_6$) (0.30 mL) and *o*-DFB (0.05 mL) and the dark red solution is transferred into a *J. Young* NMR tube. The solution is degassed with one “freeze-pump-thaw” cycle and the atmosphere is changed with dihydrogen, whereby the solution becomes slightly brighter. After 24 hours at ambient temperature the solution is light yellow. The solvent is removed under reduced pressure. The yellow solid is dissolved in *o*-DFB (0.20 mL), layered with *n*-pentane (2.00 mL) and stored at −38 °C for crystallization. The resulting orange crystals are dried under reduced pressure to yield 18.3 mg of [TbbGe(H)IrH$_2$(PMe$_3$)$_3$][BAr$^F_4$] (**13**) (10.1 µmol, 88 %). The obtained crystals were suitable for X-ray diffraction. *Analytical data.* **^{1}H** [400.11 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −11.90 (m, 2H, Ir*H*), 0.06 (s, 36H, Si(C*H*$_3$)$_3$), 1.15 (s, 2H, C*H*(SiMe$_3$)$_2$), 1.21 (m, 9H, PMe$_3$-*H*), 1.24 (s, 9H, ^{t}Bu-*H*), 1.27 (m, 18H, PMe$_3$-*H*), 6.83 (s, 2H, *m*-Tbb*H*), 7.63 (br. s, 4H, *p*-BAr^F-*H*), 8.33 (br. m, 8H, *o*-BAr^F-*H*), 13.98 (dt, 1H, Ge*H*, $^{2}J_{\mathrm{31P-1H}}$ = 32.6 Hz, $^{2}J_{\mathrm{31P-1H}}$ = 7.6 Hz). **^{11}B** [96.29 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −6.0 (s, *B*Ar$^F_4$). **^{13}C{^{1}H}** [100.62 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) 0.2 (s, Si(*C*H$_3$)$_3$), 22.3 (m, P(*C*H$_3$)$_3$), 23.9 (m, P(*C*H$_3$)$_3$), 30.6 (s, ^{t}Bu-*C*H$_3$), 31.9 (s, *C*H(SiMe$_3$)$_2$), 34.3 (s, ^{t}Bu-*C*Me$_3$), 117.6 (br. m, *p*-BAr^F-*C*), 122.1 (s, *m*-C_{Tbb}), 124.9 (q, *C*F$_3$, $^{1}J_{\mathrm{19F-13C}}$ = 273 Hz), 129.5 (br. q, *m*-BAr^F-*C*, $^{2}J_{\mathrm{19F-13C}}$ = 31.5 Hz), 135.0 (s, *o*-BAr^F-*C*), 144.0 (br. m, *i*-C_{Tbb}–Ge), 145.2 (s, *o*-C_{Tbb}), 154.1 (s, *p*-C_{Tbb}), 162.4 (q, *i*-BAr^F-*C*, $^{1}J_{\mathrm{13C-11B}}$ = 49.8 Hz). **^{19}F{^{1}H}** [376.48 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −62.3 (s, C*F*$_3$). **^{29}Si** [59.63 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) 3.0 (m, *Si*Me$_3$). **^{31}P{^{1}H}** [161.97 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −54.0 (d, 2x *P*Me$_3$, $^{2}J_{\mathrm{31P-31P}}$ = 18.7 Hz), −48.8 (t, 1x *P*Me$_3$, $^{2}J_{\mathrm{31P-31P}}$ = 18.7 Hz). **Elemental analysis** calculated for [TbbGeHIrH$_2$(PMe$_3$)$_3$][BAr$^F_4$] ($C_{65}H_{91}BF_{24}GeIrP_3Si_4$): C 43.15, H 5.07. Found: C 43.13, H 4.82.

Synthesis of [TbbSnIr(µ-H$_3$)(PMe$_3$)$_3$][BAr$^F_4$] (**14**). [TbbSnIrH(PMe$_3$)$_3$][BAr$^F_4$] (**4**) (37.0 mg, 20.0 µmol, 1.0 equiv) is dissolved in toluene(-d$_8$) (0.10 mL) and *o*-DFB (0.30 mL) and the dark brown solution is transferred into a *J. Young* NMR tube. The solution is degassed with one “freeze-pump-thaw” cycle and the atmosphere is changed with dihydrogen, whereby the solution becomes immediately brighter and orange to form quantitatively (via NMR spectroscopy) [TbbSnIrH$_3$(PMe$_3$)$_3$][BAr$^F{}_4$] (**14**). The NMR signals were assigned in the reaction mixture at low temperature. *Analytical data.* **^{1}H** [500.13 MHz, 243.20 K, toluene-d$_8$ + *o*-DFB]: δ (ppm) −7.94 (m + sat., 3H, Ir*H*, $J_{\text{Sn-H}}$ = 265 Hz), 0.10 (s, 36H, Si(C*H*$_3$)$_3$), 0.61 (s, 2H, C*H*(SiMe$_3$)$_2$), 1.30 (s, 9H, ^{t}Bu-*H*), 1.51 (m, 27H, PMe$_3$-*H*), 6.96 (s, 2H, *m*-Tbb*H*), 7.50 (br. s, 4H, *p*-BAr^F-*H*), 8.33 (br. m, 8H, *o*-BAr^F-*H*). **^{11}B{^{1}H}** [160.46 MHz, 243.20 K, toluene-d$_8$ + *o*-DFB]: δ (ppm) −6.0 (s, *B*Ar$^F{}_4$). **^{13}C{^{1}H}** [125.76 MHz, 243.20 K, toluene-d$_8$ + *o*-DFB]: δ (ppm) 0.4 (s, Si(*C*H$_3$)$_3$), 21.9 (m, P(*C*H$_3$)$_3$), 30.8 (s, ^{t}Bu-*C*H$_3$), 31.8 (s, *C*H(SiMe$_3$)$_2$), 34.1 (s, ^{t}Bu-*C*Me$_3$), 117.4 (br. m, *p*-BAr^F-*C*), 123.2 (s, *m*-*C*$_{\text{Tbb}}$), 124.7 (q, *C*F$_3$, $^1J_{\text{19F-13C}}$ = 272 Hz), 129.5 (q, *m*-BAr^F-*C*, $^2J_{\text{19F-13C}}$ = 31.6 Hz), 134.9 (s, *o*-BAr^F-*C*), 147.1 (s, *o*-*C*$_{\text{Tbb}}$), 152.3 (s, *p*-*C*$_{\text{Tbb}}$), 162.4 (q, *i*-BAr^F-*C*, $^1J_{\text{13C-11B}}$ = 49.8 Hz), 173.3 (s, *i*-*C*$_{\text{Tbb}}$–Sn). **^{19}F{^{1}H}** [282.40 MHz, 299.20 K, toluene-d$_8$ + *o*-DFB]: δ (ppm) −63.0 (s, C*F*$_3$). **^{29}Si** [99.36 MHz, 243.20 K, toluene-d$_8$ + *o*-DFB]: δ (ppm) 1.9 (br. m, *Si*Me$_3$). **^{31}P{^{1}H}** [202.46 MHz, 243.20 K, toluene-d$_8$ + *o*-DFB]: δ (ppm) −45.2 (s, *P*Me$_3$). **^{119}Sn** [186.50 MHz, 243.20 K, toluene-d$_8$ + *o*-DFB]: δ (ppm) 1592 (br. s, Tbb*Sn*Ir).

Synthesis of [TbbSn(H)IrH$_2$(PMe$_3$)$_3$][BAr$^F{}_4$] (**15**). [TbbSnIrH(PMe$_3$)$_3$][BAr$^F{}_4$] (**4**) (20.7 mg, 11.2 µmol, 1.0 equiv) is dissolved in benzene(-d$_6$) (0.30 mL) and *o*-DFB (0.05 mL) and the dark brown solution is transferred into a *J. Young* NMR tube. The solution is degassed with one "freeze-pump-thaw" cycle and the atmosphere is changed with dihydrogen, whereby the solution becomes immediately brighter and orange to form quantitatively (via NMR spectroscopy) [TbbSnIr(H)$_3$(PMe$_3$)$_3$][BAr$^F{}_4$] (**14**). After one week at ambient temperature compound **14** reacts almost completely to form the main product [TbbSn(H)IrH$_2$(PMe$_3$)$_3$][BAr$^F{}_4$] (**15**) (about 75 % via ^{1}H NMR spectrum) and at least one unknown by-product. The yield was not determined due to these circumstances. The NMR signals were assigned in the reaction mixture. *Analytical data.* **^{1}H** [400.11 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −12.68 (m, 2H, Ir*H*, $^2J_{\text{119Sn-H}}$ = 195 Hz), 0.06 (s, 36H, Si(C*H*$_3$)$_3$), 0.64 (s, 2H, C*H*(SiMe$_3$)$_2$), 1.24 (s, 9H, ^{t}Bu-*H*), 1.26 (m, 9H, PMe$_3$-*H*), 1.29 (m, 18H, PMe$_3$-*H*), 6.89 (s, 2H, *m*-Tbb*H*), 7.63 (br. s, 4H, *p*-BAr^F-*H*), 8.30 (br. m, 8H, *o*-BAr^F-*H*), 18.59 (dt + sat., 1H, Sn*H*, $^1J_{\text{119Sn-1H}}$ = 772 Hz, $^2J_{\text{31P-1H}}$ = 37.5 Hz, $^2J_{\text{31P-1H}}$ = 4.7 Hz). **^{11}B** [96.29 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −6.1 (s, *B*Ar$^F{}_4$). **^{13}C{^{1}H}** [125.76 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) 0.0 (s, Si(*C*H$_3$)$_3$), 23.8 (m, P(*C*H$_3$)$_3$), 24.4 (m, P(*C*H$_3$)$_3$), 30.7 (s, ^{t}Bu-*C*H$_3$), 34.4 (s, ^{t}Bu-*C*Me$_3$), 35.0 (s, *C*H(SiMe$_3$)$_2$), 117.6 (br. m, *p*-BAr^F-*C*), 122.4 (s, *m*-*C*$_{\text{Tbb}}$), 124.8 (q, *C*F$_3$, $^1J_{\text{19F-13C}}$ = 272 Hz), 129.5 (br. q, *m*-BAr^F-*C*, $^2J_{\text{19F-13C}}$ = 33.1 Hz), 135.0 (s, *o*-BAr^F-*C*), 146.8 (s, *o*-*C*$_{\text{Tbb}}$), 150.3 (s, *i*-*C*$_{\text{Tbb}}$–Sn), 153.8 (s, *p*-*C*$_{\text{Tbb}}$), 162.4 (q, *i*-BAr^F-*C*, $^1J_{\text{13C-11B}}$ = 49.8 Hz). **^{19}F{^{1}H}** [376.48 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −62.8 (s, C*F*$_3$). **^{29}Si** [59.63 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) 2.7 (m, *Si*Me$_3$). **^{31}P{^{1}H}** [121.49 MHz, 299.20 K, benzene-d$_6$ + *o*-DFB]: δ (ppm) −54.9 (d + sat., 2x *P*Me$_3$, $^2J_{\text{31P-31P}}$ = 15.9 Hz, $^2J_{\text{119Sn-31P}}$ = 104 Hz), −41.6 (t + sat., 1x *P*Me$_3$, $^2J_{\text{31P-31P}}$ = 15.9 Hz, $^2J_{\text{119Sn-31P}}$ = 1509 Hz). **^{119}Sn** [186.50 MHz, 299.20 K, benzene-d$_6$]: δ (ppm) 1013 (dd, Tbb*Sn*(H)Ir, $^2J_{\text{119Sn-31P}}$ = 1496 Hz, $^1J_{\text{119Sn-1H}}$ = 775 Hz). **^{119}Sn{^{1}H}** [186.50 MHz, 299.20 K, benzene-d$_6$]: δ (ppm) 1013 (d, Tbb*Sn*(H)Ir, $^2J_{\text{119Sn-31P}}$ = 1504 Hz).

TbbGeHIrH(PMe$_3$)$_3$ (**16**). **Note:** Since the thermodynamic product (TbbGeH)IrH(PMe$_3$)$_3$ already reacts in daylight to the light-induced, kinetic product TbbGe–IrH$_2$(PMe$_3$)$_3$ (**17**), work must be carried out largely in the absence of light. **Method A:** To a mixture of (TbbGeBr)IrH(PMe$_3$)$_3$ (**1**) (25.0 mg, 24.4 µmol, 1.0 equiv) and potassium triethylborohydride (3.37 mg, 24.4 µmol, 1.0 equiv) is added directly benzene (0.20 mL). After shaking for one minute the yellow, slightly turbid solution is freed from all volatiles under reduced pressure and it is co-evaporated with *n*-pentane (0.50 mL). The crude product is dissolved in *n*-pentane (1.00 mL) and filtered through a syringe filter. 21.0 mg of a product mixture of (TbbGeH)IrH(PMe$_3$)$_3$ (**16**) and TbbGe–IrH$_2$(PMe$_3$)$_3$ (**17**) in a 50:50 ratio is obtained. The assignment of the NMR signals was carried out in the product mixture. **Method B:** Starting from [TbbGeIrH(PMe$_3$)$_3$][BAr$^F{}_4$] (**3**) (30.0 mg, 16.6 µmol, 1.0 equiv) and potassium triethylborohydride (2.29 mg, 16.6 µmol, 1.0 equiv) in a mixture of benzene (0.30 mL) and *o*-DFB (0.05 mL) at room temperature the product mixture of (TbbGeH)IrH(PMe$_3$)$_3$ (**16**) and TbbGeIrH$_2$(PMe$_3$)$_3$ (**17**) can also be prepared. *Analytical data.* **^{1}H** [600.13 MHz, 273.20 K, toluene-d$_8$]: δ (ppm) −10.79 (m, 1H, Ir*H*), 0.35 (s, 36H, Si(C*H*$_3$)$_3$), 1.46 (s, 9H, ^{t}Bu-*H*), 1.58 (br. m, 27H, PMe$_3$-*H*), 3.04 (s, 2H, C*H*(SiMe$_3$)$_2$), 6.95 (s, 2H, *m*-Tbb*H*), 12.04 (dq, 1H, Ge*H*, $^{3}J_{31P\text{-}H}$ = 13.6 Hz, $^{3}J_{H\text{-}H}$ = 3.5 Hz). **^{13}C{^{1}H}** [150.92 MHz, 273.20 K, toluene-d$_8$]: δ (ppm) 0.8 (s, Si(*C*H$_3$)$_3$), 27.8 (s, *C*H(SiMe$_3$)$_2$), 29.0 (br., P(*C*H$_3$)$_3$), 31.3 (s, ^{t}Bu-*C*H$_3$), 34.1 (s, ^{t}Bu-*C*Me$_3$), 120.9 (s, *m-C*$_{\text{Tbb}}$), 144.9 (s, *o-C*$_{\text{Tbb}}$), 148.2 (s, *p-C*$_{\text{Tbb}}$), 153.3 (s, *i-C*$_{\text{Tbb}}$–Ge). **^{29}Si** [119.23 MHz, 273.20 K, toluene-d$_8$]: δ (ppm) 2.6 (m, *Si*Me$_3$). **^{31}P{^{1}H}** [242.94 MHz, 273.20 K, toluene-d$_8$]: δ (ppm) −42.1 (br. s, *P*Me$_3$).

TbbGeIrH$_2$(PMe$_3$)$_3$ (**17**). To a mixture of (TbbGeBr)IrH(PMe$_3$)$_3$ (**1**) (22.0 mg, 21.5 µmol, 1.0 equiv) and potassium triethylborohydride (2.97 mg, 21.5 µmol, 1.0 equiv) is added directly benzene (0.20 mL). After shaking for one minute the yellow, slightly turbid solution is freed from all volatiles under reduced pressure. It is co-evaporated with *n*-pentane (0.50 mL). The product mixture is dissolved in *n*-pentane (1.00 mL) and filtered through a syringe filter. The yellow solution is exposed to a blue LED (460 nm) for two hours at room temperature. The light green solution is concentrated to about one-third volume and stored at −38 °C for crystallization to yield 8.50 mg (8.99 µmol, 42 %) light green crystals of TbbGeIrH$_2$(PMe$_3$)$_3$ (**17**) as product. The obtained single crystals were suitable for X-ray diffraction. *Analytical data.* **^{1}H** [600.13 MHz, 273.20 K, toluene-d$_8$]: δ (ppm) −11.07 (m, 2H, Ir*H*$_2$), 0.18 (s, 2H, C*H*(SiMe$_3$)$_2$), 0.38 (s, 36H, Si(C*H*$_3$)$_3$), 1.33 (m, 9H, PMe$_3$-*H*), 1.42 (m, 18H, PMe$_3$-*H*), 1.60 (s, 9H, ^{t}Bu-*H*), 7.00 (s, 2H, *m*-Tbb*H*). **^{13}C{^{1}H}** [150.92 MHz, 273.20 K, toluene-d$_8$]: δ (ppm) 1.5 (s, Si(*C*H$_3$)$_3$), 22.4 (m, P(CH$_3$)$_3$), 24.8 (s, CH(SiMe3)2), 27.3 (m, P(*C*H$_3$)$_3$), 32.1 (s, ^{t}Bu-*C*H$_3$), 33.8 (s, ^{t}Bu-*C*Me$_3$), 120.4 (s, *m-C*$_{\text{Tbb}}$), 139.1 (s, *o-C*$_{\text{Tbb}}$), 149.4 (s, *p-C*$_{\text{Tbb}}$), 177.5 (dt, , *i-C*$_{\text{Tbb}}$–Ge, $^{3}J_{31P\text{-}13C}$ = 9.7 Hz, $^{3}J_{31P\text{-}13C}$ = 5.8 Hz). **^{29}Si** [119.23 MHz, 273.20 K, toluene-d$_8$]: δ (ppm) 1.9 (m, *Si*Me$_3$). **^{31}P{^{1}H}** [242.94 MHz, 273.20 K, toluene-d$_8$]: δ (ppm) −58.8 (d, 2×*P*Me$_3$, $^{2}J_{31P\text{-}31P}$ = 14.7 Hz), −30.0 (t, 1×*P*Me$_3$, $^{2}J_{31P\text{-}31P}$ = 14.7 Hz). **Elemental analysis** calculated for TbbGe–IrH$_2$(PMe$_3$)$_3$ ($C_{33}H_{78}GeIrP_3Si_4$): C 41.94, H 8.32. Found: C 42.27, H 8.31.

Synthesis of TbbSnIrH$_2$(PMe$_3$)$_3$ (**18**). TbbSnH$_3$ (22.0 mg, 38.5 µmol, 1.0 equiv) and benzyl potassium (5.02 mg, 38.5 µmol, 1.0 equiv) are weighed in and tetrahydrofuran (0.50 mL) is added at room temperature. After two minutes the solvent is removed under reduced pressure and the "TbbSnH$_2$K" anion is dissolved in benzene (0.50 mL) and directly added to (Me$_3$P)$_4$IrCl (20.5 mg, 38.5 µmol, 1.0 equiv). The reaction mixture is stirred for one hour at room temperature, while an orange suspension is formed. The solvent is removed under reduced pressure and the resulting solid is co-evaporated with *n*-pentane (1.00 mL). The dark product is extracted with *n*-pentane (1.00 mL) and filtered through a syringe filter. The orange solution is stored at −38 °C for crystallization. The resulting green-yellow crystals are dried under reduced pressure to yield 20.7 mg of TbbSnIrH$_2$(PMe$_3$)$_3$ (**18**) (20.9 µmol, 54 %). Synthesis of **18** is also possible in reaction of **2** or **4** with potassium triethylborohydride. *Analytical data.* **^{1}H** [400.11 MHz, 299.20 K, benzene-d$_6$]: δ (ppm) −12.10 (m, 2H, Ir*H*$_2$), 0.04 (s, 2H, C*H*(SiMe$_3$)$_2$), 0.35 (s, 36H, Si(C*H*$_3$)$_3$), 1.33 (br. m, 18H, PMe$_3$-*H*), 1.50 (br. m, 9H, PMe$_3$-*H*), 1.52 (s, 9H, ^{t}Bu-*H*), 7.03 (s, 2H, *m*-Tbb*H*). **^{13}C{^{1}H}** [100.62 MHz, 299.20 K, benzene-d$_6$]: δ (ppm) 1.7 (s, Si(*C*H$_3$)$_3$), 24.1 (s, PMe$_3$-*C*H$_3$), 26.3 (s, *C*H(SiMe$_3$)$_2$), 29.1 (s, PMe$_3$-*C*H$_3$), 32.0 (s, ^{t}Bu-*C*H$_3$), 33.8 (s, ^{t}Bu-*C*Me$_3$), 120.8 (s, *m-C*$_{\text{Tbb}}$), 145.0 (s, *o-C*$_{\text{Tbb}}$), 149.9 (s, *p-C*$_{\text{Tbb}}$), 186.3 (m, *i-C*$_{\text{Tbb}}$–Sn). **^{29}Si** [59.63 MHz, 299.20 K, benzene-d$_6$]: δ (ppm) 2.1 (m, *Si*Me$_3$). **^{31}P{^{1}H}** [161.97 MHz, 299.20 K, benzene-d$_6$]: δ (ppm) −60.9 (d, *P*Me$_3$, $^{2}J_{31P\text{-}31P}$ = 12.9 Hz), 24.4 (t, *P*Me$_3$, $^{2}J_{31P\text{-}31P}$ = 12.9 Hz). **^{31}P{^{1}H}** [121.49 MHz, 299.20 K, benzene-d$_6$]: δ (ppm) −60.9 (d + sat., *P*Me$_3$, $^{2}J_{119\text{-}31P}$ = 209 Hz, $^{2}J_{31P\text{-}31P}$ = 12.9 Hz), 24.4 (t + sat., *P*Me$_3$, $^{2}J_{119\text{-}31P}$ = 320 Hz, $^{2}J_{31P\text{-}31P}$ = 12.9 Hz). **^{119}Sn** [111.92 MHz, 299.20 K, benzene-d$_6$]: δ (ppm) 3835 (br. d, Tbb*Sn*Ir, $^{2}J_{119Sn\text{-}31P}$ = 327 Hz). **^{119}Sn{^{1}H}** [111.92 MHz, 299.20 K, benzene-d$_6$]: δ (ppm) 3835 (br. d, Tbb*Sn*Ir, $^{2}J_{119Sn\text{-}31P}$ = 325 Hz). **IR** [KBr, cm^{-1}] ν(Ir–H) 2018. **Elemental analysis** calculated for TbbSn–IrH$_2$(PMe$_3$)$_3$ ($C_{33}H_{78}IrP_3Si_4Sn$): C 39.99, H 7.93. Found: C 40.58, H 7.98.

Synthesis of TbbSnIrH$_2$(PEt$_3$)$_3$ (**19**). TbbSnH$_3$ (150 mg, 262 µmol, 1.0 equiv) and benzyl potassium (34.2 mg, 262 µmol, 1.0 equiv) are weighed in and tetrahydrofuran (2.00 mL) is added at room temperature. After two minutes the solvent is removed under reduced pressure and (Et$_3$P)$_3$IrCl (153 mg, 262 µmol, 1.0 equiv) dissolved in benzene (2.00 mL) is directly added to the "TbbSnH$_2$K" anion and the reaction mixture is stirred for three hours at room temperature, while the solution becomes cloudy and dark orange. The solvent is removed under reduced pressure and the resulting waxy solid is co-evaporated with *n*-pentane (2.00 mL). The dark orange solid is extracted with *n*-pentane (4.00, 4.00, 2.00 mL) and filtered through a syringe filter. Subsequently the dark orange solution is concentrated under reduced pressure till it is oily to be stored at −38 °C for crystallization. The resulting yellow crystals are dried under reduced pressure to yield 223 mg of TbbSn−IrH$_2$(PEt$_3$)$_3$ (**19**) (200 µmol, 76 %). The yielded crystals were suitable for X-ray diffraction. *Analytical data.* **^{1}H** [400.11 MHz, 299.20 K, benzene-d$_6$]: δ (ppm) −13.26 (m, 2H, Ir*H*$_2$), 0.24 (s, 2H, C*H*(SiMe$_3$)$_2$), 0.34 (s, 36H, Si(C*H*$_3$)$_3$), 0.92 (m, 9H, PEt$_3$-C*H*$_3$), 0.97 (m, 18H, PEt$_3$-C*H*$_3$), 1.52 (s, 9H, ^{t}Bu-*H*), 1.77 (m, 12H, PEt$_3$-C*H*$_2$), 1.85 (m, 6H, PEt$_3$-C*H*$_2$), 7.06 (s, 2H, *m*-Tbb*H*). **^{13}C{^{1}H}** [100.62 MHz, 299.20 K, benzene-d$_6$]: δ (ppm) 1.8 (s, Si(*C*H$_3$)$_3$), 9.0 (s, PEt$_3$-*C*H$_3$), 9.4 (br., PEt$_3$-*C*H$_3$), 25.0 (m, PEt$_3$-*C*H$_2$), 27.2 (br. m, PEt$_3$-*C*H$_2$), 27.7 (s, *C*H(SiMe$_3$)$_2$), 32.0 (s, ^{t}Bu-*C*H$_3$), 33.8 (s, ^{t}Bu-*C*Me$_3$), 121.3 (s, *m*-*C*$_{\mathrm{Tbb}}$), 145.3 (s, *o*-*C*$_{\mathrm{Tbb}}$), 149.2 (s, *p*-*C*$_{\mathrm{Tbb}}$), 190.8 (m, *i*-*C*$_{\mathrm{Tbb}}$−Sn). **^{29}Si** [59.63 MHz, 299.20 K, benzene-d$_6$]: δ (ppm) 1.8 (m, *Si*Me$_3$). **^{31}P{^{1}H}** [161.97 MHz, 299.20 K, benzene-d$_6$]: δ (ppm) −26.4 (d, PEt$_3$, $^2J_{\mathrm{31P\text{-}31P}}$ = 7.5 Hz), 62.1 (t, PEt$_3$, $^2J_{\mathrm{31P\text{-}31P}}$ = 7.5 Hz). **^{119}Sn** [111.92 MHz, 299.20 K, benzene-d$_6$]: δ (ppm) 3827 (d, Tbb*Sn*Ir, $^2J_{\mathrm{119Sn\text{-}31P}}$ = 458 Hz). **^{119}Sn{^{1}H}** [111.92 MHz, 299.20 K, benzene-d$_6$]: δ (ppm) 3827 (d, Tbb*Sn*Ir, $^2J_{\mathrm{119Sn\text{-}31P}}$ = 458 Hz). **IR** [KBr, cm^{-1}] ν(Ir–H) 2041. **Elemental analysis** calculated for TbbSn−IrH$_2$(PEt$_3$)$_3$ ($C_{42}H_{96}IrP_3Si_4Sn$): C 45.15, H 8.66. Found: C 45.32, H 8.67.

Synthesis of TbbSnIrH$_2$(CO)(PEt$_3$)$_2$ (**20**). TbbSnIrH$_2$(PEt$_3$)$_3$ (**19**) (50.5 mg, 45.2 µmol, 1.0 equiv) is dissolved in benzene(-d$_6$) (0.40 mL) and transferred into a *J. Young* NMR tube. The solution is degassed with one "freeze-pump-thaw" cycle and the atmosphere is changed with carbon monoxide, whereby the solution suddenly turns turquoise. The solvent is removed under reduced pressure immediately and the resulting solid is co-evaporated with *n*-pentane (1.00 mL) to yield 44.5 mg of TbbSnIrH$_2$(CO)(PEt$_3$)$_2$ (**20**) as a turquoise solid (43.3 µmol, 96 %). Suitable crystals for X-ray diffraction could be obtained out of a slowly evaporated *n*-pentane solution at −38 °C. *Analytical data.* **^{1}H** [400.11 MHz, 299.20 K, benzene-d$_6$]: δ (ppm) −10.49 (ddd, 1H, Ir*H*, $^2J_{\mathrm{31P\text{-}H}}$ = 21.3 Hz, $^2J_{\mathrm{31P\text{-}H}}$ = 15.6 Hz, $^2J_{\mathrm{H\text{-}H}}$ = 3.7 Hz), −9.83 (ddd, 1H, Ir*H*, $^2J_{\mathrm{31P\text{-}H}}$ = 109 Hz, $^2J_{\mathrm{31P\text{-}H}}$ = 17.1 Hz, $^2J_{\mathrm{H\text{-}H}}$ = 3.7 Hz), 0.28 (s, 2H + 18H, C*H*(SiMe$_3$)$_2$ + Si(C*H*$_3$)$_3$), 0.37 (s, 18H, Si(C*H*$_3$)$_3$), 0.76 (m, 9H, PEt$_3$-C*H*$_3$), 0.94 (m, 9H, PEt$_3$-C*H*$_3$), 1.49 (s, 9H, ^{t}Bu-*H*), 1.59 (m, 6H, PEt$_3$-C*H*$_2$), 1.89 (m, 6H, PEt$_3$-C*H*$_2$), 7.04 (s, 2H, *m*-Tbb*H*). **^{13}C{^{1}H}** [100.62 MHz, 299.20 K, benzene-d$_6$]: δ (ppm) 1.2 (s, Si(*C*H$_3$)$_3$), 1.3 (s, Si(*C*H$_3$)$_3$), 7.5 (s, PEt$_3$-*C*H$_3$), 8.3 (s, PEt$_3$-*C*H$_3$), 21.2 (m, PEt$_3$-*C*H$_2$), 24.9 (m, PEt$_3$-*C*H$_2$), 27.6 (s, *C*H(SiMe$_3$)$_2$), 31.8 (s, ^{t}Bu-*C*H$_3$), 34.0 (s, ^{t}Bu-*C*Me$_3$), 121.5 (s, *m*-*C*$_{\mathrm{Tbb}}$), 145.3 (s, *o*-*C*$_{\mathrm{Tbb}}$), 150.3 (s, *p*-*C*$_{\mathrm{Tbb}}$), 178.9 (m, *C*≡O), 182.7 (m, *i*-*C*$_{\mathrm{Tbb}}$−Sn). **^{29}Si** [59.63 MHz, 299.20 K, benzene-d$_6$]: δ (ppm) 2.0 (m, *Si*Me$_3$). **^{31}P{^{1}H}** [161.97 MHz, 299.20 K, benzene-d$_6$]: δ (ppm) −17.1 (d, PEt$_3$, $^2J_{\mathrm{31P\text{-}31P}}$ = 10.5 Hz), 42.9 (d + sat., PEt$_3$, $^2J_{\mathrm{119Sn\text{-}31P}}$ = 336 Hz, $^2J_{\mathrm{31P\text{-}31P}}$ = 10.5 Hz). **^{119}Sn** [111.92 MHz, 299.20 K, benzene-d$_6$]: δ (ppm) 3321 (d, Tbb*Sn*Ir, $^2J_{\mathrm{119Sn\text{-}31P}}$ = 336 Hz). **^{119}Sn{^{1}H}** [111.92 MHz, 299.20 K, benzene-d$_6$]: δ (ppm) 3321 (d, Tbb*Sn*Ir, $^2J_{\mathrm{119Sn\text{-}31P}}$ = 336 Hz). **IR** [KBr, cm^{-1}] ν(CO) 1964, ν(Ir–H) 2075. **Elemental analysis** calculated for TbbSn−IrH$_2$(CO)(PEt$_3$)$_2$ ($C_{37}H_{81}IrOP_2Si_4Sn$): C 43.26, H 7.95. Found: C 43.43, H 8.04.

Synthesis of TbbSnH$_2$Ir(CO)$_2$(PEt$_3$)$_2$ (**21**). TbbSnIrH$_2$(PEt$_3$)$_3$ (**19**) (26.0 mg, 23.3 µmol, 1.0 equiv) is dissolved in benzene(-d$_6$) (0.40 mL) and transferred into a *J. Young* NMR tube. The solution is degassed with one "freeze-pump-thaw" cycle and the atmosphere is changed with carbon monoxide, whereby the solution suddenly turns turquoise to yield quantitatively TbbSnIrH$_2$(CO)(PEt$_3$)$_2$ (**20**). After 96 hours the solution is yellow and the solvent is removed under reduced pressure. The resulting waxy solid is co-evaporated with *n*-pentane to yield 22.6 mg pale yellow solid of TbbSnH$_2$Ir(CO)$_2$(PEt$_3$)$_2$ (**21**) (22.6 mg, 21.4 µmol, 92 %). Suitable crystals for X-ray diffraction could be obtained out of a slowly evaporated *n*-pentane solution at −38 °C (14.0 mg, 12.3 µmol, 57 %). *Analytical data.* **^{1}H** [400.11 MHz, 299.20 K, benzene-d$_6$]: δ (ppm) 0.39 (s, 36H, Si(C*H*$_3$)$_3$), 0.80 (m, 18H, PEt$_3$-C*H*$_3$), 1.40 (s, 9H, ^{t}Bu-*H*), 1.51 (m, 12H, PEt$_3$-C*H*$_2$), 2.31 (s, 2H, C*H*(SiMe$_3$)$_2$), 4.70 (t + sat., 2H, Sn*H*$_2$, $^1J_{\mathrm{119Sn\text{-}H}}$ = 1400 Hz, $^1J_{\mathrm{117Sn\text{-}H}}$ = 1339 Hz), 7.03 (s, 2H, *m*-Tbb*H*). **^{13}C{^{1}H}** [125.76 MHz, 299.20 K, benzene-d$_6$]: δ (ppm) 0.9 (s, Si(*C*H$_3$)$_3$), 7.9 (s, PEt$_3$-*C*H$_3$), 22.1 (m, PEt$_3$-*C*H$_2$), 31.3 (s, ^{t}Bu-*C*H$_3$), 32.7 (s, *C*H(SiMe$_3$)$_2$), 34.0 (s, ^{t}Bu-*C*Me$_3$), 120.0 (s, *m*-*C*$_{\mathrm{Tbb}}$), 138.9 (m, *i*-*C*$_{\mathrm{Tbb}}$−Sn), 149.2 (s, *p*-*C*$_{\mathrm{Tbb}}$), 150.9 (s, *o*-*C*$_{\mathrm{Tbb}}$), 187.0 (s + sat., *C*≡O, $^2J_{\mathrm{119Sn\text{-}13C}}$ = 71.2 Hz).

^{29}Si [59.63 MHz, 299.20 K, benzene-d_6]: δ (ppm) 2.8 (m, *Si*Me$_3$). **^{31}P{^{1}H}** [161.97 MHz, 299.20 K, benzene-d_6]: δ (ppm) −16.5 (s + sat., *P*Et$_3$, $^2J_{119Sn-31P}$ = 320 Hz, $^2J_{117Sn-31P}$ = 305 Hz). **^{119}Sn** [111.92 MHz, 299.20 K, benzene-d_6]: δ (ppm) −388 (tt, Tbb*Sn*H$_2$Ir, $^1J_{119Sn-1H}$ = 1406 Hz, $^2J_{119Sn-31P}$ = 320 Hz). **^{119}Sn{^{1}H}** [111.92 MHz, 299.20 K, benzene-d_6]: δ (ppm) −388 (t, Tbb*Sn*H$_2$Ir, $^2J_{119Sn-31P}$ = 320 Hz). **IR** [KBr, cm^{-1}] ν(CO) 1772, ν(CO) 1899, ν(Sn−H) 1959. **Elemental analysis** calculated for TbbSnH$_2$−Ir(CO)$_2$(PEt$_3$)$_2$ ($C_{38}H_{81}IrO_2P_2Si_4Sn$): C 43.25, H 7.74. Found: C 43.54, H 7.73.

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