Supplementary Information

Selective hydrosilylation of allyl chloride with trichlorosilane

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Contents

1. General information S3
2. Supplementary tables S4
3. Experimental details and compound characterization data S7
4. $^1$H, $^{13}$C{$^1$H}, and $^{31}$P{$^1$H} NMR spectra of synthesised compounds S17
5. Supplementary references S48
Supplementary Methods

General information

All manipulations were carried out under a nitrogen or an argon atmosphere in a glovebox or using Schlenk techniques. THF and benzene were purified by a solvent purification system (MBraun SPS-800 or a Glass Contour Ultimate Solvent System). n-Pentane and n-hexane were purchased from Kanto as “Super Dehydrated” and used as received. C₆D₆, CD₂Cl₂, and THF-δ₈ were dried over CaH₂ and distilled prior to use. Other reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. 1,2-Bis(diphenylphosphino)-3,4,5,6-tetrafluorobenzene (dppbzF)¹, 1,2-bis(diphenylphosphino)-4,5-dimethoxybenzene (dppbzOMe)², 1,2-bis(bis(3,5-bis(trifluoromethyl)phenyl)phosphino)benzene (CF₃-dppbz)³, 1,2-bis(bis(4-methoxyphenyl)phosphino)benzene (MeO-dppbz)⁴, [(Et₃Si)₂IrH₂(Cl)]²⁵, [(Et₃Si)IrH₂(SiEt₂)]₂⁵, [Rh(μ-Cl)(coe)₂]₂ (coe = cyclooctene)⁶, [Rh(μ-Cl)(cod)]₂ (cod = 1,5-cyclooctadiene)⁶, [Rh(μ-Cl)(dppp)]₂ (dppp = 1,3-bis(diphenylphosphino)propane)⁷, and [Rh(Cl)(cod)(dppp)] (4)⁸ were synthesised by following the literature procedures. ¹H, ¹³C{¹H}, ³¹P{¹H} and ²⁹Si{¹H} NMR spectra were recorded on a Bruker AVANCE III HD 600 spectrometer. Chemical shifts are reported in δ (ppm) and are referenced to 1,4-bis-(trimethylsilyl)benzene (–4.20 ppm) for ²⁹Si and 85% H₃PO₄ (0.0 ppm) for ³¹P, and to the residual solvent signals for ¹H and ¹³C. High-resolution ESI mass spectra were measured on a Bruker microTOF II. Elemental analyses were performed on a Thermo Scientific FLASH2000 CHNS analyzer.
Supplementary Table 1 Reaction conditions for experiments listed in Table 1.

| entry | catalyst (mg, μmol) | ligand (mol%, mg, μmol) | % yield (1/2) |
|-------|---------------------|-------------------------|--------------|
| 1     | Speier’s catalyst⁵  | none                    | 20/32⁵       |
| 2     | Karstedt’s catalyst⁶ | none                    | 15/13⁵       |
| 3     | Karstedt’s catalyst⁶ | IMes⁸ (1, 1.5, 5)      | 53/14        |
| 4     | [Ir(μ-Cl)(cod)]₂¹,₂ | none                    | <5/<5        |
| 5     | [(Et₃Si)₂IrH₂(Cl)]₁,₂ | none                    | <5/<5        |
| 6     | [(Et₃Si)IrH₂(SiEt₂)]₁,₂ | none                    | <5/<5        |
| 7     | [Rh(μ-Cl)(coe)]₁,₂ | none                    | <5/<5        |
| 8     | [Rh(μ-Cl)(cod)]₁   | none                    | 8/<5         |
| 9     | Wilkinson’s catalyst¹⁰ | none                    | 26/<5        |
| 10    | [Rh(μ-Cl)(cod)]₁   | PPh₃ (1, 2.6, 10)      | 31/<5        |
| 11    | [Rh(μ-Cl)(cod)]₁   | PCy₃ (1, 2.8, 10)      | 45/<5        |
| 12    | [Rh(μ-Cl)(cod)]₁   | dppe¹ (0.5, 2.0, 5)    | 76/<5        |
| 13    | [Rh(μ-Cl)(cod)]₁   | dppp¹ (0.5, 2.1, 5)    | 88/6         |
| 14    | [Rh(μ-Cl)(cod)]₁   | dppbz¹ (0.5, 2.2, 5)   | 93/7         |

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⁵ Propene formation was detected based on ¹H NMR analysis of the reaction solution; 6% for entry 1 and 3% for entry 2.

⁶ Xylene stock solution (45 mM, 57 μL) was used and evaporated before adding substrates.

⁷ Toluene stock solution (45 mM, 114 μL) was used and evaporated before adding substrates.

⁸ The utility of these iridium catalysts in the hydrosilylation of allyl chloride with HSi(OR)₃ or HSiClMe₂ was reported⁹-¹³.
**Supplementary Table 2** Reaction conditions for experiments listed in Scheme 2.

![Scheme 2](image)

| entry | catalyst (mg, μmol) | % yield (1/2) |
|-------|---------------------|---------------|
| 1     | 3 (2.8, 2.5)        | 60/<5         |
| 2     | 4 (3.3, 5)          | 41/<5         |
| 3     | 5 (2.9, 2.5)        | >95/<5        |
| 4     | 6 (2.1, 2.5)        | <5/<5         |
| 5     | 7 (5.2, 5)          | <5/<5         |
Supplementary Table 3 Reaction conditions for experiments listed in Table 2.

![Chemical structures](image)

| entry | Rh catalyst | x ppm/Rh used amount (μmol)a | temp. (˚C) | time (h) | % yield (1) |
|-------|-------------|------------------------------|-----------|---------|------------|
| 1     | [Rh(μ-Cl) (dppe)]2 | 500 | 0.25 | 60 | 20 | 3 |
| 2     | 3           | 500 | 0.25 | 60 | 20 | 13 |
| 3     | [Rh(μ-Cl) (dppb)]2 | 500 | 0.25 | 60 | 20 | 22 |
| 4     | 5           | 50 | 0.025 | 60 | 20 | >95 |
| 5     | 5           | 5 | 0.0025 | 60 | 20 | 11 |
| 6     | 8           | 50 | 0.025 | 60 | 20 | <5 |
| 7     | 9           | 50 | 0.005 | 60 | 20 | <5 |
| 8     | 10          | 50 | 0.005 | 60 | 20 | <5 |
| 9     | 11          | 50 | 0.025 | 60 | 20 | >95 |
| 10    | 11          | 50 | 0.025 | 60 | 1 | 9 |
| 11    | 11          | 50 | 0.025 | 60 | 10 | 73 |
| 12    | 11          | 50 | 0.025 | 25 | 20 | 29 |
| 13    | 11          | 50 | 0.025 | 40 | 20 | 39 |
| 14    | 11          | 5 | 0.0025 | 60 | 20 | 29 |
| 15b   | 11          | 5 | 0.0025 | 60 | 20 | 70 |

a Toluene stock solution (5 mM, 1.0 mL for entries 1-3, 100 μL for entries 4, 6-9, and 10 μL for entries 5, 10, 11) was used and toluene was removed in vacuo before adding substrates. b Using 3 equiv of HSiCl3
Experimental details and compound characterization data

General procedures for catalytic hydrosilylation of allyl chloride (Table 1, Table 2, and Fig 2c)
To a 10 mL screw vial equipped with a stir bar, were added catalyst, allyl chloride (81 μL, 1.0 mmol), and trichlorosilane (100 μL, 1.0 mmol). The mixture was stirred at 60 °C. After the reaction, formation of trichloro(3-chloropropyl)silane (1), trichloropropylsilane (2), and propene were confirmed by 1H NMR spectroscopy. The yields of 1 and 2 were determined by the integral intensity ratio of the CH₂ signal at 2.78 ppm towards the signal at 2.15 ppm of mesitylene (14 μL, 0.10 mmol) as an internal standard (Fig. S1).
Detailed reaction conditions for each experiment were listed in Supplementary Tables 1-3.
1: 1H NMR (C₆D₆, ppm): 0.84 (m, 2H, SiCH₂), 1.41 (m, 2H, SiCH₂CH₂), 2.78 (t, 2H, \(^3J_{HH} = 6.6\) Hz, CH₂Cl).
2: 1H NMR (C₆D₆, ppm): 0.65 (m, 3H, SiCH₂CH₂CH₃), 0.81 (m, 2H, SiCH₂), 1.24 (m, 2H, SiCH₂CH₂).
Propene: 1H NMR (C₆D₆, ppm): 1.54 (dt, 3H, \(^3J_{HH} = 6.6\) Hz, \(^4J_{HH} = 1.6\) Hz, CH₂CHCH₃), 4.94 (m, 1H, CH₂CHCH₃), 5.00 (m, 1H, CH₂CHCH₃), 5.71 (m, 1H, CH₂CHCH₃).

Supplementary Fig. 1 An example of 1H NMR chart after reaction.
Reaction of \([\text{Rh}(\mu-\text{Cl})(\text{cod})]\)\(_2\) with dppp (Fig. 2a)

To a 6 mL screw vial containing a benzene (3 mL) solution of \([\text{Rh}(\mu-\text{Cl})(\text{cod})]\)\(_2\) (10 mg, 0.020 mmol), was added dppp (17 mg, 0.040 mmol) at room temperature. The solution was left at 60 °C for 3 h, resulting in the orange solid. After all the volatiles were evaporated under vacuum, the resulting solid was completely dissolved in \(\text{C}_6\text{D}_6\), and mesitylene (9 \(\mu\)L, 0.06 mmol) was added to the solution. The resulting solution was analyzed by \(^1\text{H}\) NMR spectroscopy to determine the yields of \([\text{Rh}(\mu-\text{Cl})(\text{dppp})]\)\(_2\) (3) (0.016 mmol, 79\%), and \([\text{RhCl(cod)(dppp)}]\) (4) (0.0024 mmol, 6\%). Identification of 3\(^7\) and 4\(^7\) was performed by comparing the authentic samples that were synthesised by the literature procedures.

Reaction of \([\text{Rh}(\mu-\text{Cl})(\text{cod})]\)\(_2\) with dppbz (Fig. 2b)

To a 6 mL screw vial containing a benzene (3 mL) solution of \([\text{Rh}(\mu-\text{Cl})(\text{cod})]\)\(_2\) (10 mg, 0.020 mmol), was added dppbz (18 mg, 0.040 mmol) at room temperature. The solution was left at 60 °C for 3 h, resulting in the orangne solid. After the volatiles were evaporated under vacuum, the resulting residue was dissolved in \(\text{CD}_2\text{Cl}_2\), and mesitylene (9 \(\mu\)L, 0.06 mmol) was added to the solution as an internal standard. The resulting solution was analyzed by \(^1\text{H}\) NMR to determine the yields of \([\text{Rh}(\mu-\text{Cl})(\text{dppbz})]\)\(_2\) (5) (0.013 mmol, 63\%), \([\text{(dppbz)Rh}(\mu-\text{Cl})(\text{cod})]\)\(_2\) \([\text{Rh(cod)}]\) (6) (0.0052 mmol, 26\%), and \([\text{Rh(dppbz)Cl]}\)\(_2\) (7) (0.0034 mmol, 8\%). Identification of 5\(^7\), 6\(^8\), and 7\(^{14}\) was performed by comparing the authentic samples that were alternatively synthesised by the literature procedures of the structurally similar complexes.
Synthesis of [Rh($\mu$-Cl)(dppbz)]$_2$ (5)

A THF solution (3 mL) of [Rh($\mu$-Cl)(cod)]$_2$ (20 mg, 0.041 mmol) was placed in a Schlenk tube (20 mL). To the solution, was added a THF (3 mL) solution containing dppbz (45 mg, 0.94 mmol) slowly over 5 min at −78 °C, and the mixture was stirred at the same temperature for 30 min. The solution was warmed to room temperature and concentrated to dryness in vacuo. The resulting residue was extracted with benzene (10 mL × 3) and hexane (10 mL × 3) and concentrated to dryness under vacuum to give 5 as an orange solid (41 mg, 0.035 mmol, 86%).

$^1$H NMR (C$_6$D$_6$, ppm): 6.80 (br, 4H, 3,6-CH), 6.94 (t, 16H, 3$^3$J$_{HH}$ = 7.5 Hz, Ph), 7.00 (t, 8H, 3$^3$J$_{HH}$ = 7.5 Hz, Ph), 7.40 (br, 4H, 4,5-CH), 7.94 (br, 16H, Ph). $^{13}$C{$^1$H} NMR (C$_6$D$_6$, ppm): 127.3 (Ar), 128.9 (Ar), 129.7 (Ar), 131.7 (m, Ar), 133.7 (Ar), 136.4 (m, Ar), 146.3 (m, Ar). $^{31}$P{$^1$H} NMR (C$_6$D$_6$, ppm): 73.6 (d, $^1$J$_{RhP}$ = 197 Hz). Anal. Calcd for C$_{60}$H$_{48}$Cl$_2$P$_4$Rh$_2$: C, 61.61; H, 4.14. Found: C, 61.84; H, 4.42.

Synthesis of [(dppbz)Rh($\mu$-Cl)$_2$Rh(cod)] (6)

A THF solution (6 mL) of [Rh($\mu$-Cl)(cod)]$_2$ (50 mg, 0.10 mmol) was placed in a Schlenk tube (20 mL). To the solution, was added a THF (6 mL) solution containing dppbz (45 mg, 0.20 mmol) slowly over 5 min at −30 °C. After stirring at room temperature for 30 min, the solution was concentrated to the dryness in vacuo, and the resulting residue was washed with pentane (10 mL × 3) and benzene (10 mL × 3) and dried under vacuum. Complex 6 was obtained as an orange solid (80%, 42 mg, 0.033 mmol).

$^1$H NMR (C$_6$D$_6$, ppm): 1.40 (m, 4H, cod), 2.09 (m, 4H, cod), 4.24 (br, 4H, cod), 6.86 (t, 16H, 3$^3$J$_{HH}$ = 7.5 Hz, Ph), 7.06 (m, 12H, Ar), 7.45 (m, 2H, Ar), 8.01 (m, 8H, Ar). $^{13}$C{$^1$H} NMR (C$_6$D$_6$, ppm): 31.5 (cod), 76.7 (d, $J = 21.9$ Hz, cod), 128.6 (Ar), 129.8 (Ar), 130.6 (Ar), 132.0 (m, Ar), 134.0 (t, $J = 5.8$ Hz, Ar), 136.6 (Ar). One Ar signal was obscured in a residual benzene signal. $^{31}$P{$^1$H} NMR (C$_6$D$_6$, ppm): 75.7 (d, $^1$J$_{RhP}$ = 198 Hz). Anal. Calcd for C$_{38}$H$_{35}$Cl$_2$P$_2$Rh$_2$: C, 54.90; H, 4.36. Found: C, 54.84; H, 4.31.
Synthesis of [Rh(dppbz)₂]Cl (7)

\[
\begin{array}{c}
\text{PP}_2 \\
\text{P}
\end{array}
\]

A benzene solution (3 mL) of [Rh(μ-Cl)(cod)]₂ (10 mg, 0.020 mmol) was placed in a Schlenk tube (20 mL). To the solution, was added a benzene (3 mL) solution containing dppbz (36 mg, 0.080 mmol). After stirring at room temperature for 30 min, the solution was concentrated to dryness in vacuo at room temperature, and the resulting residue was washed with benzene (10 mL × 3). After drying, the resulting residue was dissolved in CH₂Cl₂/hexane (2 mL/0.5 mL) and stored at –30 °C to give 7 as an orange solid (79%, 33 mg, 0.032 mmol).

¹H NMR (CD₂Cl₂, ppm): 6.88 (d, 16H, ³J_HH = 6.6 Hz, Ar), 7.11 (t, 16H, ³J_HH = 7.5 Hz, Ar), 7.38-7.46 (m, 16H, Ar).

¹³C{¹H} NMR (CD₂Cl₂, ppm): 133.5 (Ar), 135.6 (Ar), 136.7 (d, ³J = 12 Hz, Ar), 136.8 (d, ³J = 19 Hz, Ar), 136.9 (m, Ar), 137.9 (Ar), 148.4 (m, Ar).

³¹P{¹H} NMR (CD₂Cl₂, ppm): 62.3 (d, ³J_RhP = 134 Hz).

Anal. Calcd for C₆₀H₄₈Cl₄P₄Rh: C, 69.88; H, 4.69. Found: C, 70.09; H, 4.60.

Synthesis of [Rh(μ-Cl)(CF₃-dppbz)]₂ (8)

\[
\begin{array}{c}
\text{CF}_3 \\
\text{P}
\end{array}
\]

A benzene solution (3 mL) of [Rh(μ-Cl)(coe)]₂ (20 mg, 0.028 mmol) was placed in a Schlenk tube (20 mL). To the solution, was added a benzene (3 mL) solution containing CF₃-dppbz (64 mg, 0.064 mmol) slowly over 5 min at room temperature, and the mixture was stirred for 30 min. An orange precipitate was formed and filtrated to give 8 (72%, 46 mg, 0.020 mmol).

¹H NMR (THF-d₈, ppm): 7.70 (brm, 4H, 3,6-CH), 7.91 (brm, 4H, 4,5-CH), 8.15 (s, 8H, Ph), 8.18 (s, 16H, Ph).

¹³C{¹H} NMR (THF-d₈, ppm): 123.8 (q, ³J.FC = 273 Hz, CF₃), 125.5 (Ar), 132.7 (q, ²J.FC = 34 Hz, Ar), 133.2 (m, Ar), 133.6 (Ar), 134.1 (Ar), 137.5 (m, Ar), 143.4 (m, Ar).

³¹P{¹H} NMR (THF-d₈, ppm): 75.1 (d, ³J_RhP = 194 Hz). Anal. Calcd for C₇₆H₃₂Cl₂F₄₈P₄Rh₂: C, 40.43; H, 1.43. Found: C, 40.68; H, 1.30.
Synthesis of \([\text{Rh}(\mu-\text{Cl})(\text{MeO-dppbz})]_2\) (9)

A THF solution (6 mL) of \([\text{Rh}(\mu-\text{Cl})(\text{cod})]_2\) (40 mg, 0.081 mmol) was placed in a Schlenk tube (20 mL). To the solution, was added a THF (6 mL) solution containing MeO-dppbz (105 mg, 0.171 mmol) slowly over 5 min at room temperature, and the mixture was stirred for 30 min. The solution was concentrated to dryness under vacuum and the resulting residue was extract with benzene (10 mL × 3). After evaporation, 9 was obtained as an orange solid (67%, 77 mg, 0.054 mmol).

\[^1\text{H} \text{NMR (THF-}d_8, \text{ppm): } \delta 3.73 \text{ (s, 24H, OMe), 6.69 (d, 16H, }^3J_{\text{HH}} = 4.2 \text{ Hz, Ph) 7.28 (br, 4H, 4,5-CH), 7.47 (br, 4H, 3,6-CH), 7.64 (br, 16H, Ph).} \]

\[^{13}\text{C}\{^1\text{H}\} \text{NMR (THF-}d_8, \text{ppm): } 55.1 \text{ (OMe), 113.7 (Ar), 128.8 (m, Ar), 130.1 (Ar), 132.2 (m, Ar), 135.7 (Ar), 147.5 (m, Ar), 161.2 (Ar).} \]

\[^{31}\text{P}\{^1\text{H}\} \text{NMR (THF-}d_8, \text{ppm): } 70.7 \text{ (d, }^1J_{\text{RhP}} = 199 \text{ Hz). Anal. Calcd for C}_{68}\text{H}_{64}\text{Cl}_2\text{O}_8\text{P}_4\text{Rh}_2: C, 57.93; \text{H, 4.58. Found: C, 57.90; H, 4.72.} \]

Synthesis of \([\text{Rh}(\mu-\text{Cl})(\text{dppbz}^{\text{OMe}})]_2\) (10)

A THF solution (3 mL) of \([\text{Rh}(\mu-\text{Cl})(\text{cod})]_2\) (20 mg, 0.041 mmol) was placed in a Schlenk tube (20 mL). To the solution, was added a benzene (3 mL) solution containing dppbz\textsuperscript{OMe} (47 mg, 0.093 mmol) slowly over 5 min at –30 °C. After stirring at room temperature for 30 min, the solution was concentrated to dryness in vacuo at room temperature, and the resulting residue was extract with benzene (10 mL × 3). After benzene was removed by evaporation, the obtained solid was washed with hexane (10 mL × 3) to give 10 as an orange solid (80%, 42 mg, 0.033 mmol).

\[^1\text{H} \text{NMR (THF-}d_8, \text{ppm): } 3.57 \text{ (s, 12H, OMe), 6.89 (t, 4H, }J = 3.2 \text{ Hz, 3,6-CH) 7.18 (t, 16H, }^3J_{\text{HH}} = 7.5 \text{ Hz, Ph), 7.24 (t, 8H, }^3J_{\text{HH}} = 7.3 \text{ Hz, Ar), 7.72 (br, 16H, Ar).} \]

\[^{13}\text{C}\{^1\text{H}\} \text{NMR (THF-}d_8, \text{ppm): } 56.0 \text{ (OMe), 113.7 (m, Ar), 128.4 (m, Ar), 129.6 (Ar), 134.4 (m, Ar), 137.8 (m, Ar), 138.8 (m, Ar), 152.5 (Ar).} \]

\[^{31}\text{P}\{^1\text{H}\} \text{NMR} \]
(THF-d8, ppm): 72.4 (d, $^{1}J_{RhP} = 197$ Hz). Anal. Calcd for C$_{60}$H$_{56}$Cl$_{2}$O$_{4}$P$_{4}$Rh$_{2}$: C, 59.60; H, 4.38. Found: C, 59.70; H, 4.72.

**Synthesis of [Rh(μ-Cl)(dppbz$^F$)]$_2$ (11)**

![Diagram of 11]

A benzene solution (3 mL) of [Rh(μ-Cl)(coe)$_2$] (20 mg, 0.028 mmol) was placed in a Schlenk tube (20 mL). To the solution, was added a benzene (3 mL) solution containing dppbz$^F$ (33 mg, 0.064 mmol) slowly over 5 min at room temperature, and the mixture was stirred for 30 min at the temperature. The solution was concentrated to the dryness *in vacuo*, and the resulting residue was extract with benzene (10 mL × 3). After evaporation, the obtained solid was washed with hexane (10 mL × 3) to give 11 as an orange solid (72%, 26 mg, 0.020 mmol).

$^1$H NMR (THF-d$_8$, ppm): 7.26 (t, $^{16}J_{HH} = 7.5$ Hz, Ph), 7.37 (t, 8H, $^{3}J_{HH} = 7.5$ Hz, Ph), 7.78 (m, 16H, Ph).

$^{13}$C$^{{}^1}$H NMR (THF-d$_8$, ppm): 128.4 (t, $J = 4.5$ Hz, Ar), 129.0 (Ar), 130.4 (Ar), 134.0 (t, $J = 5.6$ Hz, Ar), 134.2 (d, $J = 24$ Hz, Ar), 143.4 (brd, $^{1}J_{CF} = 259$ Hz, Ar), 147.7 (brd, $^{1}J_{CF} = 253$ Hz, Ar).

$^{31}$P$^{{}^1}$H NMR (THF-d$_8$, ppm): 80.3 (d, $^{1}J_{RhP} = 200$ Hz). Anal. Calcd for C$_{60}$H$_{40}$Cl$_{2}$F$_{8}$P$_{4}$Rh$_{2}$: C, 54.86; H, 3.07. Found: C, 54.54; H, 3.35.

**Reaction of [Rh(μ-Cl)(dppbz$^F$)]$_2$ (11) with allyl chloride (Fig. 3a)**

![Diagram of Reaction 3a]

A THF (2 mL) solution of 11 (50 mg, 0.045 mmol) was placed in a Schlenk tube (20 mL). Allyl chloride (69 mg, 0.90 mmol) was added to the solution, and the mixture was stirred at room temperature for 2 h, resulting in the formation of yellow precipitates. After filtration, the obtained solid was washed with hexane (2 mL × 3) and THF (2 mL × 3) to give [Rh(π-allyl)Cl$_2$(dpppbz$^F$)] (12) (44 mg, 0.069 mmol, 74%).

$^1$H NMR (CD$_2$Cl$_2$, ppm): 2.91 (d, $^{3}J_{HH} = 9.0$ Hz, 2H, allyl), 4.32 (dt, $^{3}J_{HH} = 7.8$ Hz, $^{3}J_{HH} = 3.3$ Hz, 1H, allyl), 4.58 (dt, $^{3}J_{HH} = 14$ Hz, $^{3}J_{HH} = 4.2$ Hz, 1H, allyl), 5.03 (m, 1H, allyl), 7.36 (m, 8H, Ph), 7.50 (m, 6H, Ph), 7.57 (dd, $^{3}J_{HH} = 8.4$ Hz, $^{3}J_{HH} = 6.6$ Hz, 2H, Ph), 7.80 (dd, $^{3}J_{HH} = 12$ Hz, $^{3}J_{HH} = 7.8$ Hz, 4H, Ph).
$^{13}$C{${}^1$H} NMR (CD$_2$Cl$_2$, ppm): 55.9 (d, $J = 11$ Hz, allyl), 81.7 (dt, $J = 11$ Hz, $J = 3.5$ Hz, allyl), 107.8 (d, $J = 4.0$ Hz, allyl), 125.3 (brm, Ar), 127.4 (d, $J = 62$ Hz, Ar), 128.1 (d, $J = 12$ Hz, Ar), 129.4 (d, $J = 11$ Hz, Ar), 129.9 (d, $J = 49$ Hz, Ar), 131.8 (d, $J = 2.9$ Hz, Ar), 132.2 (d, $J = 2.4$ Hz, Ar), 132.6 (d, $J = 10$ Hz, Ar), 133.9 (brm, Ar), 143.9 (brd, $^1J_{CF} = 268$ Hz, Ar), 149.0 (brd, $^1J_{CF} = 255$ Hz, Ar). $^{31}$P{${}^1$H} NMR (CD$_2$Cl$_2$, ppm): 63.0 (brd, $^1J_{RhP} = 76$ Hz).

Anal. Calcd for C$_{33}$H$_{25}$Cl$_2$F$_4$P$_2$Rh: C, 54.05; H, 3.44. Found: C, 54.19; H, 3.44.

Reaction of [Rh($\pi$-allyl)Cl$_2$(dppbz$^F$)] (12) with HSiCl$_3$ (Fig. 3b)

![Reaction of [Rh($\pi$-allyl)Cl$_2$(dppbz$^F$)] with HSiCl$_3$](image)

A J-young NMR tube was charged with a C$_6$D$_6$ (0.5 mL) solution of 12 (3.7 mg, 0.0050 mmol). To the solution, was added HSiCl$_3$ (5 μL, 0.05 mmol) at room temperature. The solution was left at 60 °C for 3 h, and then mesitylene (6 μL, 0.06 mmol) was added. Formation of 1 (26%) and 2 (45%) were confirmed by $^1$H NMR spectroscopy. Formation of hydrido species, which exhibit hydride signals at –15.01 (dt, $J = 21$, 7.2 Hz), –15.73 (dt, $J = 25$, 9.0 Hz), and –16.85 (m) ppm with the integral intensity of 34 : 13 : 15, were observed in the $^1$H NMR spectrum. In the $^{31}$P{${}^1$H} NMR, several signals were observed in the range of 26.1 ppm to 84.2 ppm. The resulting complexes underwent further transformation under vacuum conditions to form a complicated mixture containing [Rh($\mu$-Cl)(dppbz$^F$)]$_2$ (11) and several unidentification species. Therefore, identification of the resulting hydride species were not successfull. The observed hydride signals at –15.01 and –16.85 ppm also appeared on the $^1$H NMR monitoring of the reaction of [Rh($\mu$-Cl)(dppbz$^F$)]$_2$ (11) with HSiCl$_3$ (20 equiv), which resulted in the formation of a complex mixture of unidentified complexes. The identification of these resulting complexes was not successful since these complexes were easily transferred to [Rh($\mu$-Cl)(dppbz$^F$)]$_2$ (11) and unidentified complexes after evaporation, probably via reductive elimination.
Reaction of [Rh(π-allyl)Cl₂(dpbbz)] (12) with cinnamyl chloride (Fig. 3d)

A J-young NMR tube was charged with a CD₂Cl₂ (0.5 mL) solution of 12 (4 mg, 0.006 mmol). To the solution, were added cinnamyl chloride (15 μL, 0.11 mmol) and mesitylene (1 μL, 0.01 mmol) at room temperature. The solution was left at 40 °C for 2 h, formation of free allyl chloride (0.001 mmol, 20%) was detected by ¹H NMR spectroscopy. The conversions of 12 and cinnamyl chloride were determined as 23% and 19%, respectively. In the ³¹P{¹H} NMR spectrum, a new doublet of doublets signal and the signal assignable to unreacted 12 were observed at 66.7 ppm (¹J_RhP = 130 Hz, ²J_PP = 8.9 Hz) and at 63.0 ppm with the integral intensity of 66/34, respectively.

Experimental data of A

³¹P{¹H} NMR (CD₂Cl₂, ppm): 66.7 ppm (¹J_RhP = 130 Hz, ²J_PP = 8.9 Hz). HRMS (ESI) Calculated: (C₃₉H₂₉ClF₄P₂Rh) 773.4019 ([M–Cl]⁺), Found: 773.0426.

Synthesis of [Rh(π-allyl)Cl₂(dpbb)] (13)

A THF (2 mL) solution of [Rh(μ-Cl)(dpbb)]₂ (3) (50 mg, 0.045 mmol) was placed in a Schlenk tube (20 mL). Allyl chloride (69 mg, 0.90 mmol) was added to the solution, and the mixture was stirred at room temperature for 2 h, resulting in the formation of yellow precipitates. After filtration, the obtained solid was washed with hexane (2 mL × 3) and THF (2 mL × 3) to give 13 (42 mg, 0.066 mmol, 74%).

¹H NMR (CD₂Cl₂, −30 °C, ppm): 1.34 (vsext, 1H, J = 11 Hz, C₃H₆), 1.75 (m, 1H, C₃H₆), 2.26 (m, 1H, C₃H₆), 2.57 (td, 1H, ²J_HH = 16 Hz, ³J_HH = 4.4 Hz, C₃H₆), 2.78 (m, 1H, C₃H₆), 3.08 (d, 1H, ³J_HH = 6.6 Hz, C₃H₆), 3.12 (dd, 1H, ³J_HH = 6.9 Hz, ³J_HH = 1.5 Hz, allyl), 3.54 (m, 1H, allyl) 3.68 (d, 1H, ³J_HH = 9.0 Hz, allyl), 4.15 (dd, 1H, ³J_HH = 13.5 Hz, ³J_HH = 7.8 Hz, allyl), 4.90 (m, 1H, allyl), 6.84 (dd, 2H, ³J_HH = 8.2 Hz, ³J_HH = 1.8 Hz, Ph), 7.00 (m, 2H, Ph), 7.30 (m, 2H, Ph), 7.35 (m, 2H, Ph), 7.47 (m, 2H, Ph), 7.55 (t, 1H, ³J_HH = 7.3 Hz, Ph), 7.62 (t, 2H, ³J_HH = 6.8 Hz, Ph), 7.68 (t, 1H, ³J_HH = 6.9 Hz, Ph), 7.73 (t, 2H, ³J_HH = 8.8 Hz, Ph)
Hz, Ph), 7.78 (brm, 2H, Ph), 7.84 (brm, 2H, Ph). $^{13}$C$\{^1$H$\}$ NMR (CD$_2$Cl$_2$, −30 °C, ppm): 18.6 (C$_3$H$_6$), 25.1 (dd, $J = 27$ and 4.4 Hz, C$_3$H$_6$), 26.3 (dd, $J = 38$ and 3.3 Hz, C$_3$H$_6$), 58.6 (d, $J = 18$ Hz, allyl), 74.6 (dd, $J = 31$ and 3.8 Hz, allyl), 107.3 (d, $J = 3.6$ Hz, allyl), 127.4 (d, $J = 16$ Hz, Ar), 128.1 (d, $J = 16$ Hz, Ar), 128.4 (d, $J = 16$ Hz, Ar), 128.6 (d, $J = 81$ Hz, Ar), 129.0 (d, $J = 16$ Hz, Ar), 129.6 (Ar), 130.3 (d, $J = 88$ Hz, Ar), 131.0 (Ar), 131.1 (Ar), 131.6 (Ar), 132.4 (br, Ar), 132.6 (d, $J = 11$ Hz, Ar), 133.2 (d, $J = 14$ Hz, Ar), 133.3 (d, $J = 68$ Hz, Ar), 133.7 (d, $J = 17$ Hz, Ar), 135.5 (d, $J = 83$ Hz, Ar). $^{31}$P$\{^1$H$\}$ NMR (CD$_2$Cl$_2$, −30 °C, ppm): 3.5 (dd, $^1$J$_{RhP} = 130$ Hz, $^3$J$_{PP} = 29$ Hz), 31.3 (dd, $^1$J$_{RhP} = 103$ Hz, $^3$J$_{PP} = 29$ Hz).

Anal. Calcd for C$_{30}$H$_{31}$Cl$_2$P$_2$Rh: C, 57.44; H, 4.98. Found: C, 57.26; H, 5.14.

**Reaction of [Rh(π-allyl)Cl$_2$(dppp)] (13) with HSiCl$_3$ (Fig. 3e)**

To a C$_6$D$_6$ (0.5 mL) suspension of 13 (3.1 mg, 0.0049 mmol), was added HSiCl$_3$ (20 μL, 0.20 mmol) at room temperature. The solution was left at 60 °C for overnight. After the reaction, mesitylene (2 μL, 0.02 mmol) as an internal standard was added to the solution. Based on $^1$H NMR analysis, formation of [Rh(Cl)(H)(SiCl$_3$(dppp))] (14) (0.0044 mmol, 90%), 2 (>0.0047 mmol, >95%), and propene (trace) was confirmed. In the $^{29}$Si$\{^1$H$\}$ NMR spectrum, SiCl$_4$ was observed at −18.9 ppm. Formation of 14 was confirmed by comparing the NMR of the alternatively synthesised authentic sample (vide infra).

**Alternative synthetic path for 14: Reaction of [Rh(μ-Cl)(dppp)]$_2$ with HSiCl$_3$**

A toluene solution (5 mL) of [Rh(μ-Cl)(dppp)]$_2$ (3) (50 mg, 0.045 mmol) was placed in a Schlenk tube (20 mL). HSiCl$_3$ (27 μL, 0.27 mmol) was added to the solution, and the mixture was stirred at room temperature for 2 h. The solution was concentrated to the dryness in vacuo. The resulting residue was dissolved in CH$_2$Cl$_2$/hexane (2 mL/0.5 mL) and stored at −30 °C to give 14 as an orange solid (55 mg, 0.079 mmol, 88%).
$^1$H NMR (C$_6$D$_6$, ppm): –6.17 (dd, $^2$J$_{HP}$ = 115 Hz, $^1$J$_{HRh}$ = 15.6 Hz, 1H, RhH, Rather small $^2$J$_{HPvis}$ [normally 4-18 Hz]$^{15}$ is obscured), 1.40 (m, 2H, C$_3$H$_6$), 2.22 (m, 2H, C$_3$H$_6$), 2.32 (m, 2H, C$_3$H$_6$), 6.95 (m, 12H, Ph), 7.40 (m, 8H, Ph). $^{13}$C($^1$H) NMR (C$_6$D$_6$, ppm): 18.9 (s, C$_3$H$_6$), 23.4 (d, $^1$J$_{CP}$ = 21 Hz, C$_3$H$_6$), 27.2 (m, C$_3$H$_6$), 128.5 (d, $^2$J$_{CP}$ = 10 Hz, Ar), 129.3 (d, $^2$J$_{CP}$ = 10 Hz, Ar), 130.8 (Ar), 131.1 (Ar), 132.3 (Ar), 132.4 (d, $^3$J$_{CP}$ = 20 Hz, Ar), 132.5 (Ar), 134.1 (d, $^3$J$_{CP}$ = 20 Hz, Ar). $^{31}$P($^1$H) NMR (C$_6$D$_6$, ppm): 8.17 (dd, $^1$J$_{RhP}$ = 102 Hz, $^2$J$_{PP}$ = 34 Hz), 9.52 (dd, $^1$J$_{RhP}$ = 97 Hz, $^2$J$_{PP}$ = 34 Hz). Anal. Calcd for C$_{27}$H$_{27}$Cl$_4$P$_2$RhSi: C, 47.26; H, 3.97. Found: C, 47.05; H, 3.92.

**Gram scale synthesis of 1 (Fig. 5)**

![Image of synthesis process]

A rhodium catalyst [Rh(μ-Cl)(dppbz)$_2$]$_2$ (11) (80 mg, 0.060 mmol) was placed in a three-necked flask (3 L) with condenser. Allyl chloride (187 g, 2.45 mol) and trichlorosilane (332 g, 2.45 mol) were added to the flask, and the mixture was stirred at 60 °C for 20 h. After distillation of the resulting solution under reduced pressure (36 hPa, 80 °C), analytically pure 1 was obtained as a colorless liquid (483 g, 2.28 mol, 93%).
$^1\text{H}$, $^{13}\text{C}[^1\text{H}]$, and $^{31}\text{P}[^1\text{H}]$ NMR spectra of synthesised compounds

Supplementary Fig. 2 $^1\text{H}$ NMR spectra of $[\text{Rh}(\mu-\text{Cl})(\text{dppbz})_2]$ (5) ($\text{C}_6\text{D}_6$).
Supplementary Fig. 3. $^{13}$C{H} NMR spectra of [Rh(μ-Cl)(dppbz)]$_2$ (C$_6$D$_6$).
Supplementary Fig. 4. $^{1}H$ NMR spectra of [Rh($\mu$-Cl)(dppbz)$_2$]$_2$ (5) (C6D6).
Supplementary Fig. 5 $^1$H NMR spectra of [(dppbz)Rh(μ-Cl)₂Rh(cod)] (6) (C₆D₆).
Supplementary Fig. 6 $^{13}\text{C}(^1\text{H})$ NMR spectra of $[(\text{dppbz})\text{Rh}(\mu-\text{Cl})_2\text{Rh(cod)}]$ (6) (C$_6$D$_6$).
\[ \text{Supplementary Fig. 7} \]

\[ \text{\(^{31} \text{P} \) NMR spectra of [(dppbz)Rh(µ-Cl)Rh(cod)] (C}_6 \text{D}_6}. \]
Supplementary Fig. 8: H NMR spectra of [Rh(dppbz)_2]Cl_2 (7) (CD_2Cl_2).
Supplementary Fig. 9: 13C{1H} NMR spectra of [Rh(dppbz)$_2$Cl](7)(CD$_2$Cl).

**Current Data Parameters**
- **NAME**: 20200015_473
- **EFK30**: 12
- **PROW**: 1

**F2 - Acquisition Parameters**
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- **TIME**: 3:41
- **ITEMNAME**: spect
- **FOGRED**: 5 16 06 00 00 00 00 00
- **PDIN**: 2 200
- **TD**: 65536
- **SOLVENT**: CD$_2$Cl$_2$
- **D3**: 3000
- **DS**: 3333
- **SNR**: 500000 Hz
- **ABG**: 0.983000 s
- **G5**: 120.87
- **DM**: 15000 us
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- **T1**: 296.8 S
- **D1**: 0.03800000
- **D11**: 0.03800000
- **TD**: 1

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- **SPC1**: 190.940466 MHz
- **R642**: 10.2 Hz
- **F1**: 10.4000000 MHz
- **FM1**: 57.3500070 kHz

**--- CHANNEL f2 ---**
- **SPC2**: 600.231466 MHz
- **R642**: 10.2 Hz
- **F1**: 10.400000 MHz
- **FM1**: 57.350007 kHz

**F2 - Processing parameters**
- **N**: 65536
- **AE**: 100.92725 MHz
- **DM**: o
- **LB**: 1.88 Hz
- **GB**: 0.0 Hz
- **FC**: 1.40
Supplementary Fig. 10 $^{31}$P[1H] NMR spectra of [Rh(dppbz)$_2$]Cl (7) (CD$_2$Cl$_2$).
Supplementary Fig. 11: H NMR spectra of [Rh(μ-Cl)(CF₃-dppbz)]₂ (8) (THF-d₈).
Supplementary Fig. 12 $^{13}$C($^1$H) NMR spectra of [Rh($\mu$-Cl)(CF$_3$-dppbz)$_2$]$_2$ (8) (THF-$d_8$).
Supplementary Fig. 13. $^3$P($^3$H) NMR spectra of [Rh($\mu$-Cl)(CF$_3$-dppb)2]$^{2}$ (THF-d$_8$).
Supplementary Fig. 14: H NMR spectra of [Rh₄Cl(MeO-dppbz)]₂ (9) (THF-d₈).
Supplementary Fig. 15. ¹³C(¹H) NMR spectra of [Rh(μ-Cl)(MeO-dppbz)]₂ (9) (THF-d₈).
Supplementary Fig. 16. $^3$P((H) NMR spectra of $\text{[Rh}(\mu-$Cl)(MeO-dppbz)]$_2$ (9) (THF-$d_8$).
Supplementary Fig. 17 1H NMR spectra of [Rh(µ-Cl)(dppbzOMe)]_2 (10) (THF-d8).

Current Data Parameters
NAME 20200604_622
EXPROC 27
FPROCPO 1

F2 - Acquisition Parameters
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SOLVENT THF
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TDQ 1

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SLC 12.00 ussec
FWMH 11.00000000 W

F3 - Processing parameters
ST 65.56K
SF 600.133000 MHz
NW 3EN
USR 0
LT 0.20 Hz
GR 0
FC 1.00

benzene
impurities
hexane
Supplementary Fig. 18 $^{13}$C-$^{1}$H NMR spectra of [Rh(µ-Cl)(dpbbzOMe)$_2$] (10) (THF-d$_8$).
Supplementary Fig. 19 31P{1H} NMR spectra of [Rh(μ-Cl)(dpdpbz-OMe)]2 (10) (THF-d8).
Supplementary Fig. 20. H NMR spectra of [Rh(μ-Cl)(dppbzF)]_2 (11) (THF-d8).
Supplementary Fig. 21 $^{13}$C($^1$H) NMR spectra of [Rh($\mu$-Cl)(dppbz$^F$)]$_2$ (11) (THF-$d_8$).
Supplementary Fig. 22: \( ^{1}H \) NMR spectra of \([\text{Rh}(\mu-\text{Cl})(\text{dppz})F_2]\) (11) (THF-d8).
Supplementary Fig. 23. H NMR spectra of [Rh(η-
allyl)Cl₂(dpppbz-F)] (12) (CD₂Cl₂).
Supplementary Fig. 24. 13C(1H) NMR spectra of [Rh(κ3-allyl)(C12mpppzF)](12) (CD2Cl2).
Supplementary Fig. 25. 31P{1H} NMR spectra of [Rh(π-allyl)Cl₂(dpppbzF)](12) (CD₂Cl₂).
Supplementary Fig. 26 $^1$H NMR spectra of [Rh($\pi$-allyl)Cl$_2$(dppp)] (13) (CD$_2$Cl$_2$).
Supplementary Fig. 27 \(^{13}\)C\(^{1}H\) NMR spectra of [Rh(\(\pi\)-allyl)Cl\(_2\)(dppp)] (13) (CD\(_2\)Cl\(_2\)).
Supplementary Fig. 28 $^{31}$P$^1$H NMR spectra of [Rh(π-allyl)Cl$_2$(dppp)] (13) (CD$_2$Cl$_2$).
Supplementary Fig. 29. H NMR spectra of [(dpdp)(RhCl)(H)(SiCl3)] (14) (C6D6).

impurity
Supplementary Fig. 30. $^{13}$C($^1$H) NMR spectra of $[dppp]Rh(Cl)(H)(SiCl_3)]$ (14) (C$_6$D$_6$).
Supplementary Fig. 31 $^1$H NMR spectra of [(dppp)Rh(Cl)(H)(SiCl$_3$)] (14) (C$_6$D$_6$).
Supplementary Fig. 32. H NMR spectrum of trichloro(3-chloropropyl)silane (1) (Fig. 5, C6D6).
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