# **Supporting Information**

# Selective Formylation or Methylation of Amines Using Carbon Dioxide and Catalysed by a Rhodium Perimidine-NHC Based Complex

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# **Table of Contents**

A1	General Procedure
A1.1	NMR Spectroscopy
A1.2	General Procedure for Catalysed N-Formylation and -Methylation of Amines .3
A2	Optimisation of Reaction Conditions for N-Formylation and -Methylation
	Reactions using Aniline as Model Substrate4
A3	Conversions for N-Formylation and -Methylation Reactions of Amines and
	Spectroscopic Data
A4	NMR Spectra of Isolated Products5
A5	Synthesis of [RhCl{C(NCH <sub>2</sub> PCy <sub>2</sub> ) <sub>2</sub> C <sub>10</sub> H <sub>6</sub> }]6
A6	Stoichiometric Studies with $O_2$ , $CH_2CI_2$ , $CS_2$ , $CO$ , $PhSiH_3$ , $CO_2$ and $Aniline6$
A7	References14

# A1 General Procedure

All manipulations of metal complexes and air sensitive reagents were carried out using standard Schlenk techniques; catalysis experiments were carried out using standard Schlenk techniques under  $N_{2(g)}$ ,  $Ar_{(g)}$  or  $CO_{2(g)}$  atmosphere.

Unless otherwise stated, chemicals were purchased from Alfa Aesar Inc. or Aldrich Chemical Company Inc., and used as received. Rhodium(III) chloride hydrate was purchased from Precious Metals Online P/L and used without further purification. Rhodium catalyst [RhCl{ $\kappa^3$ -P,C,P'=C(NCH<sub>2</sub>PCy<sub>2</sub>)<sub>2</sub>C<sub>10</sub>H<sub>8</sub>}] (**2b**) was synthesised according to reported procedures.<sup>[1]</sup>

For the purposes of air sensitive manipulations, preparation of metal complexes and catalysis, solvents were dispensed from a LC Technology solvent purification system and stored under nitrogen or argon atmospheres in glass ampoules fitted with Youngs<sup>©</sup> Teflon valves.

Nitrogen gas for Schlenk line operation comes from in-house liquid nitrogen boil-off. Bulk compressed gases of nitrogen (>99.5%), argon (>99.997%) and carbon dioxide (>99.9%) were obtained from BOC Australia.

# A1.1 NMR Spectroscopy

NMR spectra were recorded on Bruker DPX400 (fitted with an Autosampler, <sup>1</sup>H at 400.2 MHz, <sup>31</sup>P at 162.0 MHz), DMX500 (<sup>1</sup>H at 500.2 MHz, <sup>31</sup>P at 202.5 MHz), and Bruker Advance 600 (<sup>13</sup>C at 150.9 MHz); and on Varian Mercury 300 (<sup>1</sup>H at 300.1 MHz, <sup>31</sup>P at 121.5 MHz), Inova 300 (<sup>1</sup>H at 299.9 MHz, <sup>13</sup>C at 75.42 MHz, <sup>31</sup>P at 121.4 MHz), and MR 400 (<sup>1</sup>H at 399.9 MHz, <sup>31</sup>P at 161.9 MHz) respectively. All spectra were recorded at 298 K unless otherwise stated. Chemical shifts ( $\delta$ ) are quoted in ppm relative to residual signals of the solvent, and <sup>31</sup>P relative to an external H<sub>3</sub>PO<sub>4</sub> reference. Coupling constants (*J*) are quoted in Hz and have uncertainties of ±0.05 Hz. The following abbreviations are used to report the multiplicity of NMR resonances: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. All NMR data were acquired and processed using MestreNova<sup>TM</sup> or TopSpin<sup>TM</sup> version 3.2 from Bruker NMR software.

## A1.2 General Procedure for Catalysed N-Formylation and -Methylation of Amines

Optimisation of reaction conditions and substrate scope investigations were carried out in 50 mL Schlenk flasks. Amine substrates (0.5 mmol), hydrosilane (1-8 equiv), catalysts (25 µmol, 5 mol%) and solvent (2 mL) were charged into nitrogen filled Schlenk flasks fitted with magnetic stirrer bars. The reaction mixtures were degassed with 3 freeze-pump-thaw cycles.  $CO_{2(g)}$  was then introduced into the headspace with a balloon. The reaction mixtures were subsequently heated with stirring for 16 h. Upon cooling to r.t., the reactions were quenched with water (40 µL, 2.2 mmol).

1,1,2,2-tetrachloroethane (53  $\mu$ L, 0.5 mmol) was then added as an internal standard. Crude mixtures were diluted in CDCl<sub>3</sub> and conversions to desired products were determined using <sup>1</sup>H NMR spectroscopy.

## A2 Optimisation of Reaction Conditions for N-Formylation and -Methylation Reactions using Aniline as Model Substrate

NH <sub>2</sub> +	CO <sub>2</sub> PhSiH <sub>3</sub> (1 equiv) cat. (5 mol%) solvent, 16 h, temp. (balloon)	√=0 −NH 6a	cat. = $PCy_2$ N $H$ $ClPCy_2 PCy_2 PCy_2$
Entry	Solvent	Temp. (°C)	Conv.
1	ТИС	50	93% (86%)
2		25	83%
3	Taluana	90	91%
4		50	56%
5	Acetonitrile	70	0%

Table S1. Solvent screening for *N*-formylation of aniline, using PhSiH<sub>3</sub> as reductant.

Table S2. Hydrosilane screening for *N*-formylation of aniline. Reactions were carried out in THF solvent at 50 °C.



Table S3 Catalyst loading screening in formylating conditions. Reactions were carried out in THF at 50 °C.

✓—NH₂ + 5a	silane (1 equiv) cat. (balloon) THF, 16 h, 50 °C	$Cat. = \qquad \qquad PCy_2 \qquad \qquad$
Entry	Catalyst Loading	Total Conv.
1	0%	0%
2	1%	60%
3	2%	71%
4	5%	93% (86%)

────────────────────────────────────	CO2 CO2   (balloon) Tol, 16 h, 90 °C	√=0 NH 6a	Me NH 13a		Cat. =	N PCy <sub>2</sub> N Rh-Cl N PCy <sub>2</sub> 2b
Entry	Catalyst	6a	13a	14a	15a	Total Conv.
1	0%	0%	0%	0%	0%	0%
2	1%	0%	10%	0%	2%	12%
3	2.5%	0%	25%	0%	11%	36%
4	5%	28%	14%	<2%	47%	89%

Table S4 Catalyst loading screening in methylating conditions. Reactions were carried out in toluene at 90 °C.

### A3 Conversions for N-Formylation and -Methylation Reactions of Amines and Spectroscopic Data

The conversions of crude products were identified using <sup>1</sup>H NMR spectroscopy and 1,1,2,2-tetrachloroethane as internal standard. <sup>1</sup>H NMR spectra of the following products were compared to literature reports:

 $\begin{array}{l} 6b,^{[2]} \ 6c,^{[3]} \ 6d,^{[2]} \ 6e,^{[4]} \ 6f,^{[5]} \ 6g,^{[2]} \ 6h,^{[6]} \ 6i,^{[7]} \ 6j,^{[8]} \ 6k,^{[9]} \ 6n,^{[3]} \ 6o,^{[10]} \ 6p,^{[11]} \ 6u,^{[12]} \ 6v,^{[13]} \ 13b,^{[14]} \ 13d,^{[15]} \ 13e,^{[16]} \ 13f,^{[17]} \ 13i,^{[18]} \ 13q,^{[19]} \ 13v,^{[20]} \ 14j,^{[8]} \ 14n,^{[3]} \ 15b,^{[21]} \ 15c,^{[22]} \ 15e,^{[23]} \ 15f,^{[24]} \ 15j,^{[22]} \end{array}$ 

<sup>1</sup>H NMR spectra of the follow products were compared to commercial samples:

6a, 6l, 6m, 6q, 6r, 6s, 6t, 13a, 13c, 13j, 13k, 13n, 13r, 13s, 13u, 14a, 15a, 15d, 15i, 15k, 15n.

## A4 NMR Spectra of Isolated Products

**6a** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{H}$  7.08 (2H, d, *J*=7.44 Hz), 7.14 (1H, t, *J*=7.46 Hz), 7.20 (2H, t, *J*=7.46 Hz), 7.31-39 (4H, m), 7.54 (2H, d, *J*=7.44 Hz), 7.87 (1H, br), 8.38 (1H, m), 8.69 (1H, d, *J*=11.40 Hz). R<sub>f</sub>=0.24 (40% EtOAc in Hexane on silica), 25.8 mg (0.22 mmol, 86% yield) light brown oil recovered after purifying half the reaction mixture by column chromatography.



Figure S1 <sup>1</sup>H NMR spectrum of formanilide after purification by column chromatography.

**15a** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{H}$  2.96 (6H, s), 6.71-81 (3H, m), 7.22-32 (2H, m). R<sub>f</sub>=0.6 (10% EtOAc in Hexane on silica), 28.4 mg (0.23 mmol, 93% yield) pale yellow liquid recovered after purifying half the reaction mixture by column chromatography.



Figure S2 <sup>1</sup>H NMR spectrum of *N*,*N*-dimethylaniline after purification by column chromatography.

# A5 Synthesis of [RhCl{C(NCH<sub>2</sub>PCy<sub>2</sub>)2C<sub>10</sub>H<sub>6</sub>}]

A solution of [RhCl(PPh<sub>3</sub>)<sub>3</sub>] (0.100 g, 0.108 mmol) and H<sub>2</sub>C(NCH<sub>2</sub>PCy<sub>2</sub>)<sub>2</sub>C<sub>10</sub>H<sub>6</sub> (0.064 g, 0.11 mmol) in THF (10 mL) was stirred for 1.5 hrs. The suspension was concentrated to approximately 3 mL, and diethyl ether (2 mL) added. The orange precipitate was separated from the supernatant via cannula filtration. The product was washed with a further 3 mL diethyl ether and dried in vacuo. X-ray quality crystals of the product were obtained from slow diffusion of *n*-hexane into a THF solution. Yield: 0.073 g (93%). IR (KBr, cm<sup>-1</sup>): 2921, 2849 v<sub>CH</sub>; 1580 v<sub>aromCC</sub>. NMR  $(C_6D_6, 298 \text{ K})$  <sup>1</sup>H (300.1 MHz):  $\delta_H$  = 1.22-2.47 (series of multiplets, 44H,  $C_6H_{11}$ ), 3.58 (br s, 4H, PCH<sub>2</sub>N), 6.33 (d, 2H, naphCH,  ${}^{3}J_{HH}$  = 8 Hz), 7.27 (d, 2H, naphCH,  ${}^{3}J_{HH}$  = 8 Hz), 7.41 (m, 2H, naphCH). HSQC (500.0 MHz):  $\delta_{C}(\delta_{H}) = 26.4(1.53), 26.6(1.75)$ 26.8(1.18), 27.0(1.70), 28.7(1.68), 28.8(2.44), 28.9(2.41), 33.6(2.14), 33.7(2.12)  $(C_6H_{11})$ , 50.8(3.59), 50.9(3.56) (PCH<sub>2</sub>), 105.7(6.32), 119.4(7.25), 128.2(7.28) (naphCH). HMBC (500.0 MHz): 117.3(6.35), 117.3(7.27), (<sup>4</sup>C(naph)), 206.7(3.59) (RhC). The remaining naphCH resonances could not be unambiguously identified due to poor signal to noise.  ${}^{31}P{}^{1}H{}$  (121.5 MHz):  $\delta_{P}$  = 38.3 (d,  ${}^{1}J_{RhP}$  = 148 Hz). ESI-MS (+ve Ion, MeCN): *m*/*z* = 726.3 [M]<sup>+</sup>. Accurate Mass: Found 726.2505 [M]<sup>+</sup>, Calcd. for C<sub>37</sub>H<sub>54</sub><sup>35</sup>Cl<sup>14</sup>N<sub>2</sub><sup>31</sup>P<sub>2</sub><sup>103</sup>Rh 726.2506. Anal. Found: C, 61.08; H, 7.50; N, 3.60%. Calcd for C37H54CIN2P2Rh: C, 61.12; H, 7.48; N, 3.85%. Crystal data for  $C_{37}H_{54}CIN_2P_2Rh$ : Mr = 727.15, trigonal, R3c, a = 26.6194(4) Å, c = 27.2200(5) Å, V = 16703.8(5) Å<sup>3</sup>, Z =18,  $D_x$  = 1.301 Mg m<sup>-3</sup>,  $\mu$ (Mo K $\alpha$ ) = 0.65 mm<sup>-1</sup>, T = 200(2) K, orange block, 0.20 x 0.17 x 0.14 mm, 3312 independent reflections. F<sup>2</sup> refinement, R = 0.050, wR = 0.110 for 2736 reflections ( $I > 2\sigma(I)$ , 20max = 50°), 197 parameters.

# A6 Stoichiometric Studies withO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, CS<sub>2</sub>, CO, PhSiH<sub>3</sub>, CO<sub>2</sub> and Aniline

#### Reactions of $[RhCl{C(NCH_2PR_2)_2C_{10}H_6}]$ (R = Ph 2a, Cy 2b) with O<sub>2</sub>

A suspension of **2a** or **2b** in  $C_6D_6$  was exposed to air for 24 hrs.

R = Ph, proposed complex [RhCl( $\eta^2$ -O<sub>2</sub>){C(NCH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>C<sub>10</sub>H<sub>6</sub>}]: NMR (C<sub>6</sub>D<sub>6</sub>, 298 K) <sup>1</sup>H:  $\delta_{H}$  = 4.71 (d, PCH<sub>2</sub>N, <sup>2</sup>J<sub>PH</sub> = 5 Hz), 6.88-8.11 (set of multiplets, C<sub>6</sub>H<sub>5</sub> and naphCH). <sup>31</sup>P{<sup>1</sup>H}:  $\delta_{P}$  = 27.7.

R = Cy, proposed complex [RhCl(η<sup>2</sup>-O<sub>2</sub>){C(NCH<sub>2</sub>PCy<sub>2</sub>)<sub>2</sub>C<sub>10</sub>H<sub>6</sub>}]: IR (KBr, cm<sup>-1</sup>): 2920, 2850 v<sub>CH</sub>; 1583 v<sub>aromCC</sub>, 863 v<sub>O2</sub> (tentative). NMR (C<sub>6</sub>D<sub>6</sub>, 298 K) <sup>1</sup>H:  $\delta_{\rm H}$  = 3.74 (br d, 2H, PCH<sub>2</sub>N, <sup>2</sup>J<sub>HH</sub> = 14 Hz), 4.11 (br d, 2H, PCH<sub>2</sub>N, <sup>2</sup>J<sub>HH</sub> = 13 Hz), 6.21 (d, 2H, naphCH, <sup>3</sup>J<sub>HH</sub> = 8 Hz) (other peaks could not be unambiguously assigned due to impurities). <sup>31</sup>P{<sup>1</sup>H}:  $\delta_{\rm P}$  = 29.9 (d, <sup>1</sup>J<sub>RhP</sub> = 102 Hz). ESI-MS (+ve Ion, MeCN): *m/z* = 723.7 [M - Cl]<sup>+</sup>.

#### Synthesis of [RhCl<sub>2</sub>(CH<sub>2</sub>Cl){C(NCH<sub>2</sub>PCy<sub>2</sub>)<sub>2</sub>C<sub>10</sub>H<sub>6</sub>}]

A solution of  $[RhCl{C(NCH_2PCy_2)_2C_{10}H_6}]$ : (**2b**: 0.078 g, 0.108 mmol) in DCM (5 mL) was heated to refluxing temperature for 20 hrs. The solution was then allowed to cool to ambient temperature and 3 mL ethanol was added. This solution was concentrated under reduced pressure until a precipitate formed, which was separated from the supernatant via cannula filtration, washed with a further 3 mL ethanol, and dried in vacuo. Yield: 0.065 g (74%). IR (KBr, cm<sup>-1</sup>): 2962, 2926, 2851  $v_{CH}$ ; 1584  $v_{aromCC}$ . NMR (CDCI<sub>3</sub>, 298 K) <sup>1</sup>H:  $\delta_{H}$  = 1.35-3.21 (set of multiplets, 44H,  $C_6H_{11}$ ), 4.45 (m, 6H, PCH<sub>2</sub> and CH<sub>2</sub>Cl), 6.83 (d, 2H, naphCH, <sup>3</sup>J<sub>HH</sub> = 7 Hz), 7.39 (dd, 2H, naphCH,  ${}^{3}J_{HH}$  = 7 Hz,  ${}^{3}J_{HH}$  = 8 Hz), 7.46 (d, 2H, naphCH,  ${}^{3}J_{HH}$  = 8 Hz).  ${}^{13}C{}^{1}H{}$ :  $\delta_{\rm C}$  = 26.4, 26.5 (C<sub>6</sub>H<sub>11</sub>), 27.5-28.0 (set of multiplets, C<sub>6</sub>H<sub>11</sub>), 29.2, 29.5, 29.7, 29.8  $(C_6H_{11})$ , 35.9 (t<sup>v</sup>,  $C_6H_{11}$ ,  $J_{PC}$  = 10 Hz), 36.6 (t<sup>v</sup>,  $C_6H_{11}$ ,  $J_{PC}$  = 11 Hz), 37.2 (dt, RhCH<sub>2</sub>Cl,  ${}^{1}J_{RhC}$  = 30 Hz,  ${}^{2}J_{PC}$  = 8 Hz), 52.0 (t<sup>v</sup>, PCH<sub>2</sub>,  ${}^{1,3}J_{PC}$  = 14 Hz), 107.3 (naphCH), 119.5 (<sup>4</sup>C(naph)), 122.3, 128.2 (naphCH), 134.3 (<sup>4</sup>C(naph)), 134.4 (t<sup>v</sup>, C<sup>1,8</sup>(naph), <sup>3,5</sup>*J*<sub>PC</sub> = 4 Hz), 205.8 (dt, RhC<sub>carbene</sub>,  ${}^{1}J_{RhC}$  = 50 Hz,  ${}^{2}J_{PC}$  = 5 Hz).  ${}^{31}P{}^{1}H$ :  $\delta_{P}$  = 22.1 (d,  ${}^{1}J_{RhP}$  = 99 Hz). NMR (C<sub>6</sub>D<sub>6</sub>, 298 K) <sup>1</sup>H:  $\delta_{H}$  = 1.04-3.58 (set of multiplets, 44H, C<sub>6</sub>H<sub>11</sub>), 4.24 (d, 2H, PCH<sub>2</sub>,  ${}^{2}J_{HH}$  = 14 Hz), 4.31 (d, 2H, PCH<sub>2</sub>,  ${}^{2}J_{HH}$  = 14 Hz), 4.93 (td, CH<sub>2</sub>Cl,  ${}^{3}J_{PH}$  = 7 Hz,  ${}^{2}J_{RhH}$  = 2 Hz), 6.29 (d, 2H, naphCH,  ${}^{3}J_{HH}$  = 8 Hz), 6.98-7.12 (set of multiplets, 4H, naphCH). <sup>31</sup>P{<sup>1</sup>H}:  $\delta_P$  = 21.5 (d, <sup>1</sup>J<sub>RhP</sub> = 99 Hz). ESI-MS (+ve lon, MeCN): m/z = 775.6 [M - Cl]<sup>+</sup>, 741.5 [M - 2Cl]<sup>+</sup>. Accurate Mass: Found 775.2346 [M - Cl]<sup>+</sup>, Calcd. for C<sub>38</sub>H<sub>56</sub><sup>35</sup>Cl<sub>2</sub><sup>14</sup>N<sub>2</sub><sup>31</sup>P<sub>2</sub><sup>103</sup>Rh 775.2351.

#### Observation of [RhCl(CO){C(NCH<sub>2</sub>PCy<sub>2</sub>)<sub>2</sub>C<sub>10</sub>H<sub>6</sub>}] (proposed formulation)

In an NMR tube, a suspension of [RhCl{C(NCH<sub>2</sub>PCy<sub>2</sub>)<sub>2</sub>C<sub>10</sub>H<sub>6</sub>]] (**2b**) in C<sub>6</sub>D<sub>6</sub> was frozen using dry ice/ethanol. The atmosphere in the tube was evacuated and replaced with carbon monoxide (three times), and the solvent allowed warm to ambient temperature. Removal of solvent *in vacuo* resulted in reformation of the starting material **2b**, and hence the product was characterised by NMR spectroscopy under an atmosphere of carbon monoxide. The infrared spectrum was obtained by injecting the NMR solution into a solution infrared cell under N<sub>2</sub>. IR (benzene, cm<sup>-1</sup>): 2000, 1988 v<sub>CO</sub> (the observance of two bands rather than one is discussed in the full paper). NMR (C<sub>6</sub>D<sub>6</sub>, 298 K) <sup>1</sup>H:  $\delta_{H}$  = 1.27-2.49 (set of multiplets, 44H, C<sub>6</sub>H<sub>11</sub>), 5.25 (br s, 4H, PCH<sub>2</sub>), 7.06-7.62 (set of multiplets, 6H, naphCH). <sup>31</sup>P{<sup>1</sup>H}:  $\delta_{P}$  = 52.5 (br d)

#### Synthesis of [RhCl( $\eta^2$ -CS<sub>2</sub>){C(NCH<sub>2</sub>PCy<sub>2</sub>)<sub>2</sub>C<sub>10</sub>H<sub>6</sub>}]

In an NMR tube, a suspension of [RhCl{C(NCH<sub>2</sub>PCy<sub>2</sub>)<sub>2</sub>C<sub>10</sub>H<sub>6</sub>]] (**2b**) in C<sub>6</sub>D<sub>6</sub> was treated with 2 drops of carbon disulfide. A rapid lightening of colour was observed (orange to pale orange). The reaction was monitored by NMR spectroscopy, and conversion to the product appeared to be complete after 20 min. X-ray quality crystals were obtained upon standing of this reaction mixture. Removal of solvent *in vacuo* resulted in reformation of the starting material **2b**, hence the product was characterised by NMR spectroscopy in the presence of excess CS<sub>2</sub>. NMR (C<sub>6</sub>D<sub>6</sub>, 298 K) <sup>1</sup>H:  $\delta_{\rm H}$  = 1.11-3.04 (set of multiplets, 44H, C<sub>6</sub>H<sub>11</sub>), 4.32 (d, 2H, PCH<sub>2</sub>, <sup>2</sup>J<sub>HH</sub> = 12

Hz), 4.40 (d, 2H, PCH<sub>2</sub>, <sup>2</sup>*J*<sub>HH</sub> = 12 Hz), 6.27 (d, 2H, naphCH, <sup>3</sup>*J*<sub>HH</sub> = 8 Hz), 6.99 (dd, 2H, naphCH, <sup>3</sup>*J*<sub>HH</sub> = 8 Hz, <sup>3</sup>*J*<sub>HH</sub> = 8 Hz), 7.10 (d, 2H, naphCH, <sup>3</sup>*J*<sub>HH</sub> = 8 Hz). <sup>13</sup>C{<sup>1</sup>H}:  $\delta_{\rm C}$  = 26.1, 26.3 (C<sub>6</sub>H<sub>11</sub>), 27.4-27.8 (set of multiplets, C<sub>6</sub>H<sub>11</sub>), 28.0, 28.9, 29.0, 29.6 (C<sub>6</sub>H<sub>11</sub>), 34.4 (t<sup>v</sup>, C<sub>6</sub>H<sub>11</sub>, *J*<sub>PC</sub> = 10 Hz), 34.9 (t<sup>v</sup>, C<sub>6</sub>H<sub>11</sub>, *J*<sub>PC</sub> = 11 Hz), 53.6 (t<sup>v</sup>, PCH<sub>2</sub>, <sup>1,3</sup>*J*<sub>PC</sub> = 14 Hz), 107.3 (naphCH), 119.7 (<sup>4</sup>C(naph)), 121.9, 128.5 (naphCH), 134.2 (t<sup>v</sup>, C<sup>1.8</sup>(naph), <sup>3.5</sup>*J*<sub>PC</sub> = 10 Hz), 134.8 (<sup>4</sup>C(naph)), 212.8 (d, RhC<sub>carbene</sub>, <sup>1</sup>*J*<sub>RhC</sub> = 60 Hz), 260.3 (d, CS<sub>2</sub>, <sup>1</sup>*J*<sub>RhC</sub> = 12 Hz). <sup>31</sup>P{<sup>1</sup>H}:  $\delta_{\rm P}$  = 31.3 (d, <sup>1</sup>*J*<sub>RhP</sub> = 103 Hz). *Crystal data for* C<sub>38</sub>H<sub>54</sub>ClN<sub>2</sub>P<sub>2</sub>RhS<sub>2</sub>·2(C6H6): *M*<sub>r</sub> = 959.52, monoclinic, *P2*<sub>1</sub>/*c*, *a* = 11.8000(2) Å, *b* = 26.2914(4) Å, *c* = 15.6374(3) Å, *β* = 105.7265(9)°, *V* = 4669.72(14) Å<sup>3</sup>, *Z* = 4, *D*<sub>calcd</sub> = 1.365 Mg m<sup>-3</sup>, μ(Mo Kα) = 0.62 mm<sup>-1</sup>, *T* = 200(2) K, pale orange block, 0.17 x 0.13 x 0.09 mm, 8227 independent reflections. *F*<sup>2</sup> refinement, *R*<sub>1</sub> = 0.056, *wR*<sub>2</sub> = 0.101 for 5295 reflections (*I* > 2*σ*(*I*), 20max = 50°), 559 parameters.

#### Reactions of [RhCl{C(NCH<sub>2</sub>PCy<sub>2</sub>)<sub>2</sub>C<sub>10</sub>H<sub>6</sub>}] (2b) with PhSiH<sub>3</sub>, CO<sub>2</sub> and Aniline

Stoichiometric studies of complex **2b** with PhSiH<sub>3</sub>, CO<sub>2</sub> and aniline were carried out in NMR tubes sealed with Youngs© Teflon taps. Toluene-*d*<sub>8</sub> (0.5 mL), complex **2b** (7.00 mg, 10.0 µmol), PhSiH<sub>3</sub> (2.5 µL, 20 µmol/2 equiv or 25µL, 200 µmol/20 equiv) and aniline (1.84 µL, 20.0 µmol, 2 equiv) were charged into NMR tubes in a N<sub>2(g)</sub> glovebox. The reaction mixtures were degassed with 3 freeze-pump-thaw cycles, and the headspaces were refilled with N<sub>2(g)</sub> or CO<sub>2(g)</sub>. <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were taken at 25-90 °C.

#### Stoichiometric Studies of Complex 2b with PhSiH<sub>3</sub>



Figure S3 Stoichiometric studies of complex 2b with  $PhSiH_3$ , using <sup>1</sup>H NMR spectroscopy. On using 2 equiv  $PhSiH_3$ , all free  $PhSiH_3$  reacted upon heating to 90 °C.



**Figure S4** Hydride region of <sup>1</sup>H NMR spectrum of the reaction mixture of complex **2b** and 20 equiv PhSiH<sub>3</sub>, after heating to 90 °C for 16 h. NMR spectrum was taken at 25 °C for better resolution. Changes in multiplicity of the hydride signals suggest that phosphorus and hydride likely ligate simultaneously to the rhodium centre for <sup>31</sup>P-<sup>1</sup>H coupling to occur.

#### <sup>31</sup>P{<sup>1</sup>H} NMR Spectra

90 °C, 20	equiv Pl	nSiH₃	, mm								
90 °C, 2 e	equiv Ph	SiH₃		٨							
70 °C, 2 e	equiv Ph	SiH₃				11					
50 °C, 2 e	equiv Ph	SiH₃									
25 °C, 2 e	equiv Ph	SiH₃				U					
75 70	65	60 5	55 50	45	40	35	30	25	20	15	 ppm

**Figure S5** Stoichiometric studies of complex **2b** with PhSiH<sub>3</sub>, using <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. Complex **2b** was consumed on using 20 equiv PhSiH<sub>3</sub> and heated to 90 °C.



**Figure S6** Stoichiometric studies of complex **2b** with PhSiH<sub>3</sub>, using <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. NMR spectra were taken at 25 °C. NMR signals are sharpened and separated compared to those recorded at 90 °C (Fig. S5).

Stoichiometric Studies of Complex 2b with  $PhSiH_3$  and  $CO_2$ 



Figure S7 Stoichiometric studies of complex 2b with 2 equiv PhSiH<sub>3</sub> and CO<sub>2</sub> at 25-90  $^{\circ}$ C, using <sup>1</sup>H NMR spectroscopy.

90 °C				<b>2b</b> , δ <sub>Ρ</sub>	= 37.5 p	pm, J <sub>RhP</sub> :	= 149.3	Hz	****			
70 °C	1											
50 °C					δ <sub>P</sub> = 3	1.8 ppm	, J <sub>RhP</sub> = 9	2.0 Hz				
30 °C		~			δ <sub>P</sub> = 3	30.3 ppn	n, J <sub>RhP</sub> = 9	94.5 Hz				
25 °C					δ,	. = 29.3 p	opm, J <sub>RhF</sub>	₀= 97.0 ŀ	łz			
55	50	45	40	35	30	25	20	15	10	5	0	ppm

### <sup>31</sup>P{<sup>1</sup>H} NMR Spectra

Figure S8 Stoichiometric studies of complex 2b with 2 equiv PhSiH<sub>3</sub> and CO<sub>2</sub>, at 25-90  $^{\circ}$ C using <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy.

#### Stoichiometric Studies of Complex 2b with CO<sub>2</sub> and Aniline



**Figure S9** Stacked <sup>1</sup>H NMR spectra of stoichiometric studies of complex **2b** with 2 equiv aniline under CO<sub>2</sub> atmosphere. Minimal changes were observed before and after heating reaction mixture at 90 °C overnight.



**Figure S10** Magnified stacked <sup>1</sup>H NMR spectra (5.5-8.0 ppm region). Major aromatic peaks present in both spectra are due to aniline and residual non-deuterated toluene. Carbamate species are unlikely to have formed to a significant extent by heating aniline under  $CO_2$  in the presence of complex **2b**.

#### **Evaluation of Proposed Mechanistic Pathway 1**

Toluene-*d*<sub>8</sub> (2 mL), complex **2b** (17.5 mg, 25.0 µmol) and PhSiH<sub>3</sub> (0.25 mL, 2 mmol) were charged into a 50 mL Schlenk flask filled with  $N_{2(g)}$ . Nitrogen was removed from the headspace with 3 freeze-pump-thaw cycles, and replaced with CO<sub>2</sub> (balloon). The reaction mixture was heated at 90 °C with stirring for 16 h, then cooled to r.t. and transferred to a Youngs<sup>©</sup> NMR tube under N<sub>2</sub> atm for <sup>1</sup>H NMR analysis.

The reaction mixture was degassed with another 3 freeze-pump-thaw cycles to ensure complete removal of CO<sub>2</sub> from the system. Headspace was refilled with N<sub>2(g)</sub>. Aniline (47  $\mu$ L, 0.5 mmol) was then added to the reaction mixture, and heated at 90 °C with stirring for 16 h. Upon cooling to r.t., the reaction mixture was transferred to another Youngs<sup>©</sup> NMR tube under N<sub>2</sub> atm for <sup>1</sup>H NMR analysis.



**Figure S11** Reaction of complex **2b** with PhSiH<sub>3</sub> under CO<sub>2</sub> atm, using toluene- $d_8$  (90 °C) as the reaction solvent. Note the lack of aldehyde signals and the presences of free PhSiH<sub>3</sub> after heating. <sup>1</sup>H NMR spectrum taken at 25 °C.



**Figure S12** Reaction of aniline and *in situ* generated species from previous step under N<sub>2</sub> atm, using toluene-d<sub>8</sub> (90 °C) as the reaction solvent. <sup>1</sup>H NMR spectrum taken at 25 °C, and overlaid with <sup>1</sup>H NMR spectra of *N*,*N*-dimethylaniline, *N*-methylaniline, and aniline in toluene-d<sub>8</sub> for comparison. Sections of the <sup>1</sup>H NMR spectra are magnified and presented below.



**Figure S13** Reaction of aniline and *in situ* generated species from previous step under N<sub>2</sub> atm, using toluene-d<sub>8</sub> (90 °C) as the reaction solvent. <sup>1</sup>H NMR spectrum (6.0-6.8 ppm region) taken at 25 °C, and overlaid with <sup>1</sup>H NMR spectra of *N*,*N*-dimethylaniline, *N*-methylaniline, and aniline in toluene-d<sub>8</sub>.



**Figure S14** Reaction of aniline and *in situ* generated species from previous step under N<sub>2</sub> atm, using toluene-d<sub>8</sub> (90 °C) as the reaction solvent. <sup>1</sup>H NMR spectrum (1.6-2.6 ppm region) taken at 25 °C, and overlaid with <sup>1</sup>H NMR spectra of *N*,*N*-dimethylaniline, *N*-methylaniline, and aniline in toluene-d<sub>8</sub>.

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