Supporting Information

CO Oxidation by N₂O Homogeneously Catalyzed by Ruthenium Hydride Pincer Complexes Indicating a New Mechanism

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**1. Materials:** THF and toluene were distilled freshly over sodium and kept over 4Å MS. Other commercially available chemicals were purchased and used without additional purification unless noted otherwise. Complexes 6, 8, 9, 10, 12, 13, and 14 were prepared according to the known literature procedures. All reactions were carried out with stirring bar under an atmosphere of purified nitrogen in a Braun glovebox or by using standard Schlenk techniques. Reaction temperatures were reported as the temperatures of the oil bath. Nuclear magnetic resonance spectra (¹H NMR, ¹³C NMR, and ³¹P NMR) were recorded with a Bruker-300 MHz spectrometer (300 MHz, ¹H at 300 MHz, ¹³C at 75 MHz, and ³¹P at 121 MHz), Bruker-400 MHz spectrometer (400 MHz, ¹H at 400 MHz, ¹³C at 101 MHz), or Bruker-500 MHz spectrometer (500 MHz, ¹H at 500 MHz, ¹³C at 126 MHz). Chemical shifts are reported in parts per million (ppm, δ). In ¹H NMR, the chemical shifts were referenced to the residual hydrogen signal of the deuterated solvents. In ¹³C{¹H} NMR measurements, the signals of deuterated solvents were used as a reference. ³¹P NMR chemical shifts are reported in parts per million downfield from H₃PO₄ and referenced to an external 85% solution of phosphoric acid in D₂O. Coupling constants were reported in Hertz (Hz). Data for ¹H NMR spectra were reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet, coupling constant (Hz), and integration.

**2. Preparation of Standard Curves for CO₂ and N₂**

2.1 Preparation of Standard Curve in GC for CO₂.

| experiment | Gas Volume / µL | Area in GC |
|------------|-----------------|------------|
| 1          | 0               | 0          |
| 2          | 50              | 9320       |
| 3          | 100             | 19185      |
| 4          | 150             | 32087      |
| 5          | 200             | 40160      |

\[ y = 203.06x \]
\[ R^2 = 0.9955^{10} \]

**S2**
2.2 Preparation of Standard Curve in GC for N₂.

| experiment | Gas Volume / µL | Area in GC |
|------------|-----------------|------------|
| 1          | 0               | 0          |
| 2          | 50              | 8840       |
| 3          | 100             | 16264      |
| 4          | 150             | 23402      |
| 5          | 200             | 30979      |

3. Catalytic CO Oxidation by N₂O and determination of CO₂
3.1 Using Complex 14 as Pre-catalyst

\[
\begin{align*}
\text{N}_2\text{O} + \text{CO} & \xrightarrow{1 \text{ atm}} \text{N}_2 + \text{O} = \text{C} = \text{O} \\
\end{align*}
\]

Procedure: To a 20 mL vial were added complex 14 (4.8 mg, 0.01 mmol), t-BuOK (1.1 mg, 1.0 equiv, 0.01 mmol), and THF (1 mL) in glovebox. The resulting mixture was stirred at room temperature for 20 min to afford a green solution, which was then transferred into a 90 mL Fisher-Porter tube and 3 mL of THF were added. 1 atm of CO (14.7 psi) was added, and the solution was shaken for 30 sec, generating a blue solution. The Fisher-Porter Tube was then filled with 2 atm of N₂O and heated to 70 °C. Upon heating for 22 h, 1.97 mmol of CO₂ (197 TON) was detected in the gas phase based on analysis of the gas phase by GC using a standard calibration curve (total pressure after reaction: 3.38 atm; gas volume injected: 310 µL; CO₂ area
observed: 9978), while 0.4 mmol of CO$_2$ (partial pressure of CO$_2$: 0.54 atm; solubility: ca. 0.1 M, 4 mL) was calculated in solution according to reference 8.

GC conditions: HP 6890 Series GC System; column: SUPELCO 1-2382, 5Ftx1/8In S.S. SUPPORT 45/60 CARBOXEN$^\text{TM}$ 1000, Packed Column. Inlets: 87 °C; Flow: 29.1; Oven: 35 °C, hold 2 min; 10 °C/min to 60 °C, hold 0 min; 30 °C/min to 200 °C. Carrier Gas: He. Detector: TCD 250 °C.

i) Control experiment: 50% N$_2$ + 50% N$_2$O

![Graph](image1)

ii) Control experiment: 100% CO$_2$

![Graph](image2)

iii) Control experiment: 100% CO

![Graph](image3)

iv) Experiment of CO oxidation by using complex 14 as pre-catalyst:
3.2 Catalytic CO Oxidation by N₂O Using Complex 16

**Procedure:** To a 90 mL Fisher-Porter tube were added complex 16 (4.7 mg, 0.01 mmol) and THF (4 mL) in a glovebox. The resulting blue solution was sealed and then filled with 1 atm of CO (14.7 psi) and 2 atm of N₂O. Upon heating for 22 h, 2.72 mmol of CO₂ (272 TON) was afforded in gas phase based on analysis of the gas phase by GC using a standard calibration curve (total pressure after reaction: 3.45 atm; gas volume injected: 300 µL; CO₂ area observed: 13071), while 0.6 mmol of CO₂ was dissolved in solution (partial pressure of CO₂: 0.74 atm; solubility: ca. 0.15 M, 4 mL), calculated according to reference 8 (total TON is 332, 90% yield). And at the same time, 3.17 mmol of N₂ (317 TON, 86% yield) was afforded based on analysis of the gas phase by GC using a standard calibration curve (total pressure after reaction: 3.45 atm; gas volume injected: 300 µL; N₂ area observed: 25458; total amount of N₂: 6.85 mmol; N₂ in 90 mL tube originally: 3.67 mmol; N₂ produced: 3.17 mmol). No CO gas was detected.

2.3 Catalytic CO Oxidation Using Complex 16 with excess of CO and N₂O
Procedure: To a 90 mL Fisher-Porter tube were added 16 (5.0 mg, 0.0106 mmol) and THF (4 mL) in glovebox. The resulting blue solution was sealed and refilled with 50 psi of CO and ca. 50 psi of N$_2$O. Upon heating for 22 h, 4.97 mmol of CO$_2$ (468 TON) was afforded in the gas phase based on analysis of the gas phase by GC using a standard calibration curve (total pressure after reaction: 7.06 atm; gas volume injected: 305 µL; CO$_2$ area observed: 11880), while 1.0 mmol of CO$_2$ (partial pressure of CO$_2$: 1.35 atm; solubility: ca. 0.25 M, 4 mL) was dissolved in solution calculated according to reference 8 (total TON is 561). And at the same time, 6.16 mmol of N$_2$ (579 TON) was afforded based on analysis of the gas phase by GC using a standard calibration curve (total pressure after reaction: 7.06 atm; gas volume injected: 305 µL; N$_2$ area observed: 18157; total amount of N$_2$: 9.83 mmol; N$_2$ in 90 mL tube originally: 3.67 mmol; N$_2$ produced: 6.16 mmol).

4. Preparation of complexes 7, 16, 17, and 18.

4.1 Preparation of complex 7.

Procedure: To a 90 mL Fisher-Porter tube were added 2,6-bis((diisopropylphosphanylmethyl)pyridine (PNP ligand, 122.9 mg, 0.36 mmol), RuCl$_2$(PPh$_3$)$_3$ (334.3 mg, 0.35 mmol), and THF (10 mL) in glovebox. The resulting mixture was stirred at 70 °C for 4 h, generating an orange solution. The Fisher-Porter tube was then
filled with 3 bar of CO gas and kept at reflux for another 12 h, affording a yellow solution. The solvent was evaporated to afford a yellow solid, which was washed with pentane (4 mL × 5) and dried under vacuum. The desired product 7 (182.2 mg) was obtained in 97% yield. Crystals suitable for X-ray diffraction were obtained by laying a CHCl₃ solution with pentane. The X-ray crystal structure data is listed below as X-Ray data.

¹H NMR (500 MHz, CDCl₃, 298 K) δ: 7.62 (t, ¹JHH = 7.9 Hz, 1H, Py-H), 7.32 (d, ³JHH = 7.6 Hz, 2H, Py-H), 3.85 (t, ²JHP = 4.4 Hz, 4H, PCH₂Pt × 2), 2.90-2.75 (m, 4H, CH × 4), 1.45-1.34 (m, 24H, CH₃ × 8). ¹³C{¹H} NMR (126 MHz, CDCl₃, 298 K) δ 206.48 (t, ²JPC = 10.7 Hz, CO), 162.90 (t, JPC = 5.0 Hz, PyC), 137.89 (s, PyCH), 120.90 (t, JPC = 4.8 Hz, PyCH), 39.79 (t, JPC = 9.8 Hz, PyCH₂Pt), 23.82 (t, JPC = 11.2 Hz, PCH), 20.02 (s, CH₃), 18.85 (s, CH₃). ³¹P{¹H} NMR (121 MHz, CDCl₃, 298 K) δ: 60.36 (s). IR ν (neat, cm⁻¹) 1945.

¹H NMR of complex 7 in CDCl₃
$^1$C$^1$H NMR of complex 7 in CDCl$_3$

$^{31}$P$^1$H NMR of complex 7 in CDCl$_3$
4.2 Preparation of complex 16.

Procedure: To a 90 mL Fisher-Porter tube were added complex 14 (45.6 mg, 0.1 mmol), t-BuOK (11.0 mg, 0.1 mmol), and pre-cooled THF (-35 °C, 5 mL) in a glovebox. The resulting mixture was stirred at room temperature for 20 min, generating a green solution. The Fisher-Porter tube was then filled with 2 bar of CO gas and kept stirring at room temperature for another 10 min, affording a blue solution. After evaporation, a dark solid was obtained, which was dissolved in pentane (20 mL) and filtered through celite. The resulting solution was evaporated to ca. 5 mL and left to recrystallize in the freezer (-35 °C), affording a dark green solid. After decanting the solution and drying the solid under vacuum, the desired product 16 (33.1 mg) was obtained in 74% yield. Crystals suitable for X-ray analysis were also obtained. Note that the product is not stable in THF or benzene at room temperature, it converts to complex 17 slowly even during NMR analysis. The X-ray crystal structure data is listed below as X-Ray data.

$^1$H NMR (500 MHz, THF-$d_8$) δ 8.82 (d, $^3$J$_{HH}$ = 5.6 Hz, 1H, Py-H), 7.88 (d, $^3$J$_{HH}$ = 8.3 Hz, 1H, Py-H), 7.83 (t, $^3$J$_{HH}$ = 7.8 Hz, 1H, Py-H), 7.31 (t, $^3$J$_{HH}$ = 6.4 Hz, 1H, Ar-H), 6.56 (t, $^3$J$_{HH}$ = 8.5 Hz, 1H, Py-H), 6.30 (d, $^3$J$_{HH}$ = 6.9 Hz, 1H, Py-H), 6.25 (d, $^3$J$_{HH}$ = 8.8 Hz, 1H, Py-H), 3.41 (d, $J = 2.7$ Hz, 1H, CHP), 1.32 (t, $J = 14.1$ Hz, 18H), -4.93 (d, $^2$J$_{PH}$ = 18.6 Hz, 1H, Ru-H).

$^{13}$C($^1$H) NMR (126 MHz, THF-$d_8$) δ 204.43 (d, $^2$J$_{PC}$ = 11.5 Hz, CO), 194.80 (dd, $J = 5.4$, 2.7 Hz, CO), 168.28 (d, $J_{PC}$ = 14.8 Hz, Py), 161.04, 154.40, 152.98 (d, $J_{PC}$ = 2.7 Hz, Py), 137.57, 131.56 (d, $J_{PC}$ = 1.8 Hz, Py), 124.77 (d, $J_{PC}$ = 1.8 Hz, Py), 122.34, 116.63 (d, $J_{PC}$ = 17.3 Hz, Py), 101.69, 63.81 (d, $J_{PC}$ = 55.5 Hz, CH), 37.47 (d, $J_{PC}$ = 26.5 Hz), 36.61 (d, $J_{PC}$ = 26.5 Hz), 30.88 (d, $^2$J$_{PC}$ = 4.3 Hz), 30.17 (d, $^2$J$_{PC}$ = 4.3 Hz). $^{31}$P($^1$H) NMR (121 MHz, THF-$d_8$, 298 K) δ: 97.4 (s). IR ν(neat, cm$^{-1}$) 2013, 1950.
$^1$H NMR of complex 16 in THF-$d_8$

$^{13}$C($^1$H) NMR of complex 16 in THF-$d_8$
4.3 Preparation of complex 17.

Procedure: To a 90 mL Fisher-Porter tube were added complex 14 (25.1 mg, 0.05 mmol), t-BuOK (5.7 mg, 0.05 mmol), and pre-cooled THF (-35 °C, 5 mL) in a glovebox. The resulting mixture was stirred at room temperature for 20 min, generating a green solution. The Fisher-Porter tube was filled with 1 bar of CO gas and then kept stirring at 50 °C for 24 h, affording a purple solution. A dark purple solid was obtained after solvent evaporation, which was further dissolved in ether (20 mL) and filtered through celite. The resulting solution was allowed to slowly evaporate to ca. 0.5 mL at room temperature, affording a dark solid. After decanting the solution and drying the solid under vacuum, the desired product 17 (15.1 mg) was obtained in 61% yield. Crystals suitable for X-ray analysis were also obtained. The X-ray crystal structure data is listed below as X-Ray data.

$^1$H NMR (400 MHz, THF-$d_8$) $\delta$ 8.21-8.11 (m, 2H, Py-H), 7.78 (t, $^3$J$_{HH}$ = 7.7 Hz, 1H, Py-H), 7.39 (d, $^3$J$_{HH}$ = 7.6 Hz, 1H, Py-H), 6.92 (dd, $J = 7.5$, 4.6 Hz, 1H, Py-H), 3.75 (dd, $J_1 = 17.1$ Hz, $J_2 = 10.3$ Hz, 1H, one protone of CH$_2$), 3.54 (dd, $J_1 = 17.3$ Hz, $J_2 = 6.5$ Hz, 1H, one protone of
CH₂), 1.45 (d, J = 13.7 Hz, 9H, t-Bu), 1.25 (d, J = 13.2 Hz, 9H, t-Bu), -5.23 (d, J = 17.6 Hz, 1H, Ru-H). ¹³C{¹H} NMR (101 MHz, THF-d₈) δ 206.32 (d, ¹²JPC = 7.5 Hz, CO), 198.66 (d, ¹²JPC = 4.5 Hz, CO), 170.10 (d, ¹²JPC = 57.7 Hz, Py), 165.42 (d, JPC = 3.5 Hz, Py), 162.31 (d, JPC = 1.1 Hz, Py), 162.18 (d, JPC = 7.5 Hz, Py), 148.64, 143.36, 137.97, 124.04 (d, JPC = 4.1 Hz, Py), 120.82 (d, JPC = 8.4 Hz, Py), 119.03, 36.58 (d, ¹JPC = 14.9 Hz, CH₂), 35.46 (d, ¹JPC = 14.1 Hz), 35.33 (d, ¹JPC = 10.7 Hz), 30.08 (d, ¹JPC = 6.0 Hz, t-Bu), 28.17 (d, ¹JPC = 5.2 Hz, t-Bu). ³¹P{¹H} NMR (121 MHz, THF-d₈, 298 K) δ: 88.4 (s). IR ν (neat, cm⁻¹) 2007, 1950.

¹H NMR of complex 17 in THF-d₈
$^{13}$C($^1$H) NMR of complex 17 in THF-$d_8$

$^{31}$P($^1$H) NMR of complex 17 in THF-$d_8$
4.4 Preparation of complex 18.

**Procedure:** To a 90 mL Fisher-Porter tube were added 6-((di-tert-butylphosphaneyl)methyl)-2,2'-bipyridine (PNN ligand, 200.7 mg, 0.64 mmol), RuCl₂(PPh₃)₃ (600.3 mg, 0.63 mmol), and THF (10 mL) in a glovebox. The resulting mixture was stirred at 70 °C for 24 h, generating a dark brown solution. The Fisher-Porter tube was then filled with 3 bar of CO gas and kept at reflux for another 24 h, affording a dark orange solution together with an orange precipitate. The solvent was evaporated to afford an orange solid, which was washed with pentane (5 mL × 4) and dried under vacuum. The desired product 18 (318.3 mg) was obtained in 99% yield. Two types of crystals including 18 and 18·CHCl₃ suitable for X-ray analysis were obtained by laying a CHCl₃ solution with pentane. The X-ray crystal structure data are listed below as X-Ray data.

**1H NMR** (400 MHz, CDCl₃, 298 K) δ: 9.47 (t, J = 4.3 Hz, 1H, Ar-H), 8.08 (d, J_HH = 7.8 Hz, 1H, Ar-H), 8.00-7.91 (m, 2H, Ar-H), 7.81 (t, J_HH = 7.8 Hz, 1H, Ar-H), 7.66-7.59 (m, 1H, Ar-H), 7.56 (d, J = 7.7 Hz, 1H, Ar-H), 3.91 (dd, J₁ = 16.3 Hz, J₂ = 8.9 Hz, 1H, one protone of CH₂), 3.53 (dd, J₁ = 16.4 Hz, J₂ = 10.1 Hz, 1H, one protone of CH₂), 1.60 (d, J = 13.7 Hz, 9H, t-Bu), 1.40 (d, J = 12.9 Hz, 9H, t-Bu). 13C{1H} NMR (101 MHz, CDCl₃, 298 K) δ 200.61 (d, J_PC = 15.0 Hz, CO), 165.21 (d, J = 2.0 Hz, Ar), 157.28 (d, J = 1.4 Hz, Ar), 156.62 (d, J = 1.9 Hz, Ar), 150.34, 138.05, 137.19, 126.99 (d, J = 2.8 Hz, Ar), 123.24 (d, J = 8.2 Hz, Ar), 122.74 (d, J = 1.5 Hz, Ar), 120.41, 37.76 (d, J_PC = 17.9 Hz, C(CH₃)₃), 37.46 (d, J_PC = 11.1 Hz, CH₂), 37.17 (d, J_PC = 18.6 Hz, C(CH₃)₃), 30.38 (d, J_PC = 3.1 Hz, CH₃), 29.69 (d, J_PC = 3.3 Hz, CH₃).

**31P{1H} NMR** (121 MHz, CDCl₃, 298 K) δ: 84.81 (s). IR ν (neat, cm⁻¹) 1944.
$^1$H NMR of complex 18 in CDCl$_3$

$^{13}$C($^1$H) NMR of complex 18 in CDCl$_3$
5. Mechanistic Studies

5.1 In-situ Detection of Intermediates

**Procedure:** To a 4 mL vial were added complex 14 (3.5 mg, 0.007 mmol), t-BuOK (0.8 mg, 0.007 mmol), and THF (0.3 mL) in a glovebox. The resulting mixture was stirred at room temperature for 20 min and the afforded green solution was transferred into a high-pressure NMR tube, which was filled with 1 bar of CO gas and 3 bars of N₂O sequentially. After shaking the solution for 3 h, a mixture of complexes 16 and 17 was observed by ³¹P NMR.
5.2 Preparation of complex 16 from complex 18 with [(18-crown-6)K]OH

Procedure: To a J. Y. Young tube were added complex 18 (5.1 mg, 0.01 mmol), [(18-crown-6)K]OH (7.8 mg, 0.024 mmol), and THF (0.6 mL) in glovebox. The resulting mixture was shaken at room temperature for 40 min, affording a green solution, which was then filled with 1 bar of CO gas. After being shaken for 2 min, complex 16 was determined as the major product by $^1$H NMR and $^{31}$P NMR. CO$_2$ was detected by GC, further confirming the proposed intramolecular fast interaction between OH and CO.

i) $^{31}$P{$^1$H} NMR analysis:
complex 16

complex 18 + [(18-C-6)K]OH + CO

complex 18 + [(18-C-6)K]OH

complex 18

ii) $^1$H NMR analysis:

complex 16

complex 18 + [(18-C-6)K]OH + CO

complex 18 + [(18-C-6)K]OH

iii) GC spectra:
6. Proposed Intermediate for O-transfer from N₂O into Ru–H bond

The mechanism of oxygen-atom-transfer from N₂O to 16 is experimentally unclear at this stage. In 2008, Lin et al reported a DFT study on the reaction of N₂O with the saturated (dmpe)₂RuH₂, resulting in (dmpe)₂Ru(OH)₂.⁹a It was concluded that N₂O undergoes hydride attack at the terminal nitrogen of N₂O, followed by coordination via the O-terminus. Recently, Poater group⁹b and Xie group⁹c reported DFT studies on the hydrogenation of N₂O by a PNP pincer Ru complex [(PNP)RuH₂(CO)] reported by us,¹⁰ also concluding that the mechanism involves nucleophilic attack by the hydride ligand on the terminal nitrogen of N₂O. Based on these reported DFT studies, a similar mechanism is proposed to operate in our reaction, as outlined in the following scheme:
7. X-Ray data

X-ray diffraction data were collected in Mo radiation at 100K. The diffraction data of complex 7, complex [18+CHCl₃], and complex 18 were collected on a Bruker APEX-II Kappa CCD diffractometer and processed with SAINT. The diffraction data of complex 16 and complex 17 were collected on a Rigaku XtaLAB⁺PRO dual source diffractometer and processed with CrysAlis⁺PRO. The structures were solved by direct methods using SHELXT. All non-hydrogen atoms were further refined by SHELXL with anisotropic displacement coefficients. Hydrogen atoms were assigned isotropic displacement coefficients, and their coordinates were allowed to ride on their respective carbons. Hydride atoms were located in the electron density map. Crystallographic data and refinement parameters are summarized in Table S1.

### Table S1. Crystallographic data

| Species | Complex 7 + 2CHCl₃ | Complex 16 | Complex 17 | Complex 18 + CHCl₃ | Complex 18 |
|---------|-------------------|------------|------------|--------------------|------------|
| Formula | C₂₀H₃₅Cl₂NOP Ru₂+2CHCl₃ | C₂₁H₂₇N₂O₂PRu | C₂₁H₂₇N₂O₂PRu | C₂₅H₂₇Cl₂NOPRu+CHCl₃ | C₂₅H₂₇Cl₂NOPRu |
| Formula weight | 778.13 | 471.48 | 471.48 | 633.74 | 514.37 |
| Crystal system | Monoclinic | Monoclinic | Orthorhombic | Monoclinic | Monoclinic |
| Space group | P 2₁/c | P 2₁/c | Pbca | P 2₁/c | P 2₁/c |
| Crystal size (mm³) | 0.203x0.203x0.013 | 0.049x0.033x0.014 | 0.109x0.063x0.056 | 0.500x0.200x0.050 | 0.232x0.181x0.145 |
| Crystal color and shape | Yellow prism | Black plate | Black block | Yellow plate | Orange chunk |
| Temperature (K) | 100(2) | 100(2) | 100(2) | 100(2) | 100(2) |
| Wavelength (Å) | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| a (Å) | 12.0300(5) | 8.8526(5) | 12.0886(6) | 13.1954(7) | 7.9533(5) |
| b (Å) | 10.6729(4) | 8.5443(4) | 13.2869(11) | 15.1605(8) | 15.2254(9) |
| c (Å) | 25.4912(9) | 27.4092(13) | 26.5089(13) | 14.1886(7) | 17.5833(10) |
| α (°) | 90 | 90 | 90 | 90 | 90 |
| β (°) | 97.6750(10) | 96.433(5) | 90 | 108.745(2) | 94.4380(10) |
| γ (°) | 90 | 90 | 90 | 90 | 90 |
| Volume (Å³) | 3243.6(2) | 2060.16(18) | 4257.9(5) | 2687.9(2) | 2122.8(2) |
| Z | 4 | 4 | 8 | 4 | 4 |
| ρcalc (g cm⁻³) | 1.593 | 1.520 | 1.471 | 1.566 | 1.609 |
| μ (mm⁻¹) | 1.259 | 0.857 | 0.829 | 1.156 | 1.079 |
| No. of reflection (unique) | 64705(9901) | 28197(7092) | 32375(7240) | 72405(10263) | 87264(8095) |
|          |        |        |        |        |        |
|----------|--------|--------|--------|--------|--------|
| $R_{int}$| 0.0476 | 0.0427 | 0.0359 | 0.0453 | 0.0596 |
| Completeness to θ (%) | 99.8 | 99.7 | 99.6 | 99.8 | 99.6 |
| Data / restraints / parameters | 9901 / 24 / 361 | 7092 / 0 / 254 | 7240 / 0 / 254 | 10263 / 19/ 320 | 8095 / 0 / 263 |
| Goodness-of-fit on $F^2$ | 0.994 | 1.088 | 1.074 | 1.017 | 1.222 |
| Final $R_1$ and $wR_2$ indices ($I > 2\sigma(I)$) | 0.0304, 0.0659 | 0.0333, 0.0678 | 0.0390, 0.0762 | 0.0282, 0.0597 | 0.0348, 0.0697 |
| $R_1$ and $wR_2$ indices (all data) | 0.0404, 0.0698 | 0.0455, 0.0705 | 0.0544, 0.0804 | 0.0389, 0.0639 | 0.0432, 0.0721 |
| Largest diff. peak and hole ($e\,\text{Å}^3$) | 1.005 and -0.669 | 1.098 and -0.771 | 0.997 and -0.785 | 0.935 and -0.889 | 1.073 and -0.972 |

Crystal structure of [complex 7 + 2CHCl$_3$] at 50% probability level. The $i$-Pr groups and CHCl$_3$ moiety are shown as wireframe style for clarity. Selected bond lengths (Å) and angles (deg): N(1)–Ru(1), 2.1509(15); P(1)–Ru(1), 2.3653(5); P(2)–Ru(1), 2.3563(5); Cl(1)–Ru(1), 2.4220(4); Cl(2)–Ru(1), 2.4184(4); Ru(1)–C(20), 1.851(2); N(1)–Ru(1)–P(1), 81.15(4); N(1)–Ru(1)–P(2), 81.50(4); N(1)–Ru(1)–Cl(1), 88.02(4); N(1)–Ru(1)–Cl(2), 89.76(4); P(1)–Ru(1)–P(2), 162.653(17), N(1)–Ru(1)–C(20), 178.38(7).
Crystal structure of complex 16 at 50% probability level. Two tert-butyl groups are shown as wireframe style for clarity. Selected bond lengths (Å) and angles (deg): N(1)−Ru(1), 2.1392(16); N(2)−Ru(1), 2.0787(15); P(1)−Ru(1), 2.3358(5); H−Ru(1), 1.59(3); C(20)−Ru(1), 1.8677(19); C(21)−Ru(1), 1.9697(19); C(5)−C(6), 1.477(3); C(10)−C(11), 1.390(3); N(1)−Ru(1)−N(2), 76.74(6); N(2)−Ru(1)−P(1), 81.87(4); N(1)−Ru(1)−H, 84.9(10); P(1)−Ru(1)−H, 85.7(9); C(20)−Ru(1)−C(21), 97.86(8); N(1)−Ru(1)−P(1), 156.67(4); C(21)−Ru(1)−H, 177.0(10); N(2)−Ru(1)−C(20), 171.81(7).
Crystal structure of complex 17 at 50% probability level. Two tert-butyl groups are shown as wireframe style for clarity. Selected bond lengths (Å) and angles (deg): N(1)–Ru(1), 2.113(7); C(8)–Ru(1), 2.086(2); P(1)–Ru(1), 2.3850(6); H–Ru(1), 1.65(3); C(20)–Ru(1), 1.852(2); C(21)–Ru(1), 1.940(2); C(6)–C(7), 1.470(3); C(1)–C(2), 1.508(3); N(1)–Ru(1)–P(1), 81.37(5); C(8)–Ru(1)–N(1), 78.67(7); N(1)–Ru(1)–H, 90.2(12); P(1)–Ru(1)–H, 87.0(13); C(20)–Ru(1)–C(21), 94.00(11); C(8)–Ru(1)–P(1), 158.26(6); C(21)–Ru(1)–H, 169.7(11); N(1)–Ru(1)–C(20), 167.90(9).
Crystal structure of complex [18 + CHCl₃] at 50% probability level. Two tert-butyl groups and a disordered CHCl₃ moiety are shown as wireframe style for clarity. Selected bond lengths (Å) and angles (deg): N(1)–Ru(1), 2.0303(12); N(2)–Ru(1), 2.1362(13); P(1)–Ru(1), 2.3299(4); C(21)–Ru(1), 1.8397(16); Cl(1)–Ru(1), 2.4083(4); Cl(2)–Ru(1), 2.4804(4); C(6)–C(7), 1.478(2); C(1)–C(2), 1.505(2); N(1)–Ru(1)–P(1), 83.55(4); N(1)–Ru(1)–N(2), 78.62(5); N(1)–Ru(1)–C(21), 95.93(6); P(1)–Ru(1)–C(21), 94.11(5); C(21)–Ru(1)–Cl(1), 90.95(5); N(2)–Ru(1)–P(1), 161.52(4); Cl(1)–Ru(1)–N(1), 171.51(4); C(21)–Ru(1)–Cl(2), 168.58(5).
Crystal structure of complex 18 at 50% probability level. Two tert-butyl groups are shown as wireframe style for clarity. Selected bond lengths (Å) and angles (deg): N(1)−Ru(1), 2.0308(16); N(2)−Ru(1), 2.1281(16); P(1)−Ru(1), 2.3324(5); Cl(1)−Ru(1), 2.4245(5); Cl(2)−Ru(1), 2.4536(11); C(6)−C(7), 1.481(3); C(1)−C(2), 1.510(3); N(1)−Ru(1)−P(1), 83.41(5); N(1)−Ru(1)−N(2), 78.47(6); N(2)−Ru(1)−Cl(1), 97.33(5); P(1)−Ru(1)−Cl(1), 100.898(18); N(2)−Ru(1)−P(1), 161.71(5); Cl(1)−Ru(1)−N(1), 174.82(5).

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