

Electronic Supplementary Material

Oxidative formation of phosphinyl radicals from a trigonal pyramidal terminal phosphide Rh(I) complex, with an unusually long Rh-P bond

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1. General methods

All manipulations of air or moisture sensitive compounds were performed in a standard vacuum line in flame-dried flasks under an atmosphere of argon. Solvents were distilled under argon from Na (toluene), Na/benzophenone (THF, Et₂O), Na/benzophenone/tetraglyme (*n*-hexane), CaH₂ (dichloromethane, chloroform) and P₂O₅ (acetonitrile). Air sensitive compounds were stored and weighed in an argon filled glove box. Basic chemicals were ordered from commercial suppliers and used as received. Deuterated solvents were purchased from Eurisotop, degassed and distilled from the proper drying agent, and stored over 4Å molecular sieves. The following compounds were prepared according to literature methods: HPPH₂,¹ FcOTf² and [RhCl(trop₃P)] (**1**).³ Cyclic voltammetry studies were performed using a Princeton Applied Research potentiostat/galvanostat model 263A. The measurements were performed on an apparatus designed by Heinze *et al.*⁴ Working electrode: planar platinum electrode (approximate surface area 0.785 mm²); reference electrode: silver; counter electrode: platinum wire. At the end of each measurement, ferrocene was added as internal standard for calibration (-0.352 V vs. Ag/AgCl). IR spectra were recorded on a Perkin-Elmer-Spectrum 2000 FT-IR-Raman spectrometer with the ATR technique. Mass spectra of organic compounds were recorded on a Finnigan MAT SSQ 7000 mass spectrometer using electron ionization. Melting points were determined with a Büchi melting point apparatus and are not corrected. UV/vis spectra were recorded on a UV/vis/NIR lambda 19 spectrometer in 5 mm quartz cuvettes (200 – 1000 nm). Solution NMR spectra were recorded on Bruker Avance 400, 300, 250 and 200 spectrometers. The chemical shifts (δ) were measured according to IUPAC⁵ and expressed in parts per million (ppm) relative to TMS, CFCl₃, and H₃PO₄ for ¹H, ¹³C, ¹⁹F and ³¹P, respectively. Coupling constants *J* are given in Hertz (Hz) as absolute values, unless otherwise stated. The multiplicity of the signals is indicated as s, d, t, q, or m for singlets, doublets, triplets, quartets, or multiplets, respectively. The abbreviation br. is given for broadened signals. Quaternary carbon atoms are indicated as C^{qr}, aromatic units as CH^{ar} and CH^{ar} when not noted otherwise. The olefinic protons and carbon atoms of the C=C_{trop} unit in the central seven-membered ring are indicated as CH^{olef} and C^{olef}. The benzylic protons and C atoms in the central seven-membered ring are indicated as CH^{benzyl} and C^{benzyl}, respectively. The EPR spectrum was recorded with a Bruker EMX 080 equipped with a microwave-bridge ER 041 XG and the dielectric mixing resonator ER 4117 D-MVT. Data acquisition and analysis were carried out with ACQUISIT software (Bruker). X-ray crystallographic measurements were performed on Bruker SMART 1K and SMART APEX platforms with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The reflex intensities were measured by CCD area detectors. The collected frames were processed with the proprietary software SAINT⁶ and an absorption correction was applied (SADABS⁷). Solution and refinement of the structures was performed with SHELXS-97⁸ and SHELXL-97⁹ respectively. In general, all non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in their idealized

positions and allowed to ride on the respective carbon atoms. Associated crystallographic data and other experimental details are summarized in the crystallographic tables in section 5.

2. Synthesis of complexes 2 – 7 and spectroscopic data

2.1 Synthesis of [Rh(trop₃P)(HPPH₂)]OTf (**2**).

Dry AgOTf (139 mg, 0.54 mmol) was suspended in CH₂Cl₂ (200 mL) and the mixture was sonicated during 5 minutes. [RhCl(trop₃P)] (**1**) (257 mg, 0.346 mmol) was subsequently added and the resulting mixture was stirred for 1 hour. The solid formed (AgCl) was removed by filtration over Celite and the filtrate was concentrated to dryness. The residue was dissolved in THF (120 mL) and HPPH₂ (0.10 mL, 0.11 g, 0.58 mmol) was slowly added. After a few minutes, the product crystallized directly from the reaction mixture. The crystalline precipitate was collected by filtration and washed with THF (3 x 10 mL). The light yellow solid was recrystallized from CH₂Cl₂ and dried under vacuum. Yield: 304 mg (84 %). M.p.: 230°C (dec.). IR (ATR): ν (cm⁻¹) = 3120 (w, ν_{CH}), 2035 (w), 1587 (w), 1480 (m), 1465 (w), 1456 (w), 1288 (m), 1240 (s), 1249 (s), 1198 (s), 1012 (s), 944 (m), 876 (s), 798 (s), 634 (m). ¹H NMR (250 MHz, CD₂Cl₂, 298 K): δ (ppm) = 4.85 (dd, ²J_{PH} = 14.5 Hz, ⁴J_{PH} = 9.5 Hz, 3H, CH^{benzyl}), 5.53 (ψ -quint, *J* = 1.8 Hz, 6H, CH^{olef}), 5.80 (d, ¹J_{PH} = 335 Hz, 1H, PH), 6.12-6.78 (m, 25 H, CH^{ar}), 6.92-7.99 (m, 9 H, CH^{ar}). ¹³C{¹H} NMR (62.9 MHz, CD₂Cl₂, 298 K): δ (ppm) = 46.5 (d, ¹J_{PC} = 20 Hz, 3CH^{benzyl}), 74.9 (d, ²J_{PC} = 6.0 Hz, 6 CH^{olef}), 120.3 (q, *J*_{CF} = 320 Hz, 1C, CF₃), 127.4 (2 CH^{ar}), 128.0 (2 CH^{ar}), 128.3 (4 CH^{ar}), 128.4 (3 CH^{ar}), 130.1 (3 CH^{ar}), 130.2 (6 CH^{ar}), 131.4 (6 CH^{ar}), 131.5 (3 CH^{ar}), 131.7 (3 CH^{ar}), 133.5 (d, *J*_{PC} = 25.1 Hz, 2 C^{ar}), 135.8 (d, ²J_{PC} = 11.0 Hz, 6 C^{ar}), 141.0 (s, 6 C^{ar}). ³¹P{¹H} NMR (101.3 MHz, CD₂Cl₂, 298 K): δ (ppm) = 11.9 (dd, ²J_{PP} = 340 Hz, ¹J_{RhP} = 88 Hz, HPPH₂), 196.6 (dd, ²J_{PP} = 340 Hz, ¹J_{RhP} = 121 Hz, trop₃P). ¹⁹F (235.2 MHz, CD₂Cl₂, 298 K): δ (ppm) = -77.7 (s).

2.2 Synthesis of [Rh(trop₃P)(PPh₂)] (**3**).

To a suspension of [Rh(trop₃P)(HPPH₂)]OTf (**2**) (304 mg, 0.29 mmol) in THF (40 mL) was added dropwise a solution of KO^tBu (50 mg, 0.45 mmol) in THF (10 mL). In the course of the addition, the solution became orange and the starting complex **2** gradually dissolved. After 15 minutes, the resulting clear orange solution was concentrated to approx. 25 mL. After three days, the crystalline orange precipitate was collected by filtration, washed with THF (10 mL) and dried under high vacuum. Concentration of the filtrate gave a second crop of product. Complex **3** was isolated as bright orange microcrystalline solid. Yield: 200 mg (77 %). M.p.: 220°C (dec). IR (ATR): ν (cm⁻¹) = 3150 (w, ν_{CH}), 2520 (w), 1578 (w), 1484 (m), 1457 (w), 1422 (w), 1299 (m), 1242 (s), 1225(s), 1187 (s), 1025 (s), 923 (m), 756 (s), 730 (s), 685 (m). ¹H NMR (300 MHz, THF-d₈, 298 K): δ (ppm) = 4.18 (dd, ²J_{PH} = 14.1 Hz, ⁴J_{PH} = 3.6 Hz, 3H, CH^{benzyl}), 5.35 (s, 6H, CH^{olef}), 6.33- 6.93 (m, 23H, CH^{ar}), 7.09 – 7.53 (m, 7H, CH^{ar}), 8.03 (t, *J* = 6.8 Hz, 4H, CH^{ar}). ¹³C NMR (75.4 MHz, THF-d₈, 298 K): δ (ppm) = 59.1 (dd, ¹J_{PC} = 17.2 Hz, ³J_{PC} = 2.1 Hz, 3 CH^{benzyl}), 82.3 (dd, ²J_{PC} = 7.3 Hz, ²J_{PC} = 1.4 Hz, 6 CH^{olef}), 124.5 (s, CH^{ar}), 127.8 (s, CH^{ar}), 127.9 (d, *J*_{PC} = 4.6 Hz, CH^{ar}), 128.5 (d, *J*_{PC} = 9.5 Hz, CH^{ar}), 128.9 (d, ³J_{PC} = 1.5 Hz, CH^{ar}), 131.2 (d, *J*_{PC} = 7.8 Hz, CH^{ar}), 133.6 (d,

$^3J_{PC} = 1.6$ Hz, CH^{ar}), 135.8 (d, $^2J_{PC} = 10.3$ Hz, CH^{ar}), 136.9 (s, C^{ar}), 141.0 (d, $J_{PC} = 3.8$ Hz, C^{ar}), 147.2 (d, $J_{PC} = 7.7$ Hz, C^{ar}). $^{31}P\{^1H\}$ NMR (121.5 MHz, THF- d_8 , 298 K): δ (ppm) = 11.8 (dd, $^2J_{PP} = 172.8$ Hz, $^1J_{RhP} = 55.7$ Hz, PPh_2), 176.7 (dd, $^2J_{PP} = 172.5$ Hz, $^1J_{RhP} = 116.9$ Hz, $trop_3P$).

2.3 Synthesis of [Rh($trop_3P$)(OTf)] (5).

[RhCl($trop_3P$)] (260 mg, 0.35 mmol) and AgOTf (140 mg, 0.54 mmol) were combined in CH_2Cl_2 (200 mL) and stirred at room temperature for 2 hours. The course of the reaction was followed by ^{31}P NMR spectroscopy. The suspended AgCl was removed by filtration through Celite and the resulting solution was concentrated to dryness. The resulting yellow powder was dried under high vacuum. Yield: 273 mg (91 %). M.p.: > 325 °C. EA Calcd. C 63.16, H 4.03, P 3.54; found C 63.68, H 4.07. IR (ATR): ν (cm^{-1}) = 3042 (w, ν_{CH}), 1600 (w), 1578 (w), 1485 (m), 1454 (w), 1419 (w), 1294 (m), 1232 (s), 1218 (s), 1173 (s), 1023 (s), 901 (m), 743 (s), 733 (s), 635 (m) cm^{-1} . 1H NMR (300 MHz, THF- d_8 , 298 K): δ = 4.16 (d, $^2J_{PH} = 13.2$ Hz, 3H, CH^{benzyl}), 6.02 (d, $J_{PH} = 1.5$ Hz, 6H, CH^{olef}), 6.34 – 6.63 (m, 6H, CH^{ar}), 6.64 – 6.94 (m, 12H, CH^{ar}), 7.05 (dd, $J = 7.5, 1.5$ Hz, 6H, CH^{ar}). $^{13}C\{^1H\}$ NMR (75.5 MHz, THF- d_8 , 298 K): δ = 47.9 (d, $^1J_{PC} = 24.5$ Hz, 3 CH^{benzyl}), 80.4 (d, $^2J_{PC} = 6.5$ Hz, CH^{olef}), 126.6 (s, 6 CH_{aryl}), 127.1 (d, $J_{PC} = 7.8$ Hz, 6 CH_{aryl}), 127.3 (s, 6 CH_{aryl}), 130.4 (s, 6 CH_{aryl}), 133.5 (d, $J_{PC} = 4.5$ Hz, 6 C^{aryl}), 135.8 (s, 6 C^{aryl}). ^{19}F NMR (188.3 MHz, THF- d_8 , 298 K): δ (ppm) = -79.2 (s). $^{31}P\{^1H\}$ NMR (121.5 MHz, THF- d_8 , 298 K): δ (ppm) = 191.2 (d, $^1J_{RhP} = 161.2$ Hz).

2.4 Synthesis of [Rh($trop_3P$)(P(=O)Ph $_2$)] (7)

To a suspension of complex **2** (99 mg, 0.095 mmol) in THF (40 mL) was added dropwise a solution of KO^tBu (19 mg, 0.17 mmol) in THF (8 mL), forming in few minutes (<5 min) a clear orange solution. To the resulting solution, bis(trimethylsilyl)peroxide (30 wt% in *n*-hexane, 0.1 mmol, 60 μ L) was added dropwise. During the addition the mixture changed colour from orange to pale yellow. The mixture was stirred at room temperature for two additional hours. The solvent was then concentrated to approx. 15 mL and the crystalline product was collected by filtration and washed with THF (2 x 8 mL). The solid was dried under high vacuum resulting in a microcrystalline light yellow powder. Yield: 81 mg (94 %). M.p.: 331-333 °C (dec.). IR(ATR): ν (cm^{-1}) = 3060 (w, ν_{CH}), 2899 (w, ν_{CH}), 1574 (w), 1484 (m), 1475 (m), 1289 (w), 1095 (m), 1063 (m), 1043 (s), 895 (m), 735 (s), 701 (s), 680 (m). 1H NMR (300 MHz, CD_2Cl_2 , 298 K): δ (ppm) = 4.02 (dd, $^2J_{PH} = 13.5$ Hz, $^4J_{PH} = 9.8$ Hz, 3H, CH^{benzyl}), 5.61 (d, $J = 2.3$ Hz, 6H, CH^{olef}), 6.44 – 6.51 (m, 6H, CH^{ar}), 6.70 - 6.83 (m, 18H, CH^{ar}), 7.51 - 7.65 (m, 6H, CH^{ar}), 8.16 (dd, $^3J_{HH} = 7.4$ Hz, 7.4 Hz, 4H, CH^{ar}). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2 , 298 K): δ (ppm) = 47.9 (dd, $^1J_{PC} = 15.1$ Hz, $^3J_{PC} = 1.5$ Hz, 3 CH^{benzyl}), 74.9 (dd, $^2J_{PC} = 6.8$ Hz, $^2J_{PC} = 0.9$ Hz, 6 CH^{olef}), 126.7 (s, CH^{ar}), 127.2 (s, CH^{ar}), 127.2 (d, $J_{PC} = 4.0$ Hz, CH^{ar}), 128.0 (d, $J_{PC} = 7.7$ Hz, CH^{ar}), 128.7 (d, $^3J_{PC} = 1.5$ Hz, CH^{ar}), 129.7 (d, $J_{PC} = 8.9$ Hz, CH^{ar}), 130.6 (d, $^3J_{PC} = 1.1$ Hz, CH^{ar}), 131.4 (d, $^2J_{PC} = 9.2$ Hz, CH^{ar}), 133.8 (s, C^{ar}), 136.0 (dd, $J_{PC} = 2.6$ Hz, 0.7 Hz, C^{ar}), 142.1

(d, $J_{PC} = 8.0$ Hz, C^{ar}). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CD_2Cl_2 , 298 K): $\delta(\text{ppm}) = 59.7$ (dd, $^2J_{PP} = 423$ Hz, $^1J_{RHP} = 93$ Hz, $\text{P}(\text{O})\text{Ph}_2$), 175.5 (dd, $^2J_{PP} = 424$ Hz, $^1J_{RHP} = 110$ Hz, trop_3P).

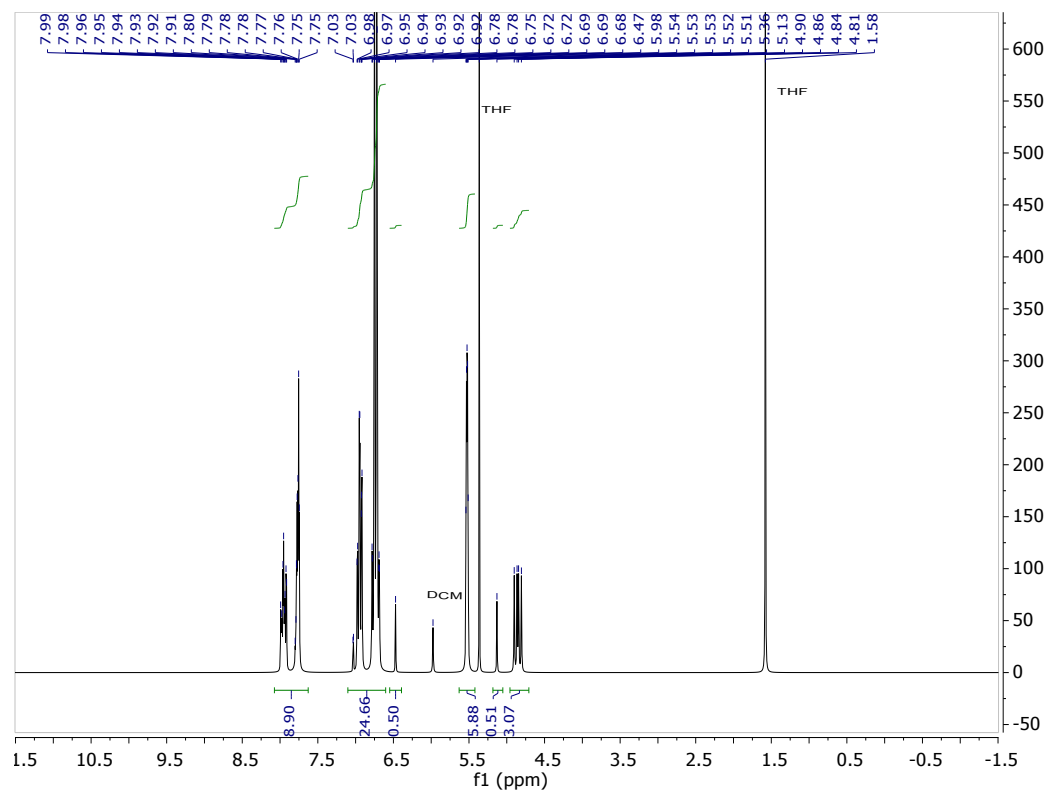
3. Generation and trapping of PPh_2 radical. Reaction of complex **3 with nitrosobenzene under oxidative conditions.**

The phosphido complex **3** (10 mg, 0.011 mmol) was suspended in THF (0.6 mL) in an NMR tube under argon atmosphere. Nitrosobenzene (3 mg, 0.028 mmol) and FcOTf (3 mg, 0.009 mmol) were added and the mixture was shaken vigorously. The initial orange suspension darkened to result in an orange-brown suspension instantly. EPR spectroscopy indicated the presence of the addition product **6**. The generation of **6** was also possible in toluene, where the three reactants were combined in solid state and toluene was added last. The reaction mixture had to be sonicated for about two hours to detect a strong EPR signal.

4. Selected NMR Spectra

Complex 2

a)



b)

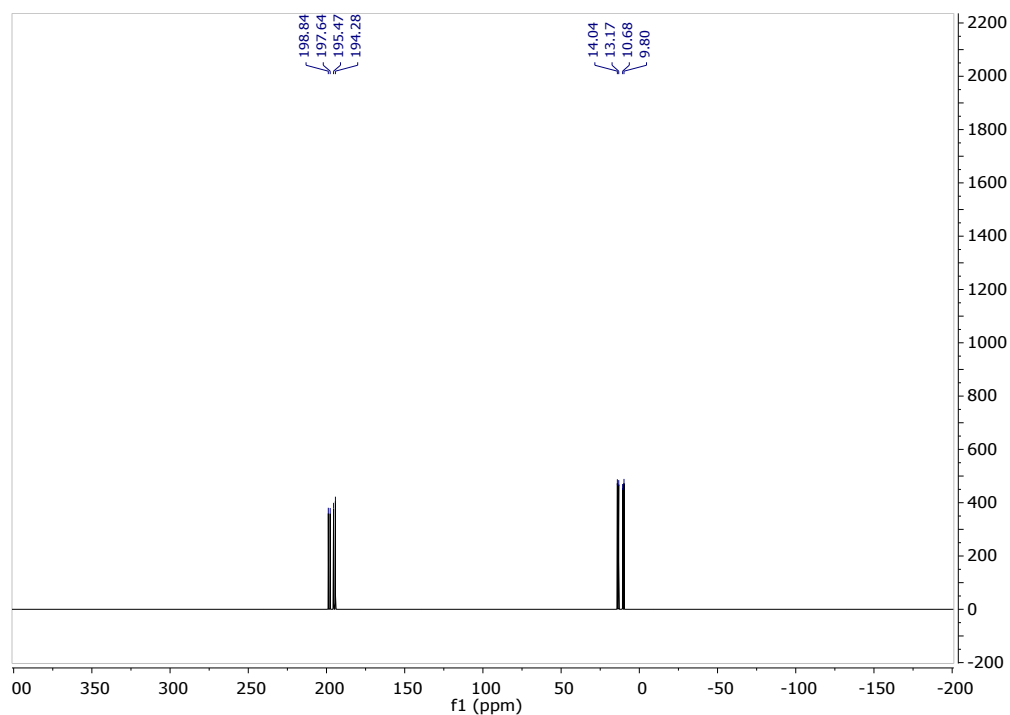
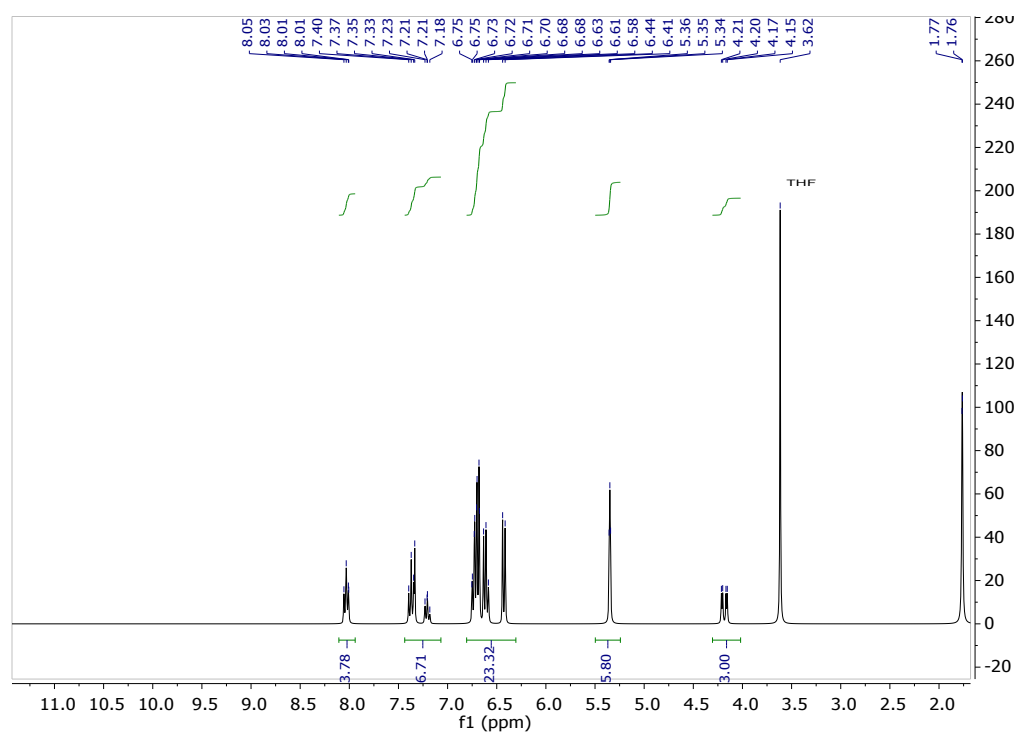


Figure S1. a) ^1H NMR (250 MHz, CD_2Cl_2 , 298 K) and b) $^{31}\text{P}\{^1\text{H}\}$ NMR (101.3 MHz, CD_2Cl_2 , 298 K) spectra of complex 2.

Complex 3

a)



b)

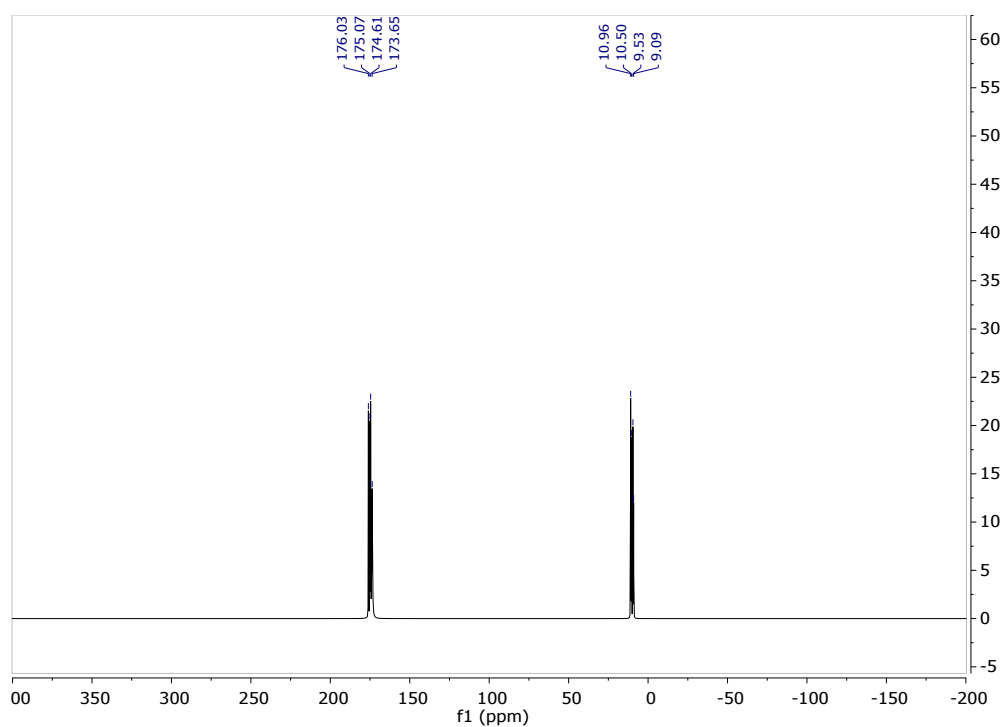
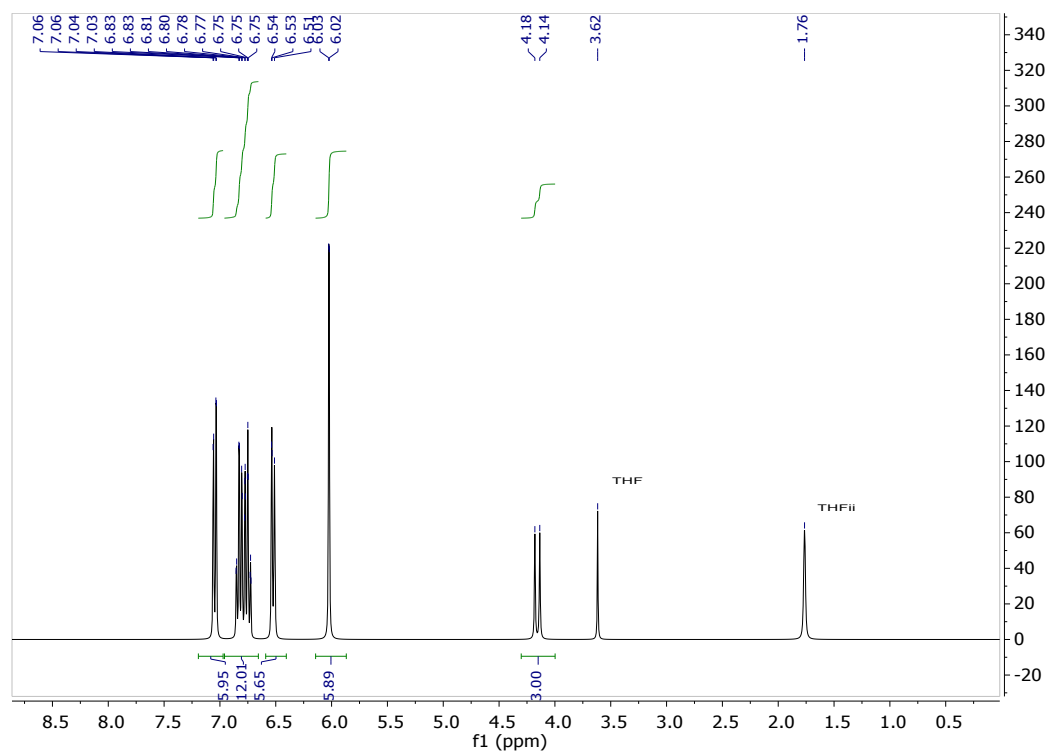


Figure S2. a) ¹H NMR (300 MHz, THF-d₈, 298 K) and b) ³¹P{¹H} NMR (121.5 MHz, THF-d₈, 298 K) spectra of complex 3.

Complex 5

a)



b)

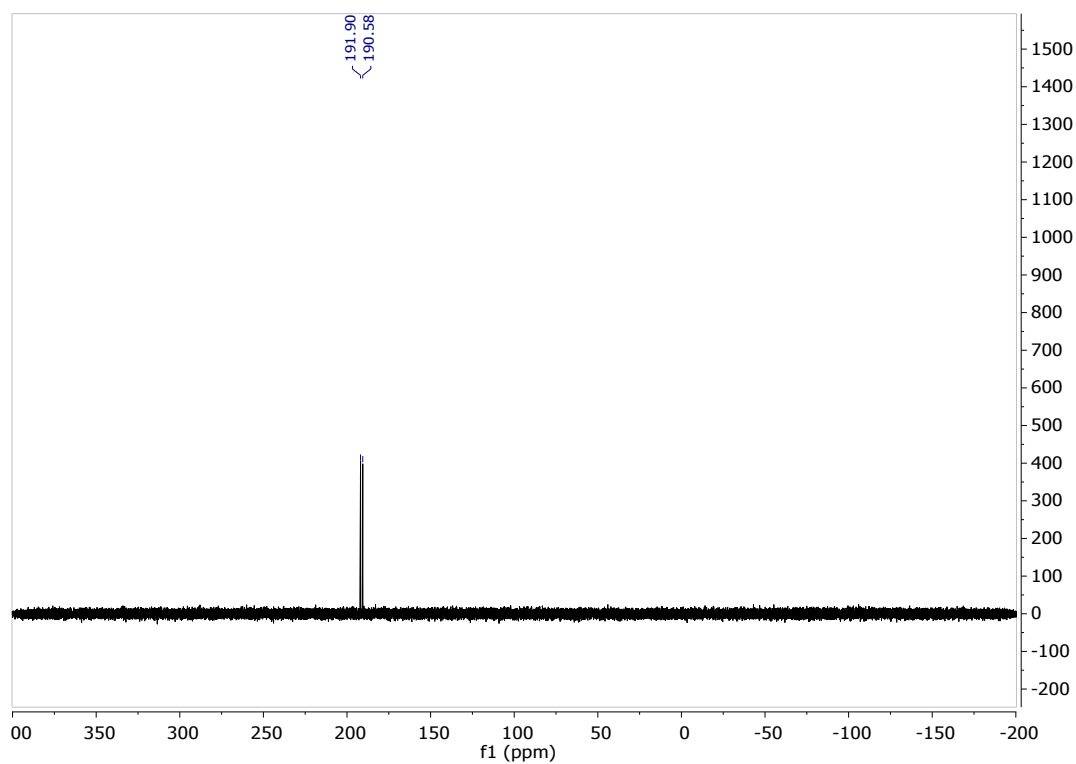
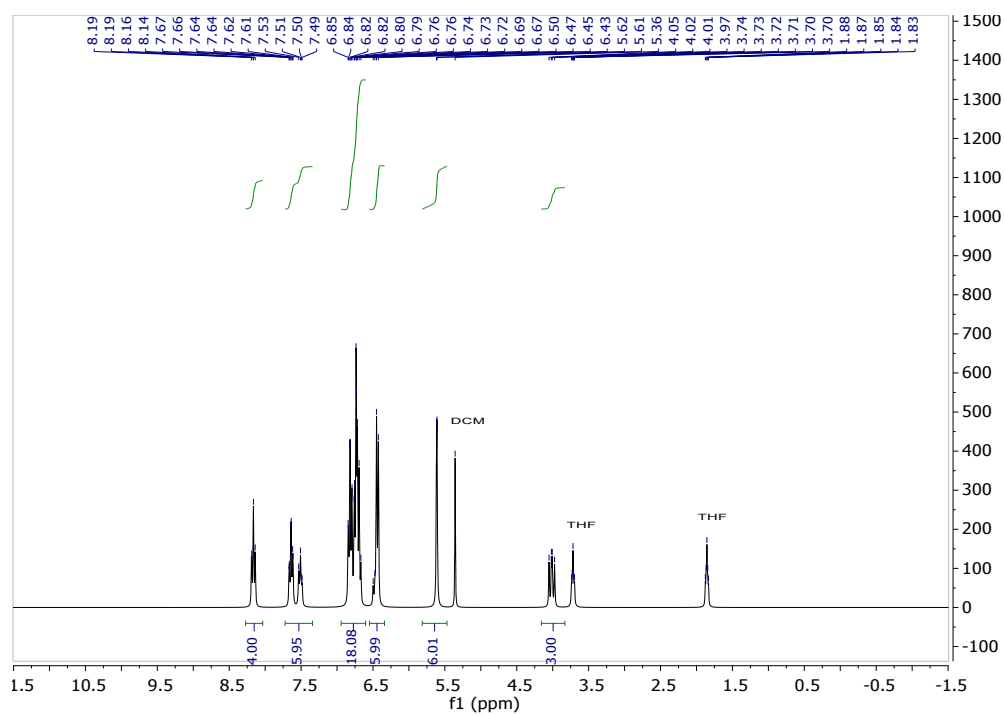


Figure S3. a) ^1H NMR (300 MHz, THF-d_8 , 298 K) and b) $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, THF-d_8 , 298 K) spectra of complex 5.

Complex 7

a)



b)

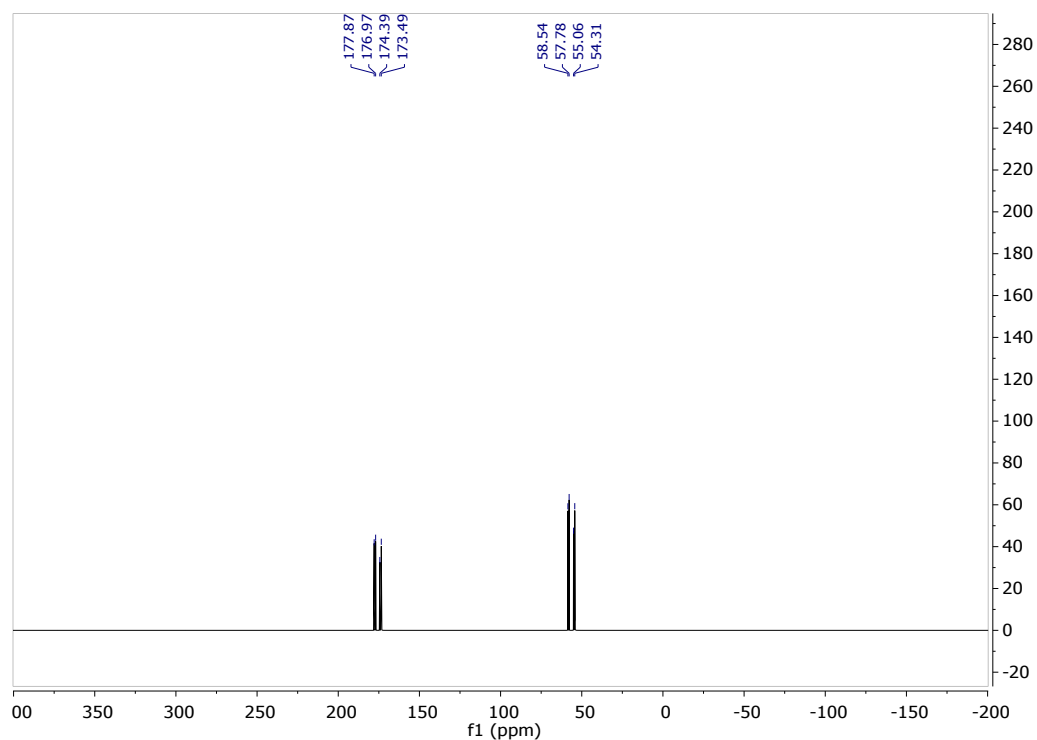


Figure S4. a) ^1H NMR (300 MHz, CD_2Cl_2 , 298 K) and b) $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CD_2Cl_2 , 298 K) spectra of complex 7.

5. Crystallographic data

| | |
|---|---|
| [Rh(trop ₃ P)(PPh ₂)] × thf (3) | |
| <hr/> | |
| Empirical formula | C ₆₁ H ₅₁ OP ₂ Rh |
| Temperature | 200(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | P2 ₁ /n |
| Unit cell dimensions | a = 11.5778(6) Å α = 90° b = 17.6871(10) Å β = 101.0040(10)° c = 22.3777(12) Å γ = 90° |
| Volume | 4498.2(4) Å ³ |
| Z | 4 |
| Density (calculated) | 1.425 gcm ⁻³ |
| Absorption coefficient | 0.496 mm ⁻¹ |
| F(000) | 2000 |
| Crystal size | 0.30 × 0.28 × 0.05 mm ³ |
| Data collection | SMART APEX PLATFORM with CCD area detector Mo Kα, graphite monochromator |
| Detector distance | 50 mm |
| Exposure time/frame | 20 s |
| Solution by | direct methods, SHELXTL 97 |
| Refinement method | full matrix least-squares on F ² |
| Theta range for data collection | 1.48° to 28.28° |
| Index range | -15 ≤ h ≤ 15, 23- ≤ k ≤ 23, -29 ≤ l ≤ 29 |
| Reflections collected | 45448 |
| Independent reflections | 11137 [R(int) = 0.0313] |
| Absorption correction | Empirical (SADABS) |
| Data / restraints / parameters | 11137 / 1 / 606 |
| Goodness-of-fit on F ² | 1.402 |
| Final R indices [I > 2σ(I)] | R ₁ = 0.0726, wR ₂ = 0.1518 |
| R indices (all data) | R ₁ = 0.0744, wR ₂ = 0.1525 |
| Largest diff. peak and hole | 2.135 and -1.060 eÅ ⁻³ |

[Rh(trop₃P) (OTf)] (5)

| | |
|-----------------------------------|--|
| Empirical formula | C ₄₆ H ₃₃ F ₃ O ₃ PRhS |
| Temperature | 200(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | P2 ₁ /n |
| Unit cell dimensions | a = 13.0718(11) Å α = 90° b = 18.2712(16) Å β = 103.4290(10)° c = 15.6047(13) Å γ = 90° |
| Volume | 3625.1(5) Å ³ |
| Z | 4 |
| Density (calculated) | 1.570 gcm ⁻³ |
| Absorption coefficient | 0.633 mm ⁻¹ |
| F(000) | 1744 |
| Crystal size | 0.33 × 0.28 × 0.18 mm ³ |
| Data collection | SMART 1K PLATFORM with CCD area detector Mo Kα, graphite monochromator |
| Detector distance | 50 mm |
| Exposure time/frame | 20 s |
| Solution by | direct methods, SHELXTL 97 |
| Refinement method | full matrix least-squares on F ² |
| Theta range for data collection | 1.74° to 24.71° |
| Index range | -15 ≤ h ≤ 15, -21 ≤ k ≤ 21, -18 ≤ l ≤ 18 |
| Reflections collected | 25467 |
| Independent reflections | 6190 [R(int) = 0.0479] |
| Absorption correction | Empirical (SADABS) |
| Data / restraints / parameters | 6190 / 0 / 496 |
| Goodness-of-fit on F ² | 1.064 |
| Final R indices [I > 2σ(I)] | R ₁ = 0.0397, wR ₂ = 0.0982 |
| R indices (all data) | R ₁ = 0.0622, wR ₂ = 0.1127 |
| Largest diff. peak and hole | 1.248 and -0.601 eÅ ⁻³ |

[Rh(trop₃P)(P(O)Ph₂)] × CH₂Cl₂ (7)

| | |
|-----------------------------------|--|
| Empirical formula | C ₅₈ H ₄₅ Cl ₂ OP ₂ Rh |
| Temperature | 200(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | P2 ₁ /n |
| Unit cell dimensions | a = 11.5568(8) Å α = 90° b = 17.6715(12) Å β = 99.3270(10)° c = 22.3047(15) Å γ = 90° |
| Volume | 4495.0(5) Å ³ |
| Z | 4 |
| Density (calculated) | 1.468 gcm ⁻³ |
| Absorption coefficient | 0.613 mm ⁻¹ |
| F(000) | 2040 |
| Crystal size | 0.33 × 0.13 × 0.10 mm ³ |
| Data collection | SMART APEX PLATFORM with CCD area detector Mo Kα, graphite monochromator |
| Detector distance | 50 mm |
| Exposure time/frame | 40 s |
| Solution by | direct methods, SHELXTL 97 |
| Refinement method | full matrix least-squares on F ² |
| Theta range for data collection | 1.48° to 30.98° |
| Index range | -16 ≤ h ≤ 16, -25 ≤ k ≤ 24, -30 ≤ l ≤ 31 |
| Reflections collected | 51483 |
| Independent reflections | 13321 [R(int) = 0.0295] |
| Absorption correction | Empirical (SADABS) |
| Data / restraints / parameters | 13321 / 1 / 596 |
| Goodness-of-fit on F ² | 1.062 |
| Final R indices [I > 2σ(I)] | R ₁ = 0.0375, wR ₂ = 0.0965 |
| R indices (all data) | R ₁ = 0.0515, wR ₂ = 0.1058 |
| Largest diff. peak and hole | 1.052 and -0.642 eÅ ⁻³ |

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