Iminophosphanes: Synthesis, Rhodium Complexes, and Ruthenium(II)-Catalyzed Hydration of Nitriles


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Iminophosphanes – Synthesis, Rhodium complexes and Ruthenium(II) catalyzed nitrile hydration

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SUPPORTING INFORMATION

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1. Experimental Details

General considerations

All experiments were performed under an atmosphere of dry nitrogen using standard Schlenk-line and glovebox techniques, unless stated otherwise. Solvents were distilled under nitrogen over the appropriate drying agent; CaCl₂ (DCM), benzophenone/NaK (Et₂O, THF, triethylamine), Na (toluene), LiAlH₄ (pentane), P₂O₅ (CD₂Cl₂, CDCl₃). C₆D₆ was dried over Na at RT. H₂O was degassed ultrasonically in vacuo. Silver salts were handled with minimum light exposure. Diphenylphosphane was purchased from Sigma-Aldrich and tri(3-methylphenyl)phosphane and di(4-methylphenyl)chlorophosphane from STREM Chemicals Inc. Di(3-trifluoromethylphenyl)chlorophosphane was provided by Arkema B.V. Known compounds 2a, 2b, 2c di(3-trifluoromethylphenyl)phosphane, di(3-methylphenyl)phosphane and di(4-methylphenyl)phosphane are reported here since their syntheses were revised and/or new analytical data was obtained. All phosphanes and chlorophosphanes were distilled under reduced pressure before use. Solids were predried in vacuo for at least 30 minutes. All other reagents were used as received. NMR spectra were recorded on a Bruker Avance 250 (1H: 250.13 MHz, 19F: 235.36 MHz, 31P: 101.25 MHz, room temperature), a Bruker Avance 400 (1H: 400.13 MHz, 13C{1H}: 100.61 MHz, 31P: 161.98 MHz, room temperature) or a Bruker Avance 500 (1H: 500.23 MHz, 13C{1H}: 125.78 MHz; room temperature). 1H-spectra and 13C{1H}-spectra were internally referenced to residual solvent resonances (CDCl₃: δ₁H = 7.26, δ₁3C{1H} = 77.16; CD₂Cl₂: δ₁H = 5.32, δ₁3C{1H} = 53.84; C₆D₆: δ₁H = 7.16, δ₁3C{1H} = 128.06) and 31P-spectra were referenced externally to H₃PO₄. Melting points were measured using a Büchi Melting Point apparatus M-565 (sealed capillaries) and are uncorrected. High resolution electrospray ionization (ESI) mass spectrometry was carried out with a Bruker micrOTOF-Q instrument in positive ion mode (capillary potential of 4500 V). Infrared spectra were recorded on a Shimadzu FT-IR 8400S spectrophotometer.

(N-methyl)(phenyl)carbonitrili um trifluoromethylsulfonate (2a)¹

Protocol 1: MeOTf (6.8 mL, 60.08 mmol, 1.0 eq.) was added dropwise to a solution of benzonitrile (6.15 mL, 60.24 mmol, 1.0 eq.) in 16 mL toluene. After stirring 18 h at RT, a microcrystalline solid had precipitated. Volatiles were removed in vacuo, and after washing with 2 x 20 mL pentane, 2a was obtained as a yellowish white solid (9.92 g, 37.12 mmol, 62%). Protocol 2: MeOTf (11.2 mL, 99.0 mmol, 1.0 eq.) was added dropwise to benzonitrile (12.0 mL, 116.3 mmol, 1.2 eq.). The colorless solution was stirred for 18 h. The resulting white/yellow crystalline solid was washed with 3 x 20 mL pentane and dried in vacuo to provide 2a as a white solid (22.80 g, 85.22 mmol, 86%).

Crystallization: Slow diffusion of ether (2.84 mL/mmol compound) into a saturated DCM solution (2.84 mL/mmol compound) at 5°C provides 2a as off-white needles. For spectroscopic details, see manuscript.

(N-methyl)(4-methyl-phenyl)carbonitrilium trifluoromethylsulfonate (2b)

MeOTf (2.84 mL g, 25.1 mmol, 1.0 eq.) was added dropwise to a solution of 4-methyl-benzonitrile (3.0 mL, 25.1 mmol, 1.0 eq.) in 6.5 mL toluene at RT. After 65 h a yellow suspension with a fine white precipitate was visible. After stirring 5 days at RT, volatiles were removed in vacuo, and washing with 2 x 10 mL pentane provided 2b (4.39 g, 15.6 mmol, 62%) as a fine off-white solid. Crystallization: Slow diffusion of ether (2.84 mL/mmol compound) into a saturated DCM solution (2.84 mL/mmol compound) at 5°C provides 2b as off-white needles. For spectroscopic details, see manuscript.

(N-methyl)(4-trifluoromethyl-phenyl)carbonitrilium trifluoromethylsulfonate (2c)

Protocol 1: MeOTf (1.70 mL, 15.02 mmol, 1.0 eq.) was added dropwise to a solution of 4-trifluoromethyl-benzonitrile (2.57 g, 15.02 mmol, 1.0 eq.) in 4 mL toluene. After stirring 6 days at RT, a brown suspension with white precipitate was obtained. Volatiles were removed in vacuo and the resulting solid was washed with 3 x 5 mL pentane. Crystallization by slow diffusion of pentane (8 mL) into a saturated DCM solution (8 mL) provided 2c as a white solid (0.70 g, 2.09 mmol, 14%). Protocol 2: MeOTf (0.91 mL, 8.04 mmol, 1.0 eq.) was added dropwise over 4-trifluoromethyl-benzonitrile (1.38 g, 8.06 mmol, 1.0 eq.) at RT. Next, the mixture was heated to 45 °C and stirred for 18 h. The resulting white/yellow solid was washed in 20 mL pentane for 22 h. After filtration, the obtained white solid was crystallized by slow diffusion of pentane (4.6 mL/mmol compound) (alternatively Et₂O) into a saturated solution in DCM (4.6 mL/mmol compound) at 5°C to provide 2c as white needles (1.87 g, 5.58 mmol, 69%). For spectroscopic details, see manuscript.

((N-methyl)phenylimidoyl)diphenylphosphane (3a)

Diphenylphosphane (1.40 mL, 8.05 mmol, 1.0 eq.) was added dropwise to a solution of 2a (2.40 g, 8.98 mmol, 1.1 eq.) in 28 mL DCM at –78 °C to give a bright yellow solution, which was allowed to warm to RT and stirred for 15 min. Triethylamine (1.2 mL, 8.61 mmol, 1.1 eq.) was added to give a yellow solution, which was stirred for 1 h. Volatiles were removed in vacuo to give a yellow oil, which was extracted into 40 mL Et2O overnight (alternatively in 3 x 20 mL Et2O). The extract was concentrated to saturation and filtered over neutral alumina (alternatively celite). Evaporation provided 3a as a yellow/white solid (2.23 g, 7.35 mmol, 91%, mixture of E/Z isomers). Crystallization: a saturated Et2O solution (6.1 mL Et2O/mmol compound) was cooled to -20°C. For spectroscopic details, see manuscript.

((N-methyl)-4-methyl-phenylimidoyl)diphenylphosphane (3b)

A solution of diphenylphosphane (1.41 mL, 1.51 g, 6.7 mmol, 1.0 eq.) in 30 mL DCM was added dropwise to a solution of 2b (2.01 g 7.1 mL, 1.1 eq.) in 30 mL DCM at –78 °C. The bright red solution was allowed to warm to RT and after 3 h, triethylamine (0.99 mL 0.72g, 7.1 mmol, 1.1 eq.) was added. The resulting red solution was stirred for 1 h. Volatiles were removed in vacuo to give a red oil, which was extracted with sequentially 50 mL Et2O for 18 h and 20 mL for 22 h to provide 3b as an off-white solid (1.59 g, 5.0 mmol, 75%). For spectroscopic details, see manuscript.

((N-methyl)-4-trifluoromethyl-phenylimidoyl)diphenylphosphane (3c)

Diphenylphosphane (1.30 mL, 7.47 mmol, 1.0 eq.) was added dropwise to a solution of 2c (2.6 g, 7.76 mmol, 1.0 eq.) in 40 mL DCM at –78 °C. The resulting bright orange solution was allowed to warm to RT, during which it colored bright yellow and was stirred for 1 h. Triethylamine (1.10 mL, 7.89 mmol, 1.1 eq.) was added to the mixture. The resulting red solution was stirred for 1 h. Volatiles were removed in vacuo to give a red oil, which was extracted with sequentially 50 mL Et2O for 18 h and 20 mL for 22 h (alternatively 3 x 20 mL Et2O). The combined extracts were concentrated to saturation and subsequently filtered over celite (alternatively neutral alumina) to give an orange solution. Evaporation provided a red oil. Crystallization from a minimal amount of Et2O at -80°C provided 3c as an orange oil, which solidified over time (0.66 mL/mmol compound) at –80 °C to provide 3c (2.23 g, 6.36 mmol, 85%) as a white solid. For spectroscopic details, see manuscript.

((N-phenylimidoyl)di(3-trifluoromethyl-phenyl)phosphane (3d)

A solution of di(3-trifluoromethyl-phenyl)phosphane (3.28 g, 10.2 mmol, 1.0 eq.) in 30 mL DCM was added dropwise to a solution of 2a (2.83 g, 10.5 mmol, 1.0 eq.) at –78 °C. The resulting red/orange solution was allowed to warm to RT and stirred for 17 h. Triethylamine (1.56 mL, 11.2 mmol, 1.1 eq.) was added to the obtained yellowish mixture. The resulting red solution was stirred for 1 h. Volatiles were removed in vacuo to give a red oil, which was extracted with sequentially 50 mL Et2O for 18 h and 20 mL for 22 h (alternatively 3 x 30 mL Et2O). The combined extracts were concentrated to saturation (approx. 15 mL) and filtered over neutral alumina (alternatively celite) to give a yellowish solution. Evaporation provided a yellow oil, which was extracted with 40 mL pentane. The extract was evaporated to give an orange solid. Crystallization by cooling a saturated Et2O solution to -80 °C, provided 3d as a white solid (45%). For spectroscopic details, see manuscript.

((N-phenylimidoyl)di(3-methyl-phenyl)phosphane (3e)

Di(3-methyl-phenyl)phosphane (1.66 g, 7.75 mmol, 1.0 eq.) was added dropwise to a solution of 2a (2.28 g, 8.53 mmol, 1.1) in 30 mL DCM at –78 °C. The yellow/orange solution was allowed to warm to RT, during which it colored red/brown, and stirred for 1 h. Triethylamine (1.15 mL, 8.25 mmol, 1.1 eq.) was added. The resulting brown solution was stirred for 1 h. Volatiles were removed in vacuo to provide a dark brown oil, which was extracted with sequentially 50 mL Et2O for 18 h and 20 mL for 22 h (alternatively 3 x 30 mL Et2O). The combined extracts were concentrated to saturation and filtered over celite (alternatively neutral alumina). The filtrate was evaporated to give an orange solid. Crystallization by cooling a saturated Et2O solution to –80 °C, provided 3e as a white solid (77%) as a white solid, which partially melts at RT. For spectroscopic details, see manuscript.

((N-phenylimidoyl)di(4-methyl-phenyl)phosphane (3f)

A solution of di(4-methyl-phenyl)phosphane (0.81 g, 3.8 mmol, 1.0 eq.) in 15 mL DCM was added dropwise to 2a (1.11 g, 4.2 mmol, 1.1 eq.) in 15 mL DCM at –78 °C. The resulting yellow solution was allowed to warm to RT and subsequently stirred for 30 min. Triethylamine (0.56 mL, 4.0 mmol, 1.1 eq.) was added dropwise. The solution was stirred for 30 min. Volatiles were removed in vacuo to give a brown oil, which was extracted with 3 x 20 mL Et2O. The combined extracts were concentrated to saturation and subsequently filtered over celite (alternatively neutral alumina), to give a yellow solution. Evaporation provided an orange-brown oil, which was extracted into 10 mL pentane. Evaporation of the extract yielded 3f as an orange oil, which solidified over time (0.66 g, 2.0 mmol, 53 %). For spectroscopic details, see manuscript.
(\((N\text{-isopropyl})\text{phenylimidoyl})\text{diphenylphosphane}\) \((3g)\)\(^2\) Prepared according to literature procedures.

**Hydrolysis of \((N\text{-methyl})\text{phenylimidoyl})\text{diphenylphosphane}\) \((3a)\)

3a (0.069 mmol, 0.021g, 1.00 eq) was dissolved in 0.6 mL acetone in an NMR tube and a solution of H\(_2\)O in acetone (10%, 6.2 µL, 0.034 mmol, 0.50 eq.) was added. The mixture was vigorously shaken and kept at RT for 21 h, during which the reaction was monitored using \(^{31}\)P-NMR spectroscopy. Using this methodology, systematically H\(_2\)O was added to the mixture, which was kept at RT during the described time span:

1. H\(_2\)O solution in acetone (10%, 6.2 µL, 0.034 mmol, 0.50 eq.), 68.5 h.
2. H\(_2\)O solution in acetone (10%, 12.4 µL, 0.069 mmol 1.00 eq.), 29 h.
3. H\(_2\)O solution in acetone (10%, 25 µL, 0.137 mmol 2.00 eq.), 26.5 h.
4. H\(_2\)O solution in acetone (10%, 50 µL, 0.275 mmol 4.00 eq.), 18.5 h.
5. H\(_2\)O (10.0 µL, 0.554 mmol, 8.03 eq.), 24.5 h.

Next, an excess of H\(_2\)O was added (0.60 mL, 33.24 mmol 481.7 eq.). The mixture was vigorously shaken, resulting in a white suspension, and kept at RT for 22.5 h. The solid was isolated by decantation of the mixture, re-providing 3a as a white solid (93% pure).

<table>
<thead>
<tr>
<th>H(_2)O added</th>
<th>3a : Ph(_2)PH</th>
<th>Time of measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100% : 0%</td>
<td>0</td>
</tr>
<tr>
<td>0.5 eq.</td>
<td>97% : 0%</td>
<td>21h05m</td>
</tr>
<tr>
<td>1.0 eq.</td>
<td>95% : 0%</td>
<td>89h26m</td>
</tr>
<tr>
<td>2.0 eq.</td>
<td>91% : 0%</td>
<td>118h13m</td>
</tr>
<tr>
<td>4.0 eq.</td>
<td>89% : 0%</td>
<td>144h37m</td>
</tr>
<tr>
<td>8.0 eq.</td>
<td>85% : 1%</td>
<td>163h16m</td>
</tr>
<tr>
<td>16.0 eq.</td>
<td>85% : 1%</td>
<td>187h39m</td>
</tr>
<tr>
<td>500 eq.</td>
<td>62% : 4%</td>
<td>210h11m</td>
</tr>
<tr>
<td>Solid</td>
<td>93% : 0%</td>
<td>216h04m</td>
</tr>
</tbody>
</table>

**Figure S1.** Water sensitivity of ligand 3a-e.

---

Hydrolysis of \((N\text{-methyl})4\text{-methyl-phenylimidoyl)diphenylphosphane (3b)\)

3b (0.023g, 0.072 mmol, 1.00 eq.) was dissolved in 0.6 mL acetone in an NMR tube and a solution of H\(_2\)O in acetone (10%, 6.5 \(\mu\)L, 0.036 mmol 0.50 eq.) was added. The mixture was vigorously shaken and kept at RT for 18 h, during which the reaction mixture was monitored using \(^{31}\text{P-NMR} \) spectroscopy. Using this methodology, systematically H\(_2\)O was added to the mixture, which was kept at RT during the described time span:

1. H\(_2\)O solution in acetone (10%, 6.5 \(\mu\)L, 0.036 mmol 0.50 eq.), 49 h.
2. H\(_2\)O (3.9 \(\mu\)L, 0.216 mmol, 3.00 eq.), 24 h.
3. H\(_2\)O 15.7 \(\mu\)L, 0.873 mmol, 12.1 eq.), 25 h.

Next, an excess of H\(_2\)O was added (0.60 mL, 33.24 mmol, 461.67 eq.). The mixture was vigorously shaken and kept at RT. After 16 days an emulsion was obtained, consisting of colorless solution and a yellow oil. The mixture was evaporated and re-dissolved in 0.6 mL acetone.

<table>
<thead>
<tr>
<th>H(_2)O added</th>
<th>3b : Ph(_2)PH</th>
<th>Time of measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>98% : 0%</td>
<td>0</td>
</tr>
<tr>
<td>0.5 eq.</td>
<td>95% : 0%</td>
<td>17h48m</td>
</tr>
<tr>
<td>1.0 eq.</td>
<td>91% : 0%</td>
<td>65h24m</td>
</tr>
<tr>
<td>4.0 eq.</td>
<td>88% : 1%</td>
<td>91h07m</td>
</tr>
<tr>
<td>16.0 eq.</td>
<td>84% : 2%</td>
<td>115h35m</td>
</tr>
<tr>
<td>Excess (redisolved)</td>
<td>36% : 6%</td>
<td>524h12m</td>
</tr>
</tbody>
</table>

Hydrolysis of \((\text{N-methyl})4\text{-trifluoromethyl-phenylimidoyl) diphenylphosphane (3c)\)

3c (0.021g, 0.059 mmol, 1.00 eq) was dissolved in 0.6 mL acetone in an NMR tube and a solution of H\(_2\)O in acetone (10%, 4.9 \(\mu\)L, 0.027 mmol 0.46 eq.) was added. The mixture was vigorously shaken and kept at RT for 47.5 h, during which the reaction mixture was monitored using \(^{31}\text{P-NMR} \) spectroscopy. Using this methodology, systematically H\(_2\)O was added to the mixture, which was kept at RT during the described time span:

1. H\(_2\)O solution in acetone (10%, 24 \(\mu\)L, 0.133 mmol 2.25 eq.), 24 h.
2. H\(_2\)O (18 \(\mu\)L, 0.997 mmol, 16.9 eq.), 23.5 h.

Next, an excess of H\(_2\)O was added (0.6 mL, 33.24 mmol, 563.34 eq.), resulting in a white suspension. The mixture was vigorously shaken and kept at RT. After 72 h an emulsion was obtained, consisting of colorless solution and a yellow oil.

<table>
<thead>
<tr>
<th>H(_2)O added</th>
<th>3c : Ph(_2)PH</th>
<th>Time of measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100% : 0%</td>
<td>0</td>
</tr>
<tr>
<td>0.5 eq.</td>
<td>95% : 0%</td>
<td>41h36m</td>
</tr>
<tr>
<td>2.8 eq.</td>
<td>94% : 0%</td>
<td>68h52m</td>
</tr>
<tr>
<td>20.0 eq.</td>
<td>92% : 1%</td>
<td>91h26m</td>
</tr>
<tr>
<td>Excess</td>
<td>72% : 3%</td>
<td>165h27m</td>
</tr>
</tbody>
</table>

Acid stability of \((\text{N-methyl})\text{phenylimidoyl)diphenylphosphane (3a)\)

3a (0.0203 g, 0.066 mmol, 1.00 eq.) was dissolved in 0.4 mL DCM to give a yellowish solution. Addition of a solution of TIOH in DCM (0.23 mL of a 0.28 M solution, 0.064 mmol, 0.98 eq.) provided a bright yellow solution, which was vigorously shaken and kept at RT for 20 h, during which the reaction was monitored using \(^{31}\text{P-NMR} \) spectroscopy. Next, again TIOH in DCM (0.23 mL of a 0.28 M solution, 0.064 mmol, 0.98 eq.) was added. The mixture was vigorously shaken and kept at RT for 24 h, during which the reaction was monitored using \(^{31}\text{P-NMR} \) spectroscopy. Excess triethylamine (0.20 ml, 1.43 mmol, 21.74 eq.) was added to the mixture at 0 °C, resulting in a light yellow solution of pure 3a.

<table>
<thead>
<tr>
<th>Reagents present</th>
<th>Mixture</th>
<th>Time of measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>99% 3a</td>
<td>0</td>
</tr>
<tr>
<td>1.0 eq. TIOH</td>
<td>98% 3aH(^+)</td>
<td>18h26m</td>
</tr>
</tbody>
</table>
Acid catalysed hydrolysis of ((N-methyl)phenylimidoyl)diphenylphosphane (3a)

3a (0.0267 mg, 0.088 mmol, 1.00 eq.) was dissolved in 0.6 ml DM to give a yellowish solution. Addition of a solution of TfOH in DCM (31 µL of a 0.28 M solution, 0.009 mmol, 0.10 eq.) provided a more intensely colored yellow solution, which was vigorously shaken and kept at RT for 1 h. Subsequently, H2O (0.8 µL, 0.044 mmol, 0.50 eq.) was added to the mixture, which then was vigorously shaken and kept at RT for 2 days, during which the reaction was monitored using 31P-NMR spectroscopy. Next, excess H2O (5.6 µL, 0.310 mmol, 3.52 eq.) was added to the mixture. After vigorous shaking, the mixture was kept at RT for 24 days.

Oxidation of ((N-methyl)phenylimidoyl)diphenylphosphane (3a)

Under N2 atmosphere, 3a (0.012 g, 0.04 mmol, 1.00 eq.) was dissolved in 0.6 mL acetone. Stepwise, O2 (21% in air) was bubbled manually through the mixture with a rate of approx. 6 bubbles per second using a needle with an inner diameter of 1.194 mm. During additions, the mixture was kept in a water bath at RT to inhibit acetone evaporation. After each addition, the NMR tube was sealed using a screw cap and the reaction mixture was monitored using 31P-NMR spectroscopy. Using this methodology, systematically O2 (21% in air) was added to the mixture at RT over the described intervals:

1. O2 (21% in air, 1 mL, 8.73 µmol, 0.22 eq.), 30s
2. O2 (21% in air, 1 mL, 8.73 µmol, 0.22 eq.), 30s
3. O2 (21% in air, 2 mL, 17.47 µmol, 0.44 eq.), 60s
4. O2 (21% in air, 2 mL, 17.47 µmol, 0.44 eq.), 60s
5. O2 (21% in air, 4 mL, 34.94 µmol, 0.87 eq.), 2 min.
6. O2 (21% in air, 4 mL, 34.94 µmol, 0.87 eq.), 2 min.
7. O2 (21% in air, 8 mL, 69.88 µmol, 1.75 eq.), 4 min.
8. O2 (21% in air, 8 mL, 69.88 µmol, 1.75 eq.), 4 min.
9. O2 (21% in air, 16 mL, 0.140 mmol, 3.49 eq.), 8 min.
10. O2 (21% in air, 16 mL, 0.140 mmol, 3.49 eq.), 8 min.

From addition #7 onwards, a white solid started to precipitate. After the additions, the mixture was allowed to fully oxidize by dissolving the mixture in 10 mL acetone (technical grade) and stirring the resulting solution in under closed air atmosphere for 42 h at RT. Subsequently, the reaction vessel was opened to the external air atmosphere and stirred for an additional 173.5 h. The resulting solution was evaporated to provide a white oil.
S7

Figure S2. Air sensitivity of ligand 3a.

((N-methyl)phenylimidoyl)diphenylphosphanyl) (pentamethylcyclopentadienyl) Rhodium(III) dichloride (4a)

Under an Argon atmosphere, a solution of 3a (102 mg 0.34 mmol, 2.4 eq.) in 9 mL DCM was added to a red/brown solution of [RhCp*Cl₂]₂ (87 mg 0.14 mmol, 1.0 eq.) in 5 mL DCM. The resulting red/brown solution was stirred for 30 min at RT. Evaporation of the obtained red solution provided a red/orange solid which was washed with 3 x 5 mL Et₂O to provide 4a as an orange solid (155 mg, 0.25 mmol, 90%). Crystallization: Subsequently Et₂O (250 mL Et₂O/mmol compound) and pentane (375 mL pentane/mmol compound) were diffused into a DCM solution (150 mL DCM/mmol compound) at RT. Next, the solution was slowly cooled to −20 °C to provide red needles. For spectroscopic details, see manuscript.

((N-methyl) 4-trifluoromethyl-phenylimidoyl) diphenylphosphanyl) (pentamethylcyclopentadienyl) Rhodium(III) dichloride (4c)

Under an Argon atmosphere, 3c (112 mg 0.30 mmol, 2.3 eq.) was dissolved in 14 mL DCM, after which [RhCp*Cl₂]₂ (81 mg 0.13 mmol, 1.0 eq.) was added to provide a red/brown solution, which was stirred for 30 min at RT. Evaporation provided a red solid which was washed with 3 x 5 mL Et₂O to provide 4c as an orange solid (121 mg, 0.18 mmol, 68%). For spectroscopic details, see manuscript.

((N-methyl) phenylimidoyl) di(3-methylphenyl)phosphanyl) (pentamethylcyclopentadienyl) Rhodium(III) dichloride (4e)

Under an Argon atmosphere, 3e (99 mg 0.30 mmol, 2.3 eq.) was dissolved in 14 mL DCM, after which [RhCp*Cl₂]₂ (81 mg 0.13 mmol, 1.0 eq.) was added to provide a red/brown solution, which was stirred for 30 min at RT. Evaporation provided a red/orange solid which was washed with 3 x 5 mL Et₂O to provide 4e as a red solid (154 mg, 0.24 mmol, 92%). Crystallization: Et₂O (45 mL/mmol compound) was diffused into a DCM/Et₂O solution (23 mL DCM/mmol compound, 32 ml Et₂O/mmol compound) at RT to provide red needles. The mother liquor was cooled to 5 °C to provide additional material. For spectroscopic details, see manuscript.

Chloro ((N-methyl) phenylimidoyl) diphenylphosphanyl) (pentamethylcyclopentadienyl) Rhodium(III) trifluoromethanesulfonate (6a)

Under an Argon atmosphere, a solution of 3a (94 mg 0.31 mmol, 2.1 eq.) in 9 mL DCM was added to a red/brown solution of [RhCp*Cl₂]₂ (93 mg 0.15 mmol, 1.0 eq.) in 5 mL DCM. The resulting red solution was stirred for 30 min at RT. Next, AgOTf (79 mg, 0.30 mmol, 2.0 eq.) was added and the resulting suspension was stirred for 60 min at RT in absence of light, during which the mixture turned bright orange. Filtration provided a red solution, which was evaporated to provide an orange solid. After washing with 3 x 5 mL Et₂O, 6a was obtained as an orange solid (218 mg, 0.30 mmol, quant.). Crystallization: Slow diffusion of pentane (3
Chloro ((N-(methyl) 4-trifluoromethyl-phenylimidoyl) diphenylphosphanyl) (pentamethylcyclopentadienyl) Rhodium(III) trifluoromethylsulfonate (6c)

Under an Argon atmosphere, to a solution of 3c (114 mg 0.31 mmol, 2.1 eq.) in 14 mL DCM, was added [RhCp*Cl2]2 (95 mg 0.15 mmol, 1.0 eq.) to provide a red solution, which was stirred for 30 min at RT. Next, AgOTf (79 mg, 0.30 mmol, 2.0 eq.) was added and the resulting suspension was stirred for 60 min at RT in absence of light, during which the mixture turned bright orange. Filtration provided an orange-red solution, which was evaporated to provide a yellow-orange solid. After washing with 3 x 5 mL pentane, 6c was obtained as an orange powder (231 mg, 0.29 mmol, 97%). For spectroscopic details, see manuscript.

Chloro ((N-(methyl)phenylimidoyl) di(3-methylphenyl) phosphanyl) (pentamethylcyclopentadienyl) Rhodium(III) trifluoromethylsulfonate (6e)

Under an Argon atmosphere, to a solution of 3e (87 mg 0.26 mmol, 2.0 eq.) in 14 mL DCM, was added [RhCp*Cl2]2 (81 mg 0.13 mmol, 1.0 eq.) to provide a red solution, which was stirred for 30 min at RT. Next, AgOTf (68 mg, 0.26 mmol, 2.0 eq.) was added and the resulting suspension was stirred for 60 min at RT in absence of light, during which the mixture turned bright orange. Filtration provided an orange-red solution, which was evaporated to provide a yellow-orange solid. After washing with 3 x 5 mL Et2O, 6e was obtained as an orange powder (190 mg, 0.25 mmol, 97%). For spectroscopic details, see manuscript.

[((N-(methyl)phenylimidoyl)diphenylphosphanyl) (pentamethylcyclopentadienyl) Rhodium(III) trifluoromethylsulfonate] [poly(disilver(I) tri(trifluoromethanesulfonate)(methylene chloride)) (7a)

Under an Argon atmosphere, to a solution of 3a (92 mg 0.30 mmol, 2.0 eq.) in 15 mL DCM, was added [RhCp*Cl2]2 (94 mg 0.15 mmol, 1.0 eq.) to provide a red solution, which was stirred for 30 min at RT. Next, AgOTf (317 mg, 1.23 mmol, 8.2 eq.) was added and the resulting suspension was stirred for 60 min at RT in absence of light, during which the mixture turned yellow. Filtration provided an orange-red solution, which was evaporated to provide an orange-red solid. After washing with 20 mL pentane, 7a was obtained as a yellow solid (306 mg, 0.21 mmol, 71%). For spectroscopic details, see manuscript.

Typical procedures [(1,3-P,N)Ru(II)]-catalysed nitrile hydration

Protocol 13: Under argon atmosphere, [M] (0.025 mmol, 5 mol% [M]) and ligand (0.05 mmol, 5 mol%) were dissolved in DME (0.5 mL) and stirred for 30 minutes. Benzonitrile (105 µL, 1.02 mmol, 1.0 eq.) and H2O (36 µL, 1.99 mmol, 2.0 eq.) were added and the vessel was sealed. The resulting mixture was stirred at 180 °C for 3 h.

Protocol 24: Under argon atmosphere, [Ru(p-cym)Cl2]2 (16 mg, 0.026 mmol, 5 mol% [Ru]) and ligand (0.052 mmol, 5 mol%) were dissolved in benzonitrile (105 µL, 1.02 mmol, 1.0 eq.) and stirred for 30 minutes. H2O (3.0 mL, 166 mmol, 163 eq.) was added and the sealed vessel was stirred at 100 °C for 24 h.

Protocol 3: Under argon atmosphere, [Ru(p-cym)Cl2]2 (15 mg, 0.024 mmol, 1.4 mol% Ru) and ligand (0.050 mmol, 1.4 mol%) were dissolved in benzonitrile (370 µL, 3.58 mmol, 1.0 eq.) and stirred for 30 minutes. H2O (130 µL, 7.2 mmol, 2.0 eq.) was added and the sealed vessel was stirred at 180 °C for 3 h. Analysis: After cooling to RT, the mixtures were extracted with i-PrOH under atmospheric conditions and analyzed by GC (internal standard: naphthalene).

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2. NMR-spectra

General considerations

NMR spectra were recorded on a Bruker Avance 250 (\(^1\text{H}: 250.13 \text{ MHz}, \quad ^{19}\text{F}: 235.36 \text{ MHz}, \quad ^{31}\text{P}: 101.25 \text{ MHz}, \text{ room temperature}), a Bruker Avance 400 (\(^1\text{H}: 400.13 \text{ MHz}, \quad ^{13}\text{C}^{1\text{H}} : 100.61 \text{ MHz}, \quad ^{31}\text{P}: 161.98 \text{ MHz}, \text{ room temperature}) or a Bruker Avance 500 (\(^1\text{H}: 500.23 \text{ MHz}, \quad ^{13}\text{C}^{1\text{H}} : 125.78 \text{ MHz}, \text{ room temperature}) ). \(^1\text{H}\)-spectra and \(^{13}\text{C}^{1\text{H}}\)-spectra were internally referenced to residual solvent resonances (CDCl\(_3\): \(\delta^1\text{H} = 7.26, \delta^{13}\text{C}^{1\text{H}} = 77.16\); CD\(_2\text{Cl}_2\): \(\delta^1\text{H} = 5.32, \delta^{13}\text{C}^{1\text{H}} = 53.84\); C\(_6\text{D}_6\): \(\delta^1\text{H} = 7.16, \delta^{13}\text{C}^{1\text{H}} = 128.06\)) and \(^{31}\text{P}\)-spectra were references externally to H\(_3\text{PO}_4\).

2a - \(^1\text{H}-\text{NMR} (500.23 \text{ MHz, CDCl}_3):\)

![NMR spectrum image]
2a - $^{13}$C($^1$H)-NMR (125.78 MHz, CDCl$_3$):
2a - $^{19}$F($^1$H)-NMR (235.36 MHz, CDCl$_3$):
2b - $^1$H-NMR (500.23 MHz, CDCl$_3$):
2b - $^{13}$C($^1$H)-NMR (125.78 MHz, CDCl$_3$):
2b - $^{19}$F$({}^1$H$)$-NMR (235.36 MHz, CDCl$_3$):
2c - $^1$H-NMR (500.23 MHz, CDCl$_3$):
2c - $^{13}$C($^1$H)-NMR (125.78 MHz, CDCl$_3$):
$^{19}$F-$^1$H-NMR (235.36 MHz, CDCl$_3$):
Di(3-trifluoromethylphenyl)phosphane - $^1$H-NMR (500.23 MHz, CDCl$_3$):
Di(3-trifluoromethylphenyl)phosphane - $^{13}$C{1H}-NMR (125.78 MHz, CDCl$_3$):
Di(3-trifluoromethylphenyl)phosphane - $^{19}$F-$^1$H-NMR (235.36 MHz, CDCl$_3$):
Di(3-trifluoromethylphenyl)phosphane - $^{31}$P-NMR (161.98 MHz, CDCl$_3$):
Di(3-methylphenyl)phosphane - $^1$H-NMR (500.23 MHz, C$_6$D$_6$):
Di(3-methylphenyl)phosphane - $^{13}\text{C}[^1\text{H}]-\text{NMR (125.78 MHz, C}_6\text{D}_6)$:
Di(3-methylphenyl)phosphane - $^{31}$P-NMR (161.98 MHz, $\text{C}_6\text{D}_6$):
Di(4-methylphenyl)phosphane - $^1$H-NMR (500.23 MHz, C$_6$D$_6$):
Di(4-methylphenyl)phosphan - $^{13}$C($^1$H)-NMR (125.78 MHz, C$_6$D$_6$):
Di(4-methylphenyl)phosphane - $^{31}$P-NMR (161.98 MHz, C$_6$D$_6$):
3a - $^1$H-NMR (500.23 MHz, CDCl$_3$):
3a - $^{13}$C($^1$H)-NMR (125.78 MHz, CDCl$_3$):

[Diagram of NMR spectra showing chemical shifts.]
3a - $^{31}$P-NMR (161.98 MHz, CDCl$_3$):
3b - ¹H-NMR (500.23 MHz, CDCl₃):
3b - $^{13}$C($^1$H)-NMR (125.78 MHz, CDCl$_3$):
3b - $^{31}$P-NMR (161.98 MHz, CDCl$_3$):
3c - $^{1}$H-NMR (500.23 MHz, CDCl$_{3}$):
$^{13}$C-H-NMR (125.78 MHz, CDCl$_3$):
$^{19}$F-$^1$H-NMR (235.36 MHz, CDCl$_3$):
$3c - ^{31}P$-NMR (161.98 MHz, CDCl$_3$):
3d - $^1$H-NMR (500.23 MHz, CDCl$_3$):
3d - $^{13}$C($^1$H)-NMR (125.78 MHz, CDCl$_3$):
3d - $^{19}\text{F}^{'\text{H}}$-NMR (235.36 MHz, CDCl$_3$):

3d - $^{31}\text{P}$-NMR (161.98 MHz, CDCl$_3$):
3e - $^1$H-NMR (500.23 MHz, CDCl$_3$):
$^{13}$C(¹H)-NMR (125.78 MHz, CDCl₃):
3e - $^{31}$P-NMR (161.98 MHz, CDCl₃):
3f - $^1$H-NMR (500.23 MHz, CDCl$_3$):
3f - \(^{13}\text{C}(\text{H})\)-NMR (125.78 MHz, CDCl\(_3\)):
3f - $^{31}$P-NMR (161.98 MHz, CDCl$_3$):
4a - $^1$H-NMR (500.23 MHz, CDCl$_3$):
$4a\ -\ ^{13}C(\text{H})$-NMR (125.78 MHz, CDCl$_3$):
4a - $^{31}$P-NMR (161.98 MHz, CDCl$_3$):
4c - $^1$H-NMR (500.23 MHz, CDCl$_3$):
4c - $^{13}$C(1H)-NMR (125.78 MHz, CDCl$_3$):
$^4c - 1^H(F)-\text{NMR} (235.36 \text{ MHz, CDCl}_3)$:
4c - $^{31}$P-NMR (161.98 MHz, CDCl$_3$):
4e - $^1$H-NMR (500.23 MHz, CDCl$_3$):
4e - $^{13}$C($^1$H)-NMR (125.78 MHz, CDCl$_3$):
4e - $^{31}$P-NMR (161.98 MHz, CDCl$_3$):
6a - $^1$H-NMR (500.23 MHz, CDCl$_3$):
6a - $^{13}$C($^1$H)-NMR (125.78 MHz, CDCl$_3$):
6a - $^{19}$F($^1$H)-NMR (235.36 MHz, CDCl$_3$):
6a - $^{31}$P-NMR (161.98 MHz, CDCl$_3$):
6c - $^1$H-NMR (500.23 MHz, CDCl$_3$):
6c - $^{13}$C(H)-NMR (125.78 MHz, CDCl$_3$):
6c - $^{19}$F($^1$H)-NMR (235.36 MHz, CDCl$_3$):
6c - $^{31}\text{P-}^{1}\text{H-NMR}$ (161.98 MHz, CDCl$_3$):
6e - \(^1\text{H-NMR (500.23 MHz, CDCl}_3\)): 

![NMR Spectrum Image]

Chemical Shift (ppm)
6e - $^{13}$C(¹H)-NMR (125.78 MHz, CDCl₃):
6e - $^{19}$F($^1$H)-NMR (235.36 MHz, CDCl$_3$):
$6e - \text{}^{31}\text{P-NMR (161.98 MHz, CDCl}_3)$:
7a - ^1^H-NMR (500.23 MHz, CDCl₃):
7a - $^{13}$C($^1$H)-NMR (125.78 MHz, CDCl$_3$):
7a - $^{19}$F($^1$H)-NMR (235.36 MHz, CDCl$_3$):
7a - $^{31}$P-NMR (161.98 MHz, CDCl$_3$):
3. Crystal structure determinations

The single-crystal X-ray diffraction study were carried out on a Bruker D8 Venture diffractometer with Photon100 detector at 123(2) K using Mo-Kα radiation (4a), an Agilent SuperNova Dual diffractometer with Atlas detector at 120(2) K using Cu-Kα radiation (4e), Bruker ApexDuo diffractometer with APEXII detector at 120(2) K using Mo-Kα radiation (6a), and a Bruker SmartApex diffractometer with APEXII detector at 120(2) K using Mo-Kα radiation (7a). Direct Methods (4e, 6a, 7a) or Patterson (heavy atom) Methods (4a) (SHELXS-97) were used for structure solution and refinement was carried out using SHELXL-2013/2014 (full-matrix least-squares on F²). Hydrogen atoms were localized by difference electron density determination and refined using a riding model. Semi-empirical absorption corrections were applied. For 6a the absolute structure was determined. In 6a the triflate anion and in 7a the solvent CH₂Cl₂ are disordered.

4a: red crystals, C₃₀H₃₃Cl₂NPRh · CH₂Cl₂, Mᵣ = 697.28, crystal size 0.18 × 0.10 × 0.04 mm, monoclinic, space group P₂₁/n (No. 14), a = 8.8092(7) Å, b = 22.8273(19) Å, c = 15.6744(13) Å, β = 105.690(3)°, V = 3034.5(4) Å³, Z = 4, ρ = 1.526 Mg/m³, μ(Mo-Kα) = 0.990 mm⁻¹, F(000) = 1424, 2θmax = 60.0°, 109477 reflections, of which 8904 were independent (Rint = 0.025), 349 parameters, R₁ = 0.022 (for 8047 I > 2σ(I)), wR₂ = 0.051 (all data), S = 1.08, largest diff. peak / hole = 0.859 / -0.779 e Å⁻³.

4e: colourless crystals, C₃₂H₃₇Cl₂NPRh · CH₂Cl₂, Mᵣ = 725.33, crystal size 0.21 × 0.04 × 0.02 mm, monoclinic, space group P₂₁/n (No. 14), a = 8.9362(1) Å, b = 23.6047(3) Å, c = 16.0910(2) Å, β = 104.980(1)°, V = 3278.83(7) Å³, Z = 4, ρ = 1.469 Mg/m³, μ(Cu-Kα) = 7.845 mm⁻¹, F(000) = 1488, 2θmax = 153.6°, 19225 reflections, of which 6858 were independent (Rint = 0.029), 369 parameters, R₁ = 0.034 (for 6296 I > 2σ(I)), wR₂ = 0.084 (all data), S = 1.02, largest diff. peak / hole = 1.447 / -1.838 e Å⁻³.

6a: orange crystals, C₃₀H₃₃ClNPRh · CF₃O₃S, Mᵣ = 725.97, crystal size 0.30 × 0.10 × 0.03 mm, orthorhombic, space group Pna2₁ (No. 33), a = 14.4195(3) Å, b = 14.5992(3) Å, c = 15.1828(3) Å, V = 3196.18(11) Å³, Z = 4, ρ = 1.509 Mg/m³, μ(Mo-Kα) = 0.783 mm⁻¹, F(000) = 1480, 2θmax = 55.4°, 25974 reflections, of which 7166 were independent (Rint = 0.045, 370 parameters, 92 restraints, R₁ = 0.036 (for 6737 I > 2σ(I)), wR₂ = 0.097 (all data), S = 1.03, largest diff. peak / hole = 0.427 / -0.319 e Å⁻³, Parsons’ x = -0.037(15).

7a: orange crystals, C₁₁H₁₂F₆NO₃PRhS · C₃Ag₂F₉OₙS₃ · CH₂Cl₂, Mᵣ = 1438.40, crystal size 0.20 × 0.12 × 0.08 mm, monoclinic, space group P2₁/c (No. 14), a = 11.7349(2) Å, b = 41.0647(6) Å, c = 19.590(1) Å, β = 91.496(1)°, V = 4797.14(12) Å³, Z = 4, ρ = 1.992 Mg/m³, μ(Mo-Kα) = 1.572 mm⁻¹, F(000) = 2832, 2θmax = 55.0°, 79507 reflections, of which 11006 were independent (Rint = 0.025), 645 parameters, 25 restraints, R₁ = 0.030 (for 10140 I > 2σ(I)), wR₂ = 0.065 (all data), S = 1.17, largest diff. peak / hole = 0.859 / -0.860 e Å⁻³.

CCDC 1487761 (4a), 1487762 (4e), 1487763 (6a), and 1487764 (7a) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Figure S3. Molecular structure of 4a (displacement parameters are drawn at 50 % probability level).
Figure S4. Molecular structure of 4a (displacement parameters are drawn at 50 % probability level, solvent omitted for clarity).
Figure S5. Molecular structure of 4e (displacement parameters are drawn at 50 % probability level).
Figure S6. Molecular structure of 4e (displacement parameters are drawn at 50 % probability level, solvent omitted for clarity).
Figure S7. Molecular structure of 6a (displacement parameters are drawn at 50 % probability level).

Figure S8. Structure of the cation of 6a (displacement parameters are drawn at 50 % probability level).
Figure S9. Content of the asymmetric unit of 7a (displacement parameters are drawn at 50 % probability level).
Figure S10. Structure of the cation of 7a (displacement parameters are drawn at 50 % probability level).
4. Optimized Structures

General considerations:
Density functional calculations were performed at the ωB97X-D \(^7\) level of theory using Gaussian09, revision A.02 \(^8\). Geometry optimizations were performed using the 6-31+G(d,p)\(^9\) basis set (Def2-TZVP for Rh),\(^10\) and the nature of each stationary point was confirmed by frequency calculations.

Iminophosphane isomers

\[
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**Z-3a**

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Analysis donor capacity 3a,c,e

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[k2-3a-RhCp*Cl+]   E = -2129.53417269 a.u.
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