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# Unusually large 'yaw' angle upon coordination of a new bulky unsymmetrical 3-hydroxyadamantyl-functionalized N-heterocyclic carbene ligand to rhodium(I)

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## Content

## A. Experimental details

**General considerations**. The synthesis of the imidazolium salt, **1**, was performed under air. All other reactions and characterization were performed under inert atmosphere using an MBraun glovebox under an atmosphere of purified argon (<1 ppm $O_2$/$H_2O$). Glassware was stored in an oven at ~100 °C for at least 12 h prior to use. THF and *n*-pentane were purified by passage through a column of activated alumina, dried over Na/benzophenone, vacuum-transferred to a storage flask and freeze-pump-thaw degassed prior to use. All other reagents were acquired from commercial sources and used as received. All other reagents were acquired from commercial sources and used as received. NMR spectra were recorded on Bruker AV-300, AVQ-400 and AV-500 spectrometers. Chemical shifts were measured relative to residual solvent peaks, which were assigned relative to an external TMS standard set at 0.00 ppm. $^{31}P$ and $^{19}F$ chemical shifts were referenced to an external standard ($Ph_3PO$ for $^{31}P$ set at 23 ppm and $BF_3.OEt_2$ for $^{19}F$ set at 0.0 ppm). $^{1}H$ and $^{13}C$ NMR assignments were routinely confirmed by $^{1}H$–$^{1}H$ COSY and $^{1}H$–$^{13}C$ HSQC and HMBC experiments. Samples for IR spectroscopy were prepared in a glovebox, sealed under argon in a DRIFT cell equipped with KBr windows and analyzed on a Nicolet 6700 FT-IR spectrometer. The uncorrected melting points were determined using sealed capillaries prepared under argon.

**Synthesis of 1.**

3-amino-1-adamantanol (0.958 g, 5.73 mmol, 1 eq.), 1,3,5-trimethylaniline (0.8 mL, 5.73mmol, 1 eq.) and acetic acid (3.5 mL, 60.17 mmol, 10.5 eq.) were added in a 50mL round-bottom flask. The solution was then stirred and heated at 60°C during 5 min (brown mixture A). Formaldehyde (0.46 g, 5.73 mmol, 1 eq.), glyoxal (0.66 mL, 5.73 mmol, 1 eq.) and acetic acid (1.5 mL, 25.79 mmol, 4.5 eq.) were added in another 50 mL round-bottom flask. The obtained solution was stirred and heated at 60°C during 5 min (colorless mixture B). Mixture B was then added to mixture A at 60°C. The resulting brown solution was heated at 60°C during 10 min and then cooled down at room temperature. Diethylether (40 mL) and distilled water (40 mL) were added to the solution. The aqueous layer was washed with diethylether (3x40 mL). Brine (50 mL) was then added to the aqueous layer and washed with diethylether again (3x40 mL).

Potassium hexafluorophosphate (1.05 g, 5.73 mmol, 1 eq.) and dichloromethane (120 mL) were then added to the aqueous layer in a 500mL round-bottom flask. The two layers solution was stirred vigorously during one hour. The organic DCM layer was separated, dried with magnesium sulfate, filtered and evaporated to dryness to yield a pale orange solid (2.34 g, 85% yield).

The product was purified by flash chromatography (60M silica gel, eluent: $CH_2Cl_2$/acetone [85/15]) yielding **1** as a white powder (1.89 g, 3.92 mmol, 69% yield). Single crystals suitable for X-ray diffraction were grown by slow evaporation of a concentrated $CH_2Cl_2$ solution of **1**.

**TLC** (silica gel, $CH_2Cl_2$/acetone [85/15]): $R_f$= 0.59.

**Melting point**: 198.9-199.8 °C.

**$^1$H NMR** (298 K, 300 MHz, $CD_2Cl_2$): 8.47 (s, 1H, $CH_{imid}$), 7.76 (s, 1H, $CH_{imid}$), 7.34 (s, 1H, $CH_{imid}$), 7.08 (s, 2H, C-$H_{Mes}$), 2.50 (s, 2H, $CH_{Ad}$), 2.37 (s, 3H, *p*-$CH_{3Mes}$), 2.33 (s, 1H, OH), 2.20 (s, 2H, $CH_{Ad}$), 2.15 (m, 4H, $CH_{Ad}$), 2.03 (s, 6H, *o*-$CH_{3Mes}$), 1.84 (m, 4H, $CH_{Ad}$), 1.68 (m, 2H, $CH_{Ad}$).

**$^{13}$C{$^1$H}-NMR** (298 K, 75 MHz, $CD_2Cl_2$): 142.04 ($C_{imid}$), 134.74 ($C_{Ar}$), 133.47 ($C_{Ar}$), 131.02 ($C_{Ar}$), 130.11 ($C_{Ar}$), 124.75 ($C_{imid}$), 120.49 ($C_{imid}$), 69.31 (HO$C_{Ad}$), 63.71 (N$C_{Ad}$), 49.72 ($C_{Ad}$), 43.22 ($C_{Ad}$), 41.69 ($C_{Ad}$), 34.09 ($C_{Ad}$), 31.12 ($C_{Ad}$), 21.25 (*o*-$C$H$_{3Mes}$), 17.32 (*p*-$C$H$_{3Mes}$).

**$^{19}$F{$^1$H}-NMR** (298 K, 282 MHz, $CD_2Cl_2$): 72.15 (d, $J_{P-F}$=711Hz).

**$^{31}$P{$^1$H}-NMR** (298 K, 121 MHz, $CD_2Cl_2$): 144.45 (septet, $J_{P-F}$=711Hz).

**MS ESI**: [$M^+$]: $C_{22}H_{29}N_2O^+$, m/z = 337.2; $C_{12}H_{15}N_2^+$; m/z = 187.3. [$M^-$]: $PF_6^-$, m/z = 145.3; $[(PF_6)_2Na]^-$, m/z = 313.5.

**IR** (298 K, $cm^{-1}$): 3566.6 (w, $\nu_{O-H}$), 3139.6 (w, $\nu_{Ar-H}$), 2926.4 (w, $\nu_{C-H}$), 2858.3 (w, $\nu_{C-H}$), 1535.3 (w), 1311.2 (w), 1188.8 (m), 1156.3 (m), 1124.2 (m), 1099.0 (m), 1076.3 (m), 823.9 (s, $\nu_{P-F}$), 753.4 (s, $\nu_{P-F}$), 555.9 (s).

**Synthesis of 2.**

Under an argon atmosphere, a 10 mL THF solution of potassium bis(trimethylsilyl)amide (0.571 g, 2.86 mmol, 1 eq.) was added to a 30 mL THF solution of **1** (1.382 g, 2.86 mmol, 1 eq.). The resulting pale yellow solution was stirred at r.t. for 18 hours, yielding a pale yellow suspension. The solid $KPF_6$ residue was removed by filtration and the THF filtrate was evaporated to dryness. The resulting crude solid was extracted with 6 mL THF, 10 mL pentane were added and the mixture was filtered to yield a colorless solution that was stored at -40°C for 15 hours. This yielded a cream-colored crystalline material that was recovered by filtration and dried *in vacuo* to yield 955 mg of **2** (2.84 mmol, 99% yield).

**$^{1}$H NMR** (298 K, 300 MHz, THF-$d_8$) δ 7.24 (d, 1H, $CH_{imid}$), 6.91 (s, 2H, $CH_{Mes}$), 6.82 (s, 1H, $CH_{imid}$), 5.03 (s, 1H, OH), 2.28 (s, 3H, *p*-$CH_{3Mes}$), 2.21 (m, 2H, $CH_{Ad}$), 2.14-2.00 (m, 6H, $CH_{Ad}$), 1.96 (s, 6H, *o*-$CH_{3Mes}$), 1.61-1.48 (m, 6H, $CH_{Ad}$).

**$^{13}$C{$^{1}$H}-NMR** (298 K, 75 MHz, THF-$d_8$) δ 211.86 ($C_{NHC}$), 139.88 ($C_{Mes}$), 137.39 ($C_{Mes}$), 135.81 ($C_{Mes}$), 129.05 ($CH_{Mes}$), 119.90 ($CH_{imid}$), 115.72 ($CH_{imid}$), 68.03 ($HOC_{Ad}$), 59.37 ($NC_{Ad}$), 52.75 ($CH_{2Ad}$), 45.11 ($CH_{2Ad}$), 44.17 ($CH_{2Ad}$), 35.86 ($CH_{Ad}$), 32.09 ($CH_{2Ad}$), 20.90 (*o*-$CH_{3Mes}$), 17.84 (*p*-$CH_{3Mes}$).

**Synthesis of 3.**

Under an argon atmosphere, A 6 mL THF solution of **2** (150 mg, 0.45 mmol, 1 eq.) was added dropwise to a 6 mL THF solution of $[Rh(COD)Cl]_2$ (100 mg, 0.20 mmol, 0.5 eq.). The reaction mixture was stirred at room temperature for 30 minutes, yielding a yellow solution. The solution was layered with 10 mL pentane and stored at -40°C for 24h. This produced a yellow solid that was recovered and dried in vacuo to yield Rh(L)(COD)(Cl), **3**, as a bright yellow solid (183 mg, 0.31 mmol, 70 %). Single crystals suitable for X-ray diffraction were grown by pentane vapor diffusion into a concentrated THF solution of **3**.

**$^1$H NMR** (298 K, 300 MHz, THF-$d_8$) δ 7.55 (d, 1H, $^3J_{HH}$ = 1.8 Hz, $CH_{imid}$), 7.10 (s, 1H, $CH_{Mes}$), 7.02 (d, 1H, $^3J_{HH}$ = 1.8 Hz, $CH_{imid}$), 6.93 (s, 1H, $CH_{Mes}$), 4.63 (m, 2H, COD), 3.84 (s, 1H, OH), 3.43 (m, 1H, COD), 3.03 (m, 1H, COD), 2.99-2.95 (m, 2H, $CH_{Ad}$), 2.70 (m, 3H, $CH_{Ad}$), 2.58 (m, 1H, $CH_{Ad}$), 2.48 (s, 3H, *o*-$CH_{3Mes}$), 2.41 (m, 3H, $CH_{Ad}$), 2.36 (s, 3H, *o*-$CH_{3Mes}$), 2.10 (m, 1H, COD), 1.82 (m, 6H, COD), 1.77 (s, 3H, *p*-$CH_{3Mes}$), 1.68-1.59 (m, 3H, $CH_{Ad}$), 1.50 (m, 1H, COD), 1.35-1.28 (m, 2H, $CH_{Ad}$).

**$^{13}$C{$^1$H}-NMR** (298 K, 75 MHz, THF-$d_8$) δ 181.33 (d, $J_{Rh-C}$ = 51 Hz, Rh-$C_{NHC}$), 138.94 ($C_{Mes}$), 138.84 ($C_{Mes}$), 138.33 ($C_{Mes}$), 135.55 ($C_{Mes}$), 130.07 ($CH_{Mes}$), 128.24 ($CH_{Mes}$), 123.61 ($CH_{imid}$), 119.99 ($CH_{imid}$), 94.89 (d, $J_{Rh-C}$ = 8 Hz, $CH_{COD}$), 91.30 (d, $J_{Rh-C}$ = 8 Hz, $CH_{COD}$), 69.03 (d, $J_{Rh-C}$ = 14 Hz, $CH_{COD}$), 68.89 ($HOC_{Ad}$), 68.09 (d, $J_{Rh-C}$ = 14 Hz, $CH_{COD}$), 62.49 ($NC_{Ad}$), 52.62 ($CH_{2Ad}$), 44.98 ($CH_{2Ad}$), 44.85 ($CH_{2Ad}$), 43.62 ($CH_{2Ad}$), 35.67 ($CH_{Ad}$), 34.38 ($CH_{Ad}$), 32.34 ($CH_{2COD}$), 31.55 ($CH_{2Ad}$), 30.13 ($CH_{2Ad}$), 27.90 ($CH_{2COD}$), 20.92 (*o*-$CH_{3Mes}$), 20.48 (*o*-$CH_{3Mes}$), 17.81 (*p*-$CH_{3Mes}$).

**IR** (298 K, $cm^{-1}$): 3485.0 (s, $\nu_{O-H}$), 3168.8 (m, $\nu_{C-H}$), 3096.3 (m, $\nu_{C-H}$), 2991.8 (m, $\nu_{C-H}$), 2925.5 (s, $\nu_{C-H}$), 2860.4 (s, $\nu_{C-H}$), 2822.4 (s, $\nu_{C-H}$), 1573.0 (w), 1489.1 (w), 1455.9 (w), 1396.5 (m), 1352.7 (w), 1324.6 (m), 1306.1 (w), 1277.4 (w), 1266.2 (m), 1235.0 (w), 1215.3 (w), 1189.9 (m), 1162.6 (w), 1116.7 (m), 1096.6 (m), 1068.5 (w), 1031.8 (m), 992.5 (w), 974.6 (w), 950.0 (w), 926.9 (w), 850.5 (m), 816.8 (w), 749.9 (w), 701.6 (m), 589.5 (m), 554.4 (w).

**Elemental analysis** calcd for $C_{30}H_{40}N_2OClRh$: C, 61.80; H, 6.92; N, 4.80. Found: C, 61.54; H, 6.69; N, 4.63.

## B. NMR spectroscopy

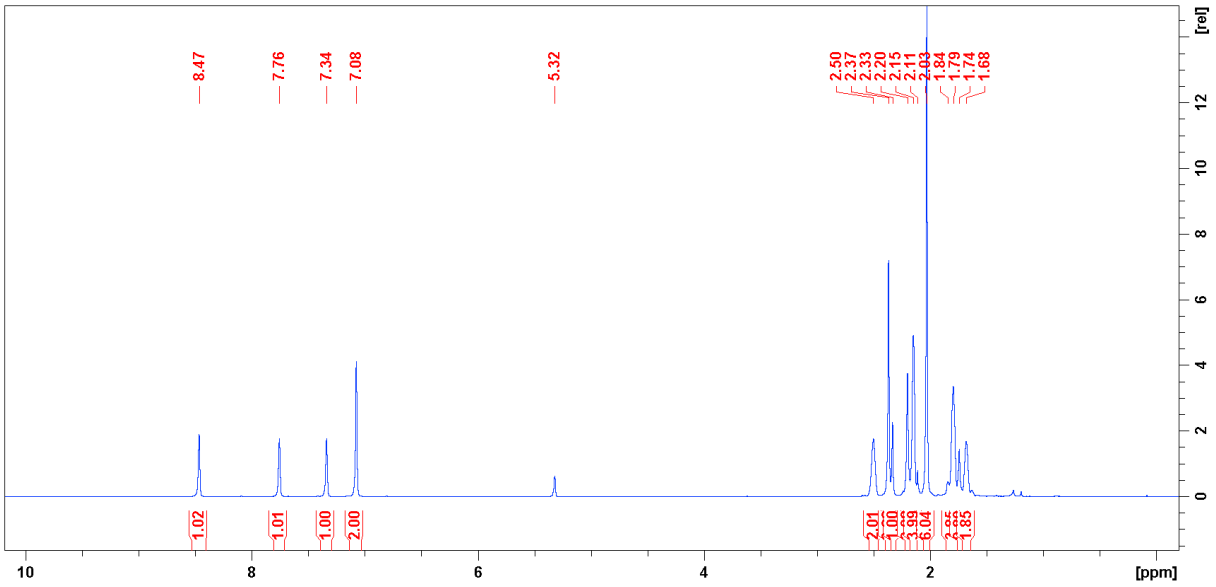


**Figure S1.** $^{1}H$ NMR spectrum (298 K, 300 MHz, $CD_2Cl_2$) of compound **1.**

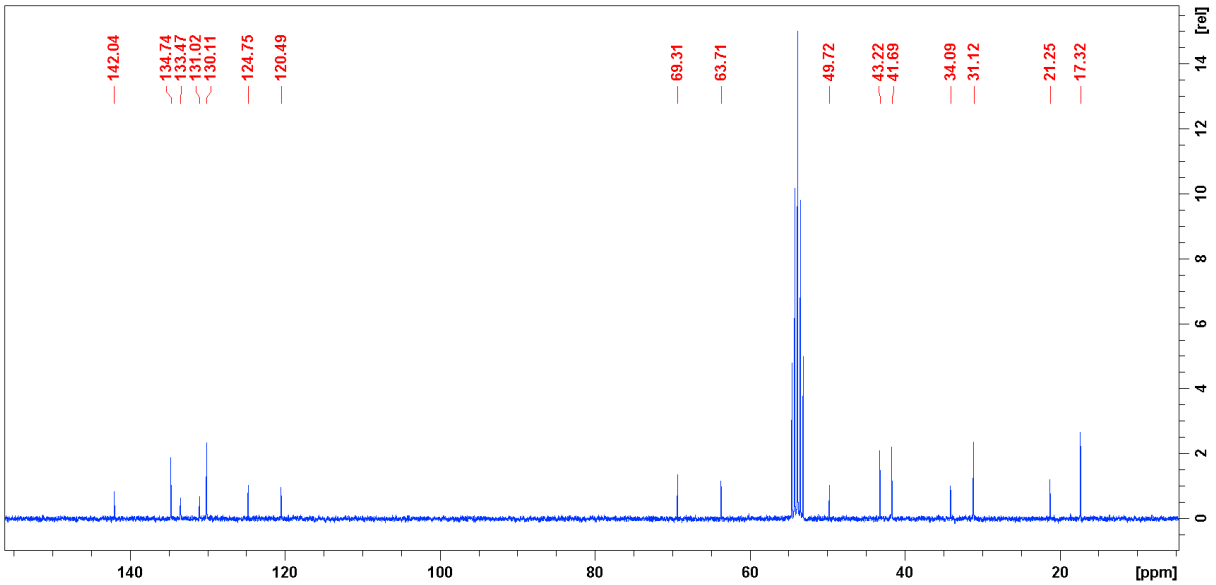


**Figure S2.** $^{13}C\{^{1}H\}$ NMR spectrum (298 K, 75 MHz, $CD_2Cl_2$) of compound **1.**

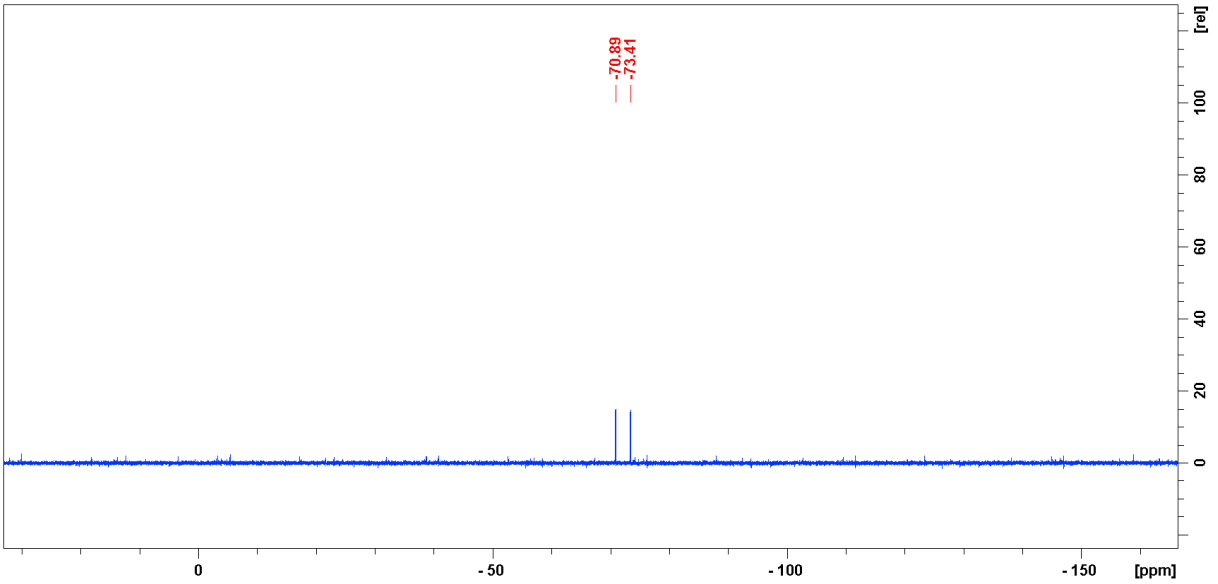


**Figure S3.** $^{19}F\{^{1}H\}$ NMR spectrum (298 K, 282 MHz, $CD_2Cl_2$) of compound **1**.

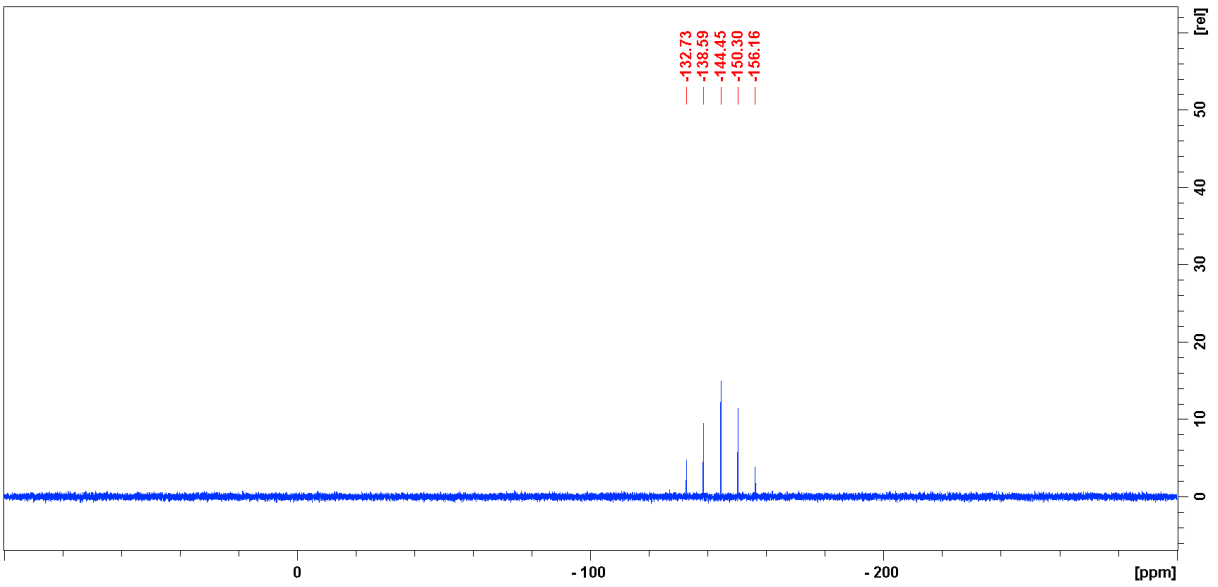


**Figure S4.** $^{31}P\{^{1}H\}$ NMR spectrum (298 K, 121 MHz, $CD_2Cl_2$) of compound **1**.

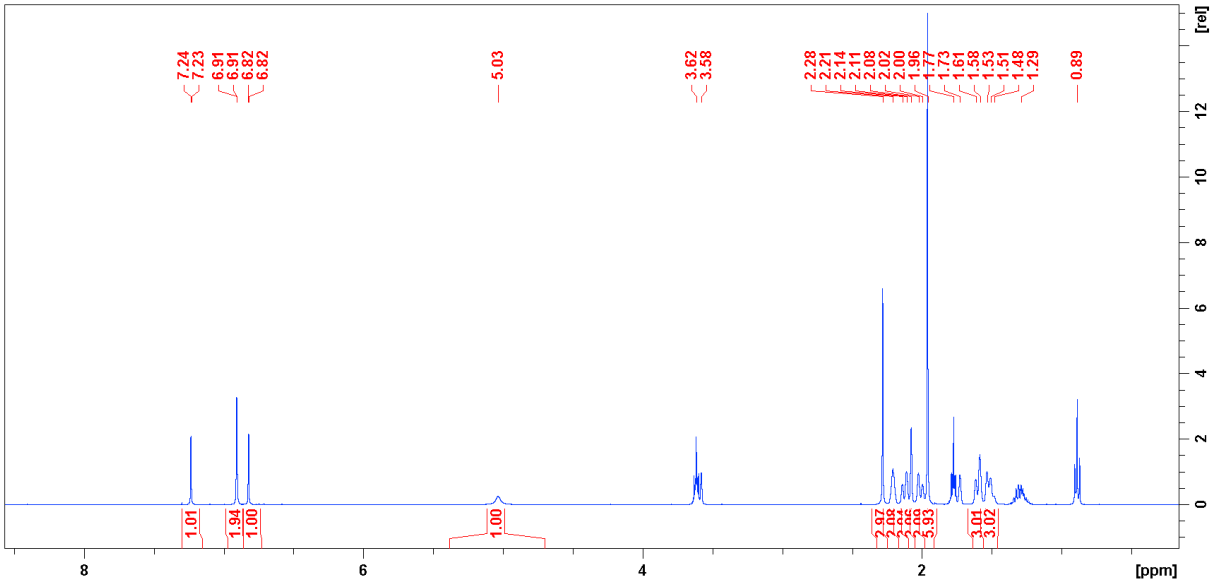


**Figure S5.** $^{1}$H NMR spectrum (298 K, 300 MHz, THF-$d_8$) of compound **2.**

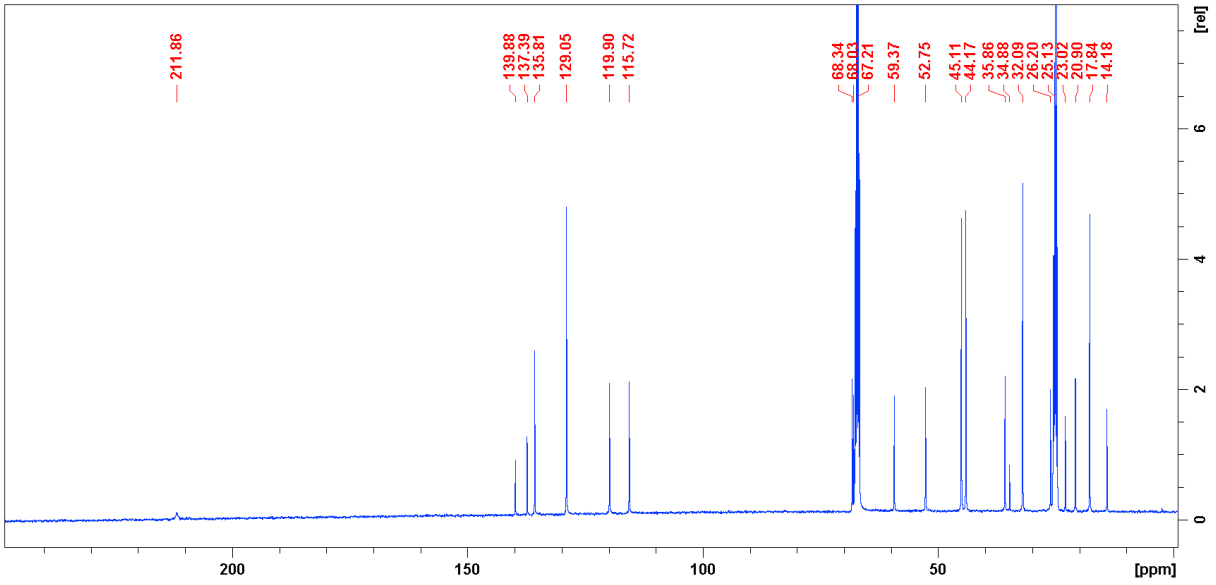


**Figure S6.** $^{13}$C{$^{1}$H} NMR spectrum (298 K, 75 MHz, THF-$d_8$) of compound **2.**

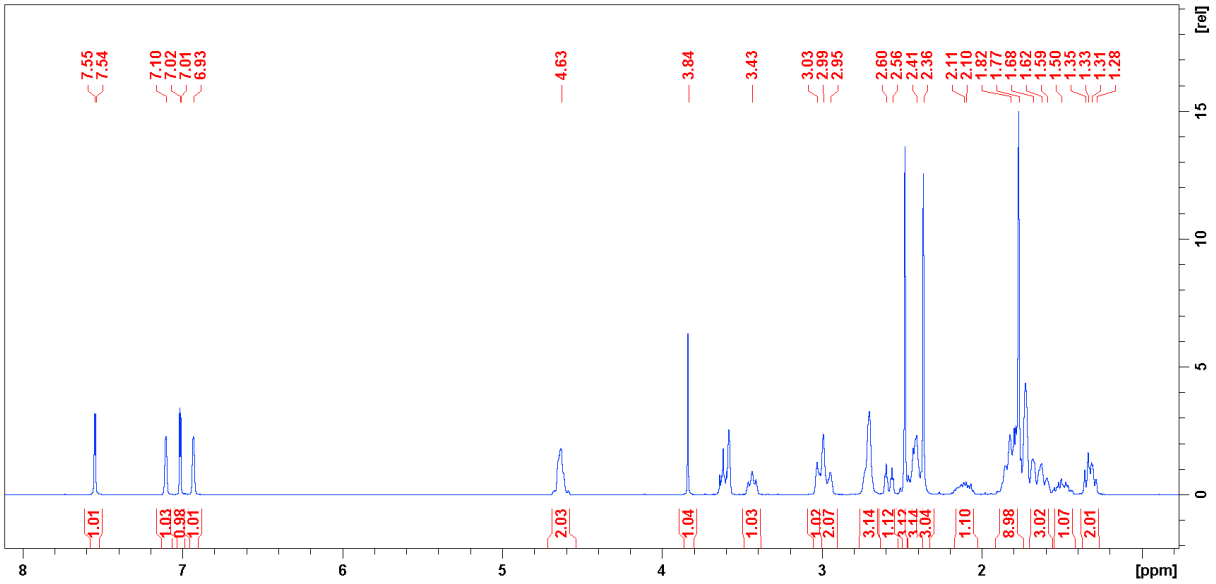


**Figure S7.** $^{1}$H NMR spectrum (298K, 300 MHz, THF-$d_8$) of compound **3.**

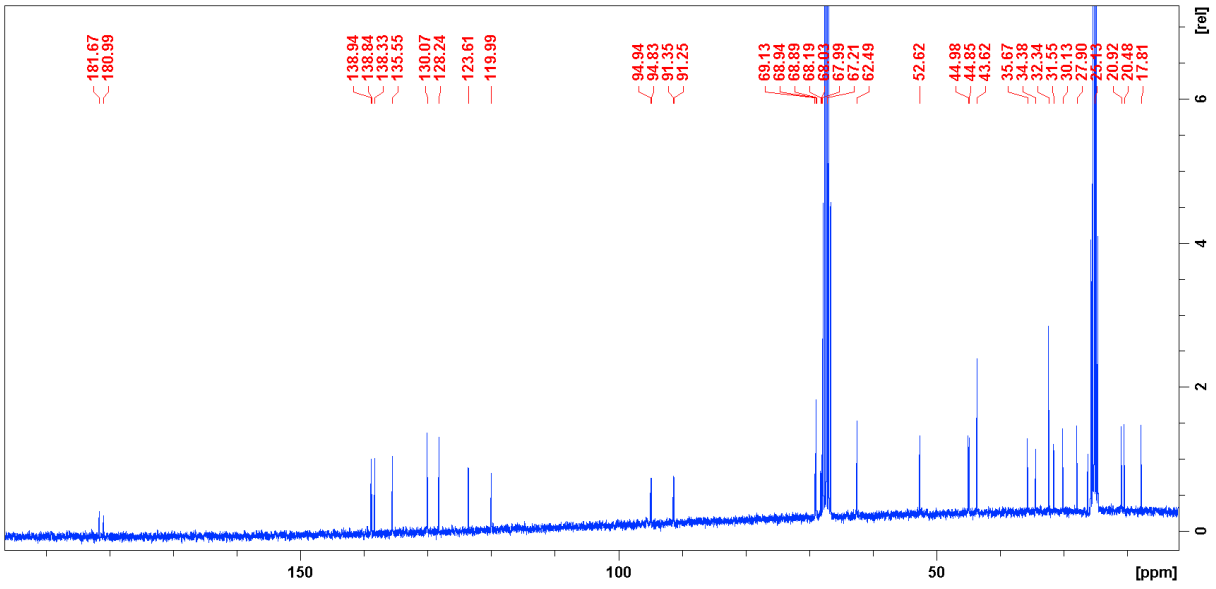


**Figure S8.** $^{13}$C{$^{1}$H} NMR spectrum (298K, 75.4MHz MHz, THF-$d_8$) of compound **3.**

## C. IR spectroscopy

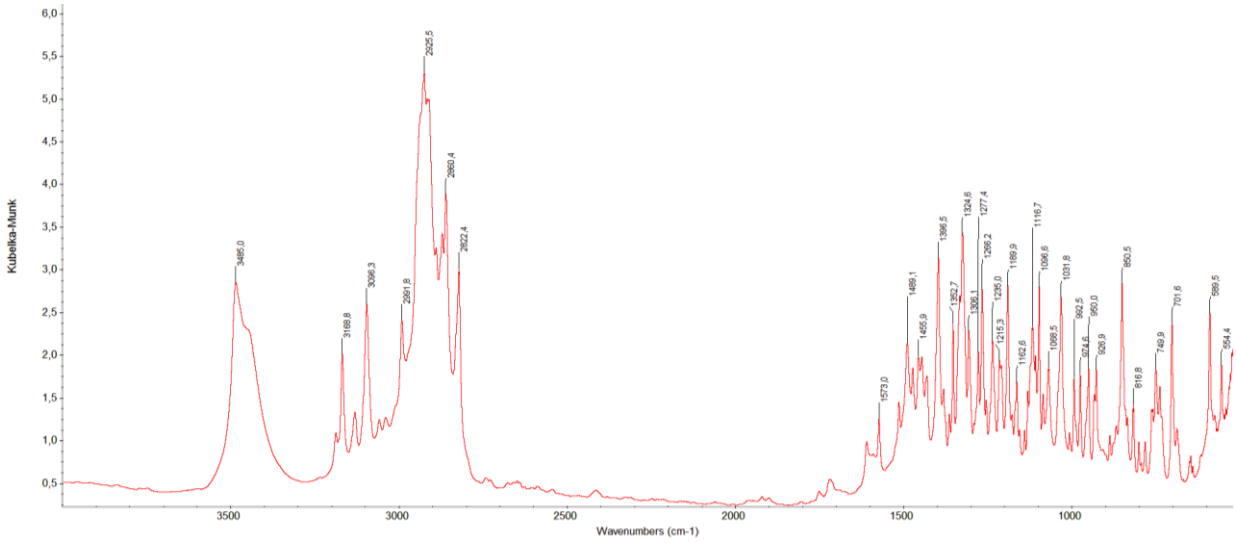


**Figure S9.** DRIFT spectrum (25°C) for compound **3.**

## D. X-Ray crystallography

The X-ray structural determinations were performed at the Centre de Diffractométrie Henri Longchambon, UCBL, Villeurbanne. A suitable crystal coated in Parabar oil was selected and mounted on a Gemini kappa-geometry diffractometer (Rigaku Oxford Diffraction) equipped with an Atlas CCD detector and using Mo radiation (λ= 0.71073 Å). Intensities were collected at 150 K by means of the CrysalisPro software. Reflection indexing, unit-cell parameters refinement, Lorentz-polarization correction, peak integration and background determination were carried out with the CrysalisPro software. An analytical absorption correction was applied using the modeled faces of the crystal.[1] The resulting set of hkl was used for structure solution and refinement. The structures were solved by direct methods with SIR97[2]and the least-square refinement on $F^2$ was achieved with the CRYSTALS software.[3] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were all located in a difference map, but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C---H in the range 0.93--0.98 Å, O---H =0.82 Å) and Uiso(H) (in the range 1.2-1.5 times Ueq of the parent atom), after which the positions were refined with riding constraints. CCDC 2026408 and 2026409 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the Cambridge Crystallographic Data Centre.

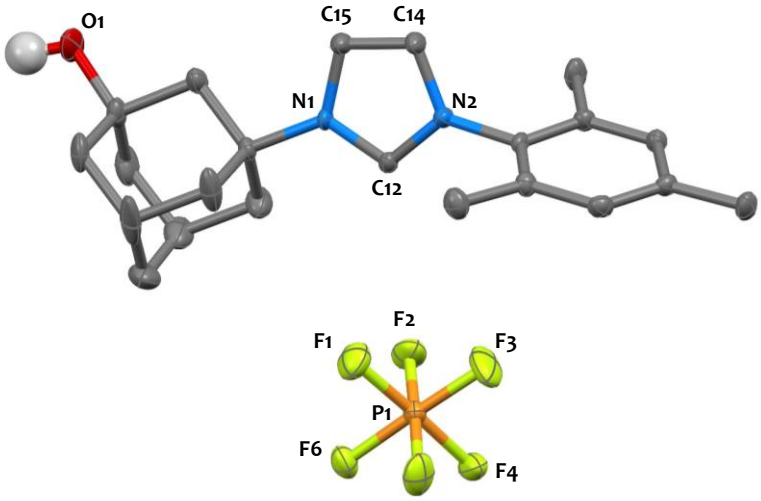


**Figure S10.** Solid-state molecular structure of 1 (30% probability ellipsoids). Hydrogen atoms, except that of the hydroxyl group have been omitted for clarity. Selected bond distances (Å) and angles (°): N1-C12 = 1.336(4); N2-C12 = 1.333(4); N1-C12-N2 = 108.4(2).

[1]Clark, R. C.; Reid, J. S. *Acta Crystallogr. Sect. A Found. Crystallogr.***1995**, *51* (6), 887–897.
[2]Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.***1999**, *32* (1), 115–119.
[3]Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, K.; Watkin, D. J. *J. Appl. Crystallogr.***2003**, *36* (6), 1487–1487.

**Table S1.** Crystallographic parameters for compounds **1** and **3**.

| Compound | **1** | **3** |
|---|---|---|
| Formula | $C_{22}H_{29}N_2O_1F_6P_1$ | $C_{30}H_{40}N_2O_1Cl_1Rh_1$ |
| cryst syst | Monoclinic | Monoclinic |
| space group | C c | I 2/a |
| volume (Å$^3$) | 2236.2(3) | 5693.7(7) |
| a (Å) | 9.1401(7) | 13.1921(8) |
| b (Å) | 18.740(1) | 10.3410(7) |
| c (Å) | 13.090(1) | 41.759(3) |
| α (deg) | 90 | 90 |
| β (deg) | 94.175(7) | 91.872(7) |
| γ (deg) | 90 | 90 |
| Z | 4 | 8 |
| formula weight (g/mol) | 482.44 | 583.02 |
| density (g cm$^{-3}$) | 1.433 | 1.360 |
| absorption coefficient (mm$^{-1}$) | 1.702 | 0.718 |
| $\theta_{max}$ (°) | 66.850 | 29.749 |
| temp (K) | 150.0(1) | 150.0(1) |
| total no. reflections | 11814 | 49488 |
| unique reflections [R(int)] | 3636 [0.050] | 7489 [0.084] |
| no. refined parameters | 293 | 319 |
| Final R indices [I > 2σ(I)] | R1 = 0.0608, wR2 = 0.1682 | R1 = 0.0689, wR2 = 0.1290 |
| GooF | 0.9732 | 0.9696 |

## E. Comparative structural analysis

**Table S2.** Selected metrical and $^{13}C$ NMR data for a series of representative [Rh(NHC)(COD)Cl] complexes.

| Entry | wingtips R1, R2 | Rh-C [Å] | yaw distortion θ [deg] | $^{13}C$ NMR $\delta C_{carbene}$ [ppm] | reference |
|---|---|---|---|---|---|
| **1** | $Ad^{OH}$, Mes | 2.068(5) | 6.8 | 181.3 | Camp, *this work* |
| **2** | *t*-Bu, *n*-Bu | 2.038(6) | 5.9 | 212.8 | Hahn[4] |
| **3** | *t*-Bu, Me | 2.020(1) | 5.5 | 213.3 | Orru[5] |
| **4** | *t*-Bu, Et | 2.031(2) | 4.7 | 212.3 | Hahn[4] |
| **5** | $CF_3$, Ph | 2.015(2) | 3.7 | 200.5 | Togni[6] |
| **6** | Mes, fluoren-9-yl | 2.043(3) | 1.7 | 184.0 | César[7] |
| **7** | Mes, $CH_2CMe_2OH$ | 2.042(4) | 1.2 | 181.9 | Camp[8] |
| **8** | Me, *n*-Bu | 2.023(6) | 0.8 | *not reported* | Chung[9] |
| **9** | Ad, Ad | 2.073(3) | 0.7 | 198.0 | Bielawski[10] |
| **10** | *t*-Bu, *t*-Bu | 2.049(5) | 0.3 | 211.25 | Tapu[11] |
| **11** | Np, Np | 2.032(2) | 0.2 | 205.2 | Heinicke[12] |

[4] F. E. Hahn, M. Paas, D. Le Van and T. Lügger, *Angew. Chemie - Int. Ed.*, 2003, **42**, 5243–5246.
[5] R. S. Bon, F. J. J. De Kanter, M. Lutz, A. L. Spek, M. C. Jahnke, F. E. Hahn, M. B. Groen and R. V. A. Orru, *Organometallics*, 2007, **26**, 3639–3650.
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[12] F. Ullah, G. Bajor, T. Veszprémi, P. G. Jones and J. W. Heinicke, *Angew. Chemie - Int. Ed.*, 2007, **46**, 2697–2700.