

## Electronic supplementary information

# USE OF PHENYL-SUBSTITUTED CYCLOPENTADIENYL RHODIUM COMPLEXES IN the C–H ACTIVATION

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## General experimental remarks

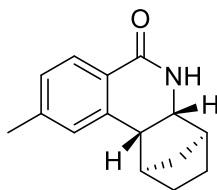
All reactions were carried out under air using distilled solvents. Isolation of all products was carried out in air. The rhodium complexes  $[\text{Cp}^*\text{RhCl}_2]_2$ ,  $[\text{Cp}^{\text{Ph}2}\text{RhCl}_2]_2$  and  $[\text{Cp}^{\text{Ph}3}\text{RhCl}_2]_2$  were synthesized according to published protocols [1]. All other reagents were purchased from Acros or Aldrich and used as received. Column chromatography was carried out using Macherey-Nagel silica gel 60 (particle sizes: 0.04–0.063 mm). The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded on a Varian Inova 400 spectrometer operating at 400 and 101 MHz, respectively. The chemical shifts are given in ppm using the residual solvent signals as an internal standard. The HRMS spectrum (ESI) was recorded using a TripleTOF 5600+ mass spectrometer (SCIEX).

### Rhodium-catalyzed reaction of 4-methyl-*N*-(pivaloyloxy)benzamide with norbornene

4-Methyl-*N*-(pivaloyloxy)benzamide (23.5 mg, 0.1 mmol, 1 equiv.), rhodium complex (1 mol %), CsOAc (4.8 mg, 0.025 mmol, 0.25 equiv.), AgOAc (2 mg, 0.01 mmol, 0.1 equiv.), and solvent (1 mL) were placed in a tube equipped with a magnetic stirring bar. After 5 min, norbornene (19 mg, 0.2 mmol, 2 equiv.) was added. The reaction mixture was stirred at room temperature for 1 h. For the NMR spectroscopic monitoring, after the evaporation of the solvent, the residue was dissolved in  $\text{DMSO}-d_6$ . The conversion was determined as the ratio of the integrals of Me proton signals of the target product and the starting benzamide.

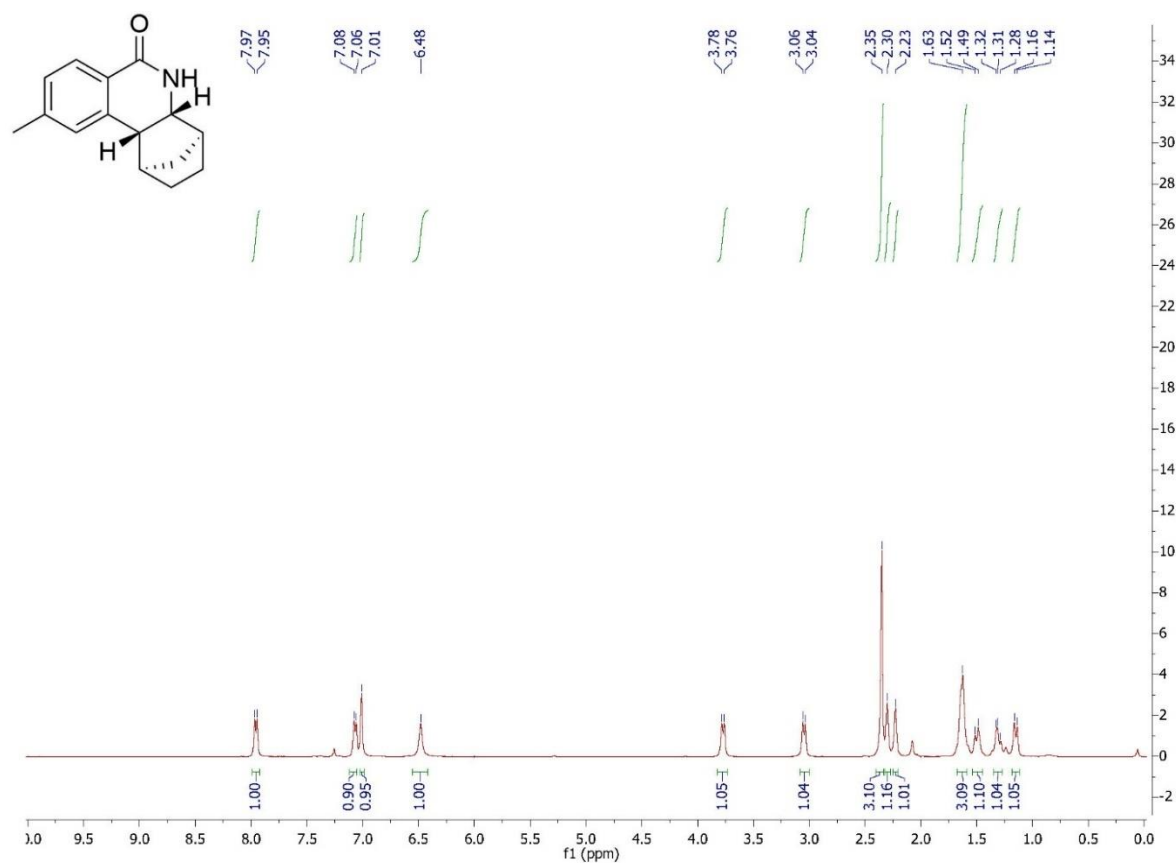
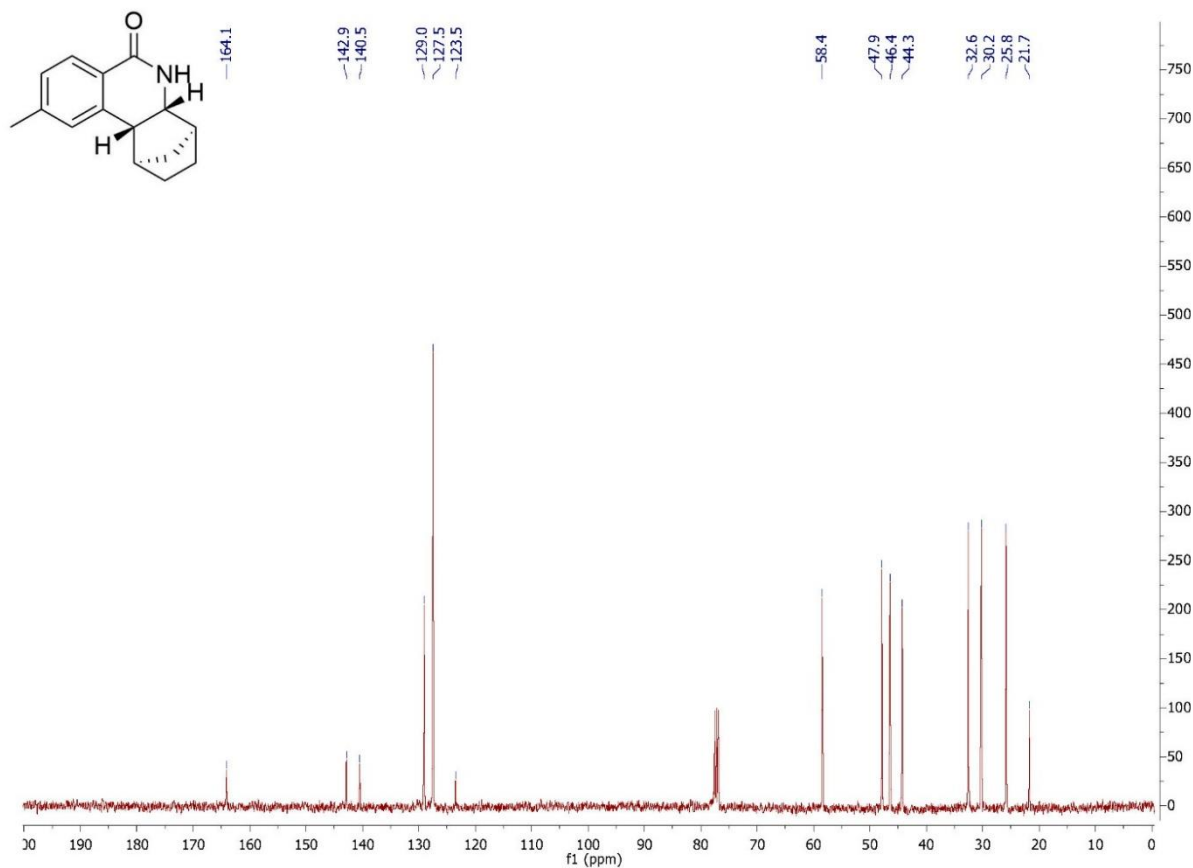
For the isolation of compound **1**, in the case of  $[\text{Cp}^{\text{Ph}2}\text{RhCl}_2]_2$  (0.8 mg, 1 mol %), after stirring the reaction mixture for 1 h, the solvent was removed under vacuum without heating, and the residue was purified by chromatography on silica gel ( $1 \times 15$  cm). The first colorless band containing the unreacted alkene was eluted with  $\text{CH}_2\text{Cl}_2$ . The second band was eluted with  $\text{CH}_2\text{Cl}_2$ –EtOAc (4:1) to give target compound **1** as a colorless solid. Yield: 22.5 mg (99%).

### 9-Methyl-1,3,4,4a,5,10b-hexahydro-1,4-methanophenanthridin-6(2*H*)-one (**1**)



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.96 (d,  $J = 8.1$  Hz, 1H), 7.07 (d,  $J = 7.3$  Hz, 1H), 7.03–6.99 (m, 1H), 6.48 (s, 1H), 3.77 (d,  $J = 8.5$  Hz, 1H), 3.05 (d,  $J = 9.1$  Hz, 1H), 2.35 (s, 3H), 2.32–2.27 (m, 1H), 2.25–2.21 (m, 1H), 1.68–1.59 (m, 3H), 1.54–1.44 (m, 1H), 1.34–1.27 (m, 1H), 1.18–1.11 (m, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.1, 142.9, 140.5, 129.0, 127.5 (2C), 123.5, 58.4, 47.9, 46.4, 44.3, 32.6, 30.2, 25.8, 21.7. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{15}\text{H}_{18}\text{NO}$  228.1383; found, 228.1386.

## NMR spectra

<sup>1</sup>H NMR (400 MHz) spectrum of **1** in CDCl<sub>3</sub><sup>13</sup>C NMR (400 MHz) spectrum of **1** in CDCl<sub>3</sub>

## Computational details

All calculations were performed using ADF 10 program at the GGABP-D3/TZP level with corrections for solvation in methanol (the COSMO model implemented in the ADF 10 program).

To estimate the stabilization effect of cyclopentadienyl ligand on the Rh–Cl bonding, we performed energy decomposition analysis (EDA) for complexes of the type  $[\text{Cp}^{\text{R}}\text{RhCl}_2(\text{MeOH})]$  at the GGABP-D3/TZP level using the COSMO solvation model with methanol as a solvent (Table S1). According to the EDA Scheme [2] the energy of interaction between two fragments of the molecule  $\Delta E_{\text{int}}$  can be divided into three main components:  $\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}}$ , where  $E_{\text{elstat}}$  is the electrostatic attraction between the fragments with a frozen electron density,  $\Delta E_{\text{Pauli}}$  is the repulsive interactions between occupied orbitals (Pauli repulsion), and  $\Delta E_{\text{orb}}$  is the stabilizing orbital interactions. We found that the interaction energy ( $\Delta E_{\text{int}}$ ) of the bonding between the  $[\text{Cp}^{\text{R}}\text{Rh}(\text{MeOH})]^{2+}$  fragment and two chlorine anions is higher by *ca.* 4 kcal mol<sup>−1</sup> for the Cp\* derivative than for the Cp<sup>Ph2</sup> derivative. Although the sum of attractive interactions ( $\Delta E_{\text{elstat}} + \Delta E_{\text{orb}}$ ) for the complex with Cp<sup>Ph2</sup> is higher than that with Cp\*, this positive effect is overruled by an increase in the  $\Delta E_{\text{Pauli}}$  value for the Cp<sup>Ph2</sup> derivative, indicating a significant contribution of steric effects to Rh–Cl bonding.

**Table S1.** Results of energy decomposition analysis (energy values in kcal mol<sup>−1</sup>) for  $[\text{Cp}^{\text{R}}\text{RhCl}_2(\text{MeOH})]$  with  $[\text{Cp}^{\text{R}}\text{Rh}(\text{MeOH})]^{2+} + [\text{Cl}_2]^{2-}$  as interacting fragments at the GGABP-D3/TZP level

Cp <sup>R</sup>	$\Delta E_{\text{int}}$	$\Delta E_{\text{elstat}}$	$\Delta E_{\text{orb}}$	$\Delta E_{\text{elstat}} + \Delta E_{\text{orb}}$	$\Delta E_{\text{Pauli}}$
Cp*	−467.39	−432.50	−114.64	−547.14	125.15
Cp <sup>Ph2</sup>	−463.28	−421.64	−138.32	−559.96	140.25

### Cp\*RhCl<sub>2</sub>(MeOH)

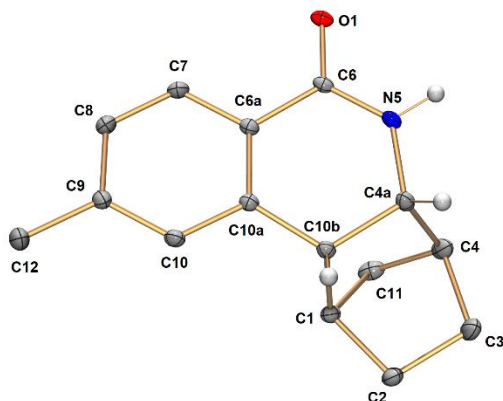
1.Rh	-0.930495	0.086480	-0.149368
2.H	1.728282	-1.389745	-2.172817
3.H	2.960139	1.503533	-1.139103
4.C	0.472518	-1.105397	1.066251
5.H	0.724953	3.315302	0.363474
6.C	1.098112	-0.800757	-0.196025
7.C	1.216740	0.648001	-0.290519
8.C	0.153134	0.144084	1.728410
9.H	-1.052729	1.206285	3.150199
10.H	-0.607322	-2.485245	2.314084
11.C	0.646160	1.229948	0.892031
12.Cl	-2.733179	1.764353	0.305282
13.H	-0.325874	2.937659	1.750120
14.H	1.442657	2.899921	1.936140
15.C	-0.440468	0.299328	3.087619
16.H	-1.059095	-0.562774	3.359813
17.H	0.369001	0.384786	3.830227
18.Cl	-2.613937	-1.764490	-0.352157
19.C	0.233648	-2.470932	1.612861
20.H	0.038155	-3.195350	0.814890
21.H	1.136597	-2.795613	2.155079
22.C	1.651086	-1.798114	-1.159497
23.H	2.663466	-2.093277	-0.840879
24.H	1.036669	-2.705348	-1.194808
25.C	1.892404	1.394495	-1.389914
26.H	1.836921	0.860065	-2.344537
27.H	1.474836	2.398970	-1.517976
28.C	0.612634	2.677648	1.246862
29.O	-1.625905	0.375137	-2.367079
30.H	-2.490002	-0.063567	-2.196407
31.C	-0.923243	-0.456947	-3.333841
32.H	-1.454005	-0.438908	-4.294631
33.H	-0.836096	-1.489021	-2.967008
34.H	0.071491	-0.019645	-3.461176

**Cp<sup>Ph2</sup>RhCl<sub>2</sub>(MeOH)**

1.Rh	1.457030	-0.232598	0.119934
2.Cl	3.660482	-1.365112	-0.046478
3.H	-5.044021	-1.508474	0.411055
4.H	-4.626924	-3.693491	-0.719108
5.Cl	0.843739	-0.959603	-2.169269
6.C	-0.516544	-0.749993	1.065199
7.C	0.594990	-1.338498	1.773869
8.C	1.404561	-0.281004	2.320008
9.C	0.846737	0.951196	1.891538
10.C	-0.341739	0.693483	1.099067
11.H	0.732484	-2.402196	1.938244
12.H	2.297696	-0.405450	2.923060
13.H	1.258354	1.936521	2.092311
14.C	-1.191191	1.733290	0.502917
15.C	-1.411240	2.933434	1.202453
16.C	-1.770718	1.558897	-0.769126
17.C	-2.222210	3.930039	0.652338
18.C	-2.570204	2.559452	-1.318248
19.C	-2.804167	3.745323	-0.607161
20.H	-0.964090	3.075377	2.186831
21.H	-1.561090	0.646683	-1.329180
22.H	-2.397569	4.851341	1.208128
23.H	-3.007739	2.418060	-2.306294
24.H	-3.433255	4.525529	-1.037150
25.C	-1.630683	-1.524477	0.502976
26.C	-1.399753	-2.763043	-0.124366
27.C	-2.951289	-1.073947	0.681717
28.C	-2.473924	-3.533607	-0.568351
29.C	-4.023839	-1.857346	0.251154
30.C	-3.788332	-3.085055	-0.378636
31.H	-0.376500	-3.101263	-0.284072
32.H	-3.135342	-0.121773	1.178917
33.H	-2.287211	-4.486203	-1.064265
34.O	2.473571	1.382073	-1.126532
35.H	2.338293	0.893479	-1.974345
36.C	1.745563	2.642149	-1.244192
37.H	2.234813	3.270651	-1.999159
38.H	1.797889	3.127481	-0.265063
39.H	0.696278	2.463236	-1.516346

## X-ray diffraction study

Crystals of **1** were grown by slow evaporation of a solution in dichloromethane. X-ray diffraction data were collected at 120 K with a Bruker APEX2 CCD diffractometer, using graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å,  $\omega$ -scans). Using Olex2 [3], the structure was solved with the ShelXT [4] structure solution program using Intrinsic Phasing and refined with the XL [5] refinement package using Least-Squares minimization against  $F^2$  in the anisotropic approximation for non-hydrogen atoms. Hydrogen atom of the NH group was located from difference Fourier synthesis while positions of other hydrogen atoms were calculated, and they all were refined in the isotropic approximation in the riding model. Crystal data and structure refinement parameters are given in Table S2. CCDC 2385702 contains the supplementary crystallographic information for **1**.



**Figure 1.** General view of **1** in representation of atoms as thermal ellipsoids ( $p = 50\%$ ); the hydrogen atoms, except those at the carbon atoms C4a and C10b and in the NH group, are omitted. Bond lengths [Å]: O1–C6 1.2478(15), C4A–C10B 1.5594(18), N5–C4A 1.4661(16), C6–C6A 1.4831(17), N5–C6 1.3343(17), C6A–C7 1.3980(18), C1–C2 1.5317(18), C6A–C10A 1.3923(17), C1–C10B 1.5561(17), C7–C8 1.3805(19), C1–C11 1.5293(19), C8–C9 1.3995(18), C2–C3 1.552(2), C9–C10 1.3888(18), C3–C4 1.5442(19), C9–C12 1.5030(19), C4–C4A 1.5390(19), C10–C10A 1.3935(18), C4–C11 1.535(2), C10A–C10B 1.5079(17).

**Table S2.** Crystal data and structure refinement parameters for **1**

	<b>1</b>
Formula unit	C <sub>15</sub> H <sub>17</sub> NO
Formula weight	227.29
Crystal system	Monoclinic
Space group	P2 <sub>1</sub> /n
Z	4
a, Å	10.745(2)
b, Å	9.972(2)
c, Å	12.161(2)
$\alpha$ , °	90
$\beta$ , °	114.480(5)
$\gamma$ , °	90
V, Å <sup>3</sup>	1185.9(4)
$D_{\text{calc}}$ (g cm <sup>−3</sup> )	1.273
Linear absorption, $\mu$ (cm <sup>−1</sup> )	0.79
F(000)	488
2 $\Theta_{\text{max}}$ , °	58
Reflections measured	13621
Independent reflections	3149
Observed reflections [ $I > 2\sigma(I)$ ]	2378
Parameters	155

R1	0.0463
wR2	0.1258
GOOF	1.066
$\Delta\rho_{\max}/\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.346/−0.261

## References

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