

SUPPORTING INFORMATION

The Structures of Reactive Donor/Acceptor and Donor/Donor Rhodium Carbenoids in the Solid State and their Implications for Catalysis

Christophe Werlé, Richard Goddard, Petra Philipps, Christophe Farès, and Alois Fürstner*

Max-Planck-Institut für Kohlenforschung, D-45470 Mülheim/Ruhr, Germany

E-mail: fuerstner@kofo.mpg.de

Table of Contents

Crystallographic Information	S-2
General	S-14
General Procedures for the Preparation of the Rhodium Carbenoids	S-14
Characterization Data	S-15
Cyclopropanation Reactions	S-18
Cp*Rh(III)-Catalysis	S-19
References	S-20
Spectra	S-21

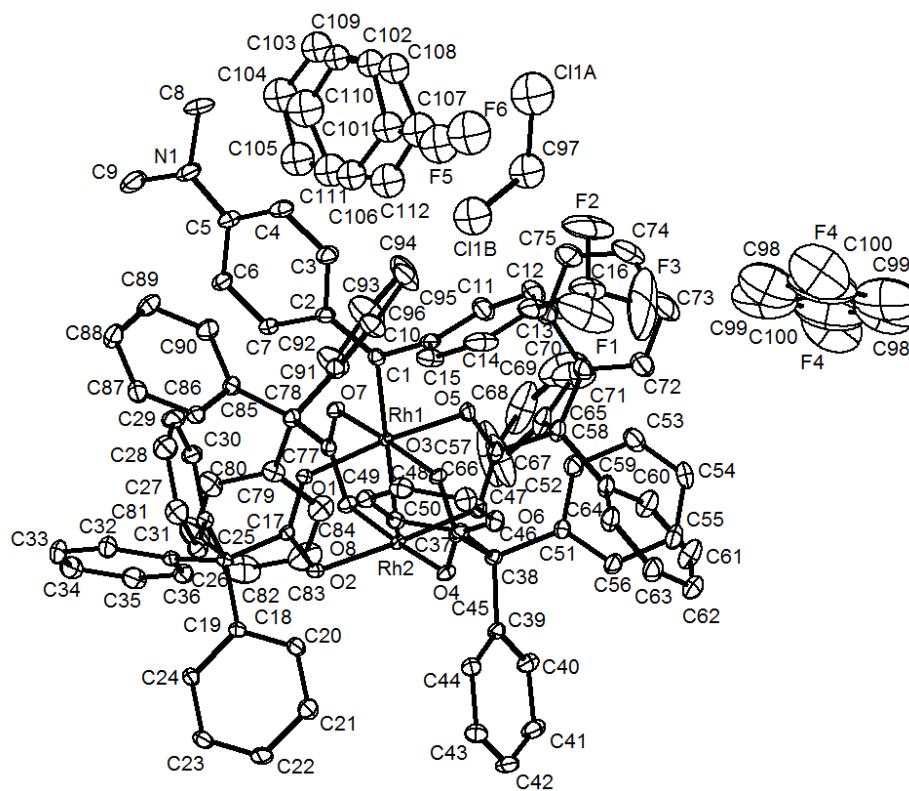


Figure S2. Molecular structure of **4c**.

X-ray Crystal Structure Analysis of 4c: $2(\text{C}_{96}\text{H}_{74}\text{F}_3\text{NO}_8\text{Rh}_2) \cdot (\text{CH}_2\text{Cl}_2) \cdot 3(\text{C}_6\text{H}_5\text{F})$, $M_r = 3637.98 \text{ g} \cdot \text{mol}^{-1}$, red prism, crystal size $0.09 \times 0.14 \times 0.19 \text{ mm}^3$, triclinic, space group $P1$, $a = 12.859(5) \text{ \AA}$, $b = 14.447(5) \text{ \AA}$, $c = 25.005(9) \text{ \AA}$, $\alpha = 103.770(7)^\circ$, $\beta = 94.190(7)^\circ$, $\gamma = 110.200(6)^\circ$, $V = 4172(3) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 1$, $D_{\text{calc}} = 1.448 \text{ g} \cdot \text{cm}^{-3}$, $\lambda = 0.71073 \text{ \AA}$, $\mu(\text{Mo-K}\alpha) = 0.500 \text{ mm}^{-1}$, Gaussian absorption correction ($T_{\text{min}} = 0.91222$, $T_{\text{max}} = 0.96384$), Bruker AXS Enraf-Nonius KappaCCD diffractometer, $2.402 < \theta < 30.946^\circ$, 93124 measured reflections, 26222 independent reflections, 20711 reflections with $I > 2\sigma(I)$, $R_{\text{int}} = 0.043$. The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.051 [I > 2\sigma(I)]$, $wR_2 = 0.129$, 1069 parameters. Several low angle reflections were shadowed by the beamstop and removed from the data for refinement. The structure contains disordered and partially occupied fluorobenzene as well as disordered dichloromethane. The C atoms of the phenyl groups of one disordered fluorobenzene (C101–C106, C107–C112) were constrained to be idealized six-membered rings with a C–C distance of 1.39 \AA and refined as rigid bodies. The atomic displacement parameters of the F atoms of the CF_3 group are somewhat prolate. H atoms riding, $S = 1.159$, residual electron density $1.88 (0.45 \text{ \AA} \text{ from Cl1A}) / -3.02 (0.48 \text{ \AA} \text{ from Cl1A}) \text{ e}^{-3}$. CCDC-1443590.

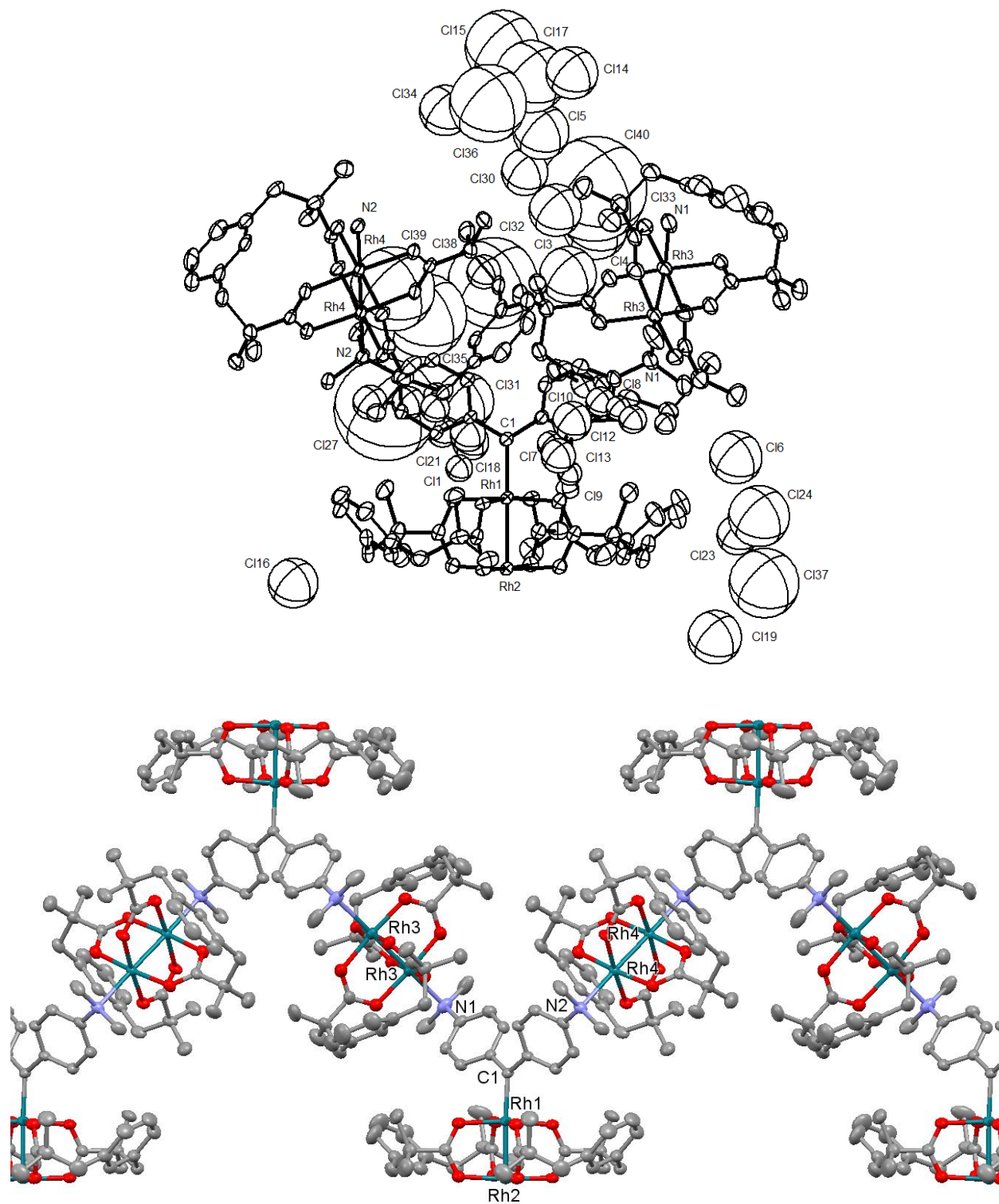


Figure S3. Molecular structure of the coordination polymer **6b**.

X-ray Crystal Structure Analysis of 6b: (C₈₁H₁₀₀N₂O₁₆Rh₄)·18.26(Cl), $M_r = 2416.58 \text{ g} \cdot \text{mol}^{-1}$, red prism, crystal size 0.05 x 0.15 x 0.18 mm³, triclinic, space group *P1*, $a = 15.143(2) \text{ \AA}$, $b = 18.179(3) \text{ \AA}$, $c = 21.930(2) \text{ \AA}$, $\alpha = 111.878(8)$, $\beta = 96.135(9)$, $\gamma = 91.520(9)^\circ$, $V = 5555.7(12) \text{ \AA}^3$, $T = 150 \text{ K}$, $Z = 2$, $D_{\text{calc}} = 1.445 \text{ g} \cdot \text{cm}^3$, $\lambda = 0.71073 \text{ \AA}$, $\mu(\text{Mo-K}\alpha) = 1.076 \text{ mm}^{-1}$, Gaussian absorption correction ($T_{\text{min}} = 0.89313$, $T_{\text{max}} = 0.97104$), Bruker AXS Enraf-Nonius KappaCCD diffractometer, $3.158 < \theta < 26.372^\circ$, 69697 measured reflections, 22608 independent reflections, 17646 reflections with $I > 2\sigma(I)$, $R_{\text{int}} = 0.064$. The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.066 [I > 2\sigma(I)]$, $wR_2 = 0.204$, 1108 parameters.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.78	511	545	93.8	4.52	61.26	24.30	0.0604	0.0334
2.78 - 1.89	1177	1180	99.7	3.68	63.00	21.88	0.0522	0.0386
1.89 - 1.50	1711	1711	100.0	3.55	34.26	18.27	0.0486	0.0414
1.50 - 1.31	1742	1745	99.8	3.50	24.44	16.61	0.0506	0.0442
1.31 - 1.19	1715	1722	99.6	3.33	17.51	14.36	0.0576	0.0492
1.19 - 1.11	1608	1613	99.7	3.23	14.44	13.08	0.0629	0.0543
1.11 - 1.04	1829	1838	99.5	3.10	11.81	11.71	0.0700	0.0607
1.04 - 0.99	1638	1643	99.7	3.06	10.87	11.08	0.0745	0.0643
0.99 - 0.95	1564	1565	99.9	2.94	9.24	10.02	0.0817	0.0720
0.95 - 0.91	1862	1863	99.9	2.86	7.96	8.76	0.0869	0.0806
0.91 - 0.88	1668	1672	99.8	2.78	6.79	8.06	0.0970	0.0901
0.88 - 0.85	1837	1840	99.8	2.66	5.41	6.92	0.1095	0.1082
0.85 - 0.83	1386	1392	99.6	2.60	5.06	6.50	0.1142	0.1161
0.83 - 0.80	2382	2395	99.5	2.53	4.18	5.71	0.1340	0.1355
0.80 - 0.78	1777	1791	99.2	2.42	3.91	5.48	0.1385	0.1484
0.78 - 0.77	966	973	99.3	2.34	3.42	4.85	0.1542	0.1705
0.77 - 0.75	2069	2096	98.7	2.24	3.15	4.42	0.1690	0.1911
0.75 - 0.73	2260	2293	98.6	2.15	2.87	3.99	0.1881	0.2163
0.73 - 0.72	1281	1302	98.4	2.09	2.83	3.88	0.1778	0.2214
0.72 - 0.71	1298	1318	98.5	2.08	2.47	3.46	0.2109	0.2541
0.71 - 0.70	1398	1424	98.2	1.99	2.13	2.99	0.2363	0.3032

0.80 - 0.70	11049	11197	98.7	2.19	2.99	4.18	0.1737	0.2045
Inf - 0.70	33679	33921	99.3	2.78	11.87	9.22	0.0685	0.0667

Several low-angle reflections were shadowed by the beamstop and removed from the data set before refinement. The crystal contains a large volume of disordered solvent (ca. 2018.45 Å³, 36%). Bond distances suggest that the solute is dichloromethane. The disordered solute was modeled by chlorine atoms of various occupancies. There are no additional solvent accessible voids (calculated with CCDC Mercury 3.7; probe radius 1.2 Å, grid spacing 0.7 Å). In order not to falsify the data, SQUEEZE was not used. The residual electron density close to the Rh atoms may be a result of anharmonic motion of the atoms as a result of loss of solvent from the crystal. Final refinement cycles were undertaken using data to a resolution of 0.8 Å. H atoms riding, $S = 1.402$, residual electron density 1.52 (0.76 Å from Rh3)/ -2.01 (0.79 Å from Rh1) e Å⁻³. CCDC-1443591.

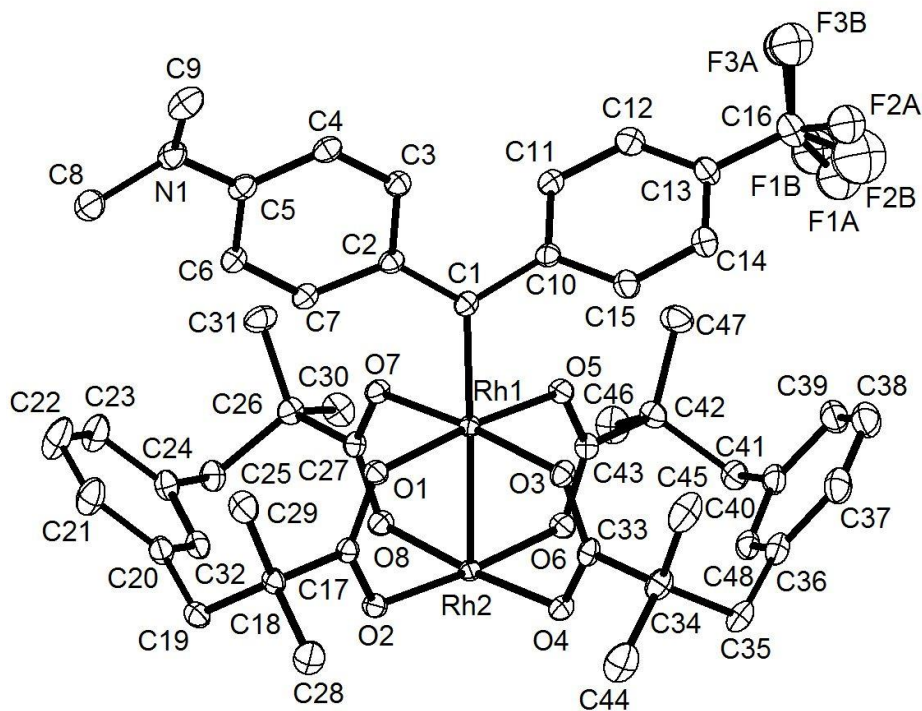


Figure S4. Molecular structure of **6c**. The fluorine atoms of the trifluoromethyl group are disordered over two positions (0.5:0.5).

X-ray Crystal Structure Analysis of 6c: $[C_{48}H_{54}F_3NO_8Rh_2]$, $M_r = 1035.74 \text{ g} \cdot \text{mol}^{-1}$, green plate, crystal size $0.040 \times 0.203 \times 0.423 \text{ mm}^3$, orthorhombic, space group $Pbca$, $a = 18.314(2) \text{ \AA}$, $b = 17.591(2) \text{ \AA}$, $c = 27.537(3) \text{ \AA}$, $V = 8871.1(3) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 8$, $D_{calc} = 1.551 \text{ g} \cdot \text{cm}^3$, $\lambda = 0.71073 \text{ \AA}$, $\mu(Mo-K_{\alpha}) = 0.812 \text{ mm}^{-1}$, Gaussian absorption correction ($T_{min} = 0.90458$, $T_{max} = 0.98374$), Bruker AXS Enraf-Nonius KappaCCD diffractometer, $2.673 < \theta < 33.146^\circ$, 247615 measured reflections, 16904 independent reflections, 14234 reflections with $I > 2\sigma(I)$, $R_{int} = 0.041$. The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.033 [I > 2\sigma(I)]$, $wR_2 = 0.108$, 558 parameters. Several low angle reflections were shadowed by the beamstop and removed from the data for refinement. The largest residual peak is close to F1A. In view of the position of this peak, it cannot be ruled out that the trifluoromethyl group is partially occupied by a dimethylaminyl group. Disordered atoms were refined with isotropic atomic displacement parameters. H atoms riding, $S = 1.273$, residual electron density 2.35 (0.69 \AA from F1A)/ -1.39 (0.40 \AA from F1A) $e \text{ \AA}^{-3}$. CCDC-1443592.

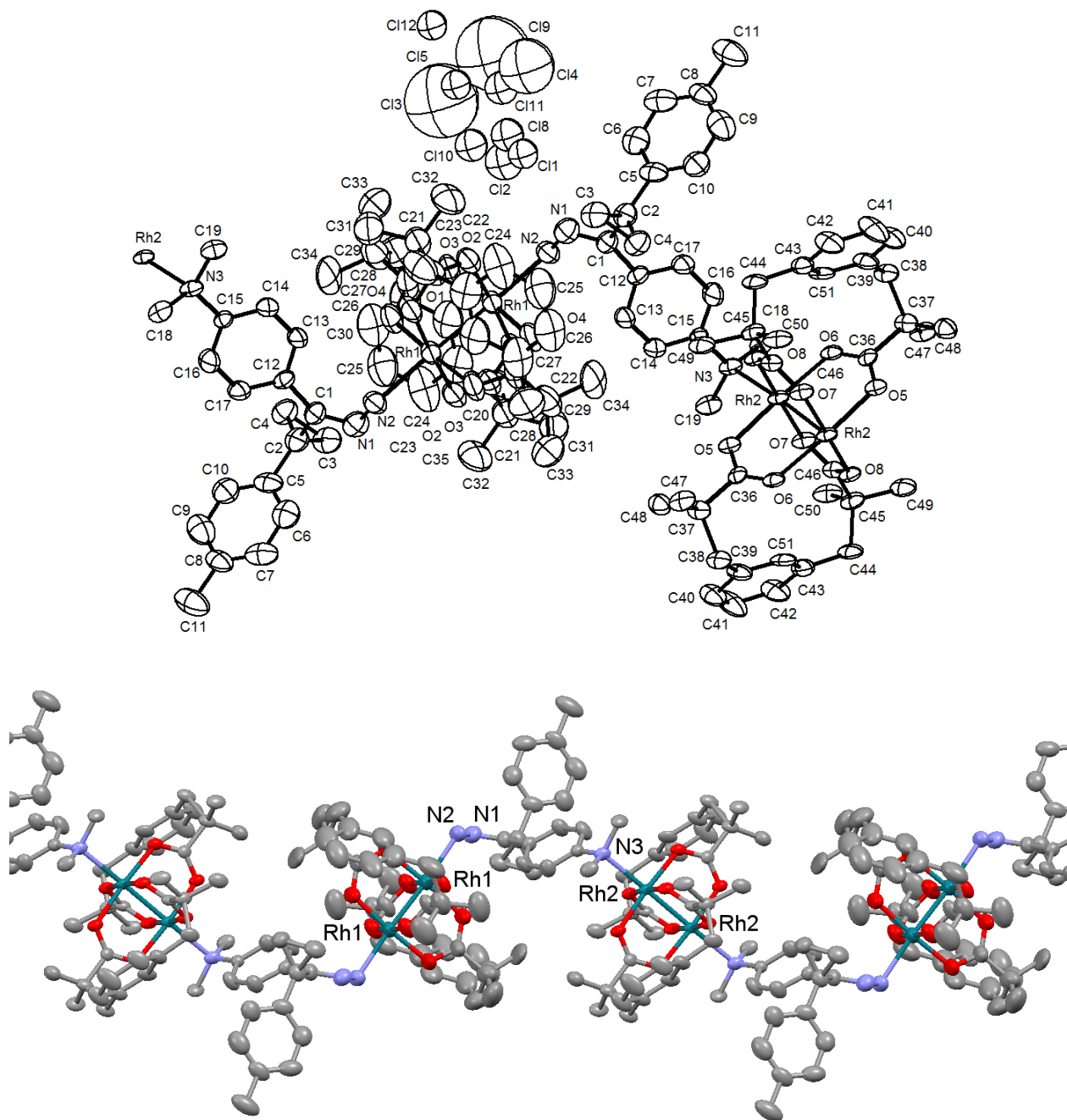


Figure S6. Molecular structure of **14**.

X-ray Crystal Structure Analysis of 14: $(C_{51}H_{61}N_3O_8Rh_2) \cdot 2(CH_2Cl_2)$, $M_r = 1191.64 \text{ g} \cdot \text{mol}^{-1}$, pink needle, crystal size $0.010 \times 0.025 \times 0.070 \text{ mm}^3$, triclinic, space group $P1$, $a = 9.6489(18) \text{ \AA}$, $b = 16.895(3) \text{ \AA}$, $c = 18.414(4) \text{ \AA}$, $\alpha = 71.271(4)$, $\beta = 89.960(4)$, $\gamma = 78.602(4)^\circ$, $V = 2780.5(9) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 2$, $D_{calc} = 1.423 \text{ g} \cdot \text{cm}^3$, $\lambda = 0.71073 \text{ \AA}$, $\mu(Mo-K\alpha) = 0.837 \text{ mm}^{-1}$, Gaussian absorption correction ($T_{min} = 0.98215$, $T_{max} = 0.99689$), Bruker AXS Enraf-Nonius KappaCCD diffractometer, $3.029 < \theta < 26.242^\circ$, 33017 measured

reflections, 11205 independent reflections, 6601 reflections with $I > 2\sigma(I)$, $R_{\text{int}} = 0.103$. The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.075$ [$I > 2\sigma(I)$], $wR_2 = 0.230$, 636 parameters. Several low angle reflections were shadowed by the beamstop and removed from the data for refinement. The crystal contains strongly disordered solute, such as is often observed in coordination polymers. Residual electron density and distances indicate that it may be dichloromethane. The solute was modeled by Cl atoms with various refined occupancies, which were rounded and fixed for the final refinement cycles. The residual void was 13.53 \AA^3 , with no significant residual electron density in this region. H atoms riding, $S = 1.170$, residual electron density 0.98 (0.59 \AA from Rh2)/ -1.67 (0.53 \AA from Rh1) $e \text{ \AA}^{-3}$. CCDC-1443594.

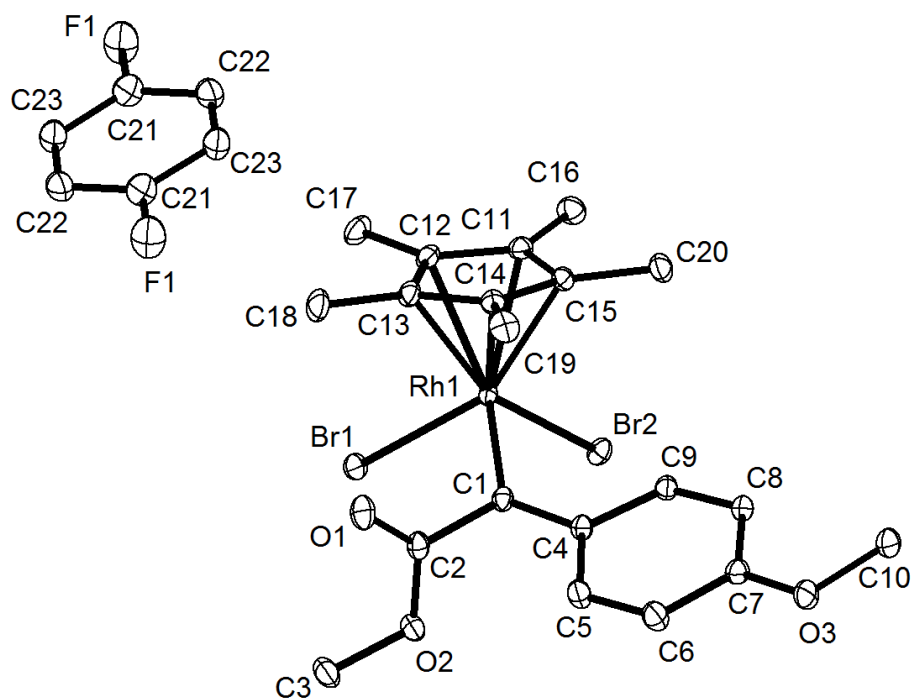


Figure S7. Molecular structure of **19b**. The F atom attached to C21 of the disordered solute fluorobenzene molecule is disordered over two positions (0.5:0.5).

X-ray Crystal Structure Analysis of 19b: $(\text{C}_{20}\text{H}_{25}\text{Br}_2\text{O}_3\text{Rh}) \cdot 0.5 (\text{C}_6\text{H}_5\text{F})$, $M_r = 624.18 \text{ g} \cdot \text{mol}^{-1}$, red-brown plate, crystal size $0.042 \times 0.092 \times 0.161 \text{ mm}^3$, triclinic, space group $P1$, $a = 8.5625(9) \text{ \AA}$, $b = 8.6439(9) \text{ \AA}$, $c = 15.8135(17) \text{ \AA}$, $\alpha = 83.2837(19)$, $\beta = 80.4591(17)$, $\gamma = 81.2873(17)^\circ$, $V = 1135.8(2) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 2$, $D_{\text{calc}} = 1.825 \text{ g} \cdot \text{cm}^3$, $\lambda = 0.71073 \text{ \AA}$, $\mu(\text{Mo-K}\alpha) = 4.296 \text{ mm}^{-1}$, Gaussian absorption correction ($T_{\text{min}} = 0.58925$, $T_{\text{max}} = 0.86452$), Bruker AXS Enraf-Nonius KappaCCD diffractometer, $3.177 < \theta < 37.441^\circ$, 44713

measured reflections, 11241 independent reflections, 9653 reflections with $I > 2\sigma(I)$, $R_{\text{int}} = 0.031$. The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.022$ [$I > 2\sigma(I)$], $wR_2 = 0.050$, 278 parameters. Several low angle reflections were shadowed by the beamstop and removed from the data for refinement. The structure contains disordered fluorobenzene. H atoms riding, $S = 1.017$, residual electron density 0.84 (0.65 Å from Rh1)/ -1.0 (0.64 Å from Rh1) e Å⁻³. CCDC-1443596.

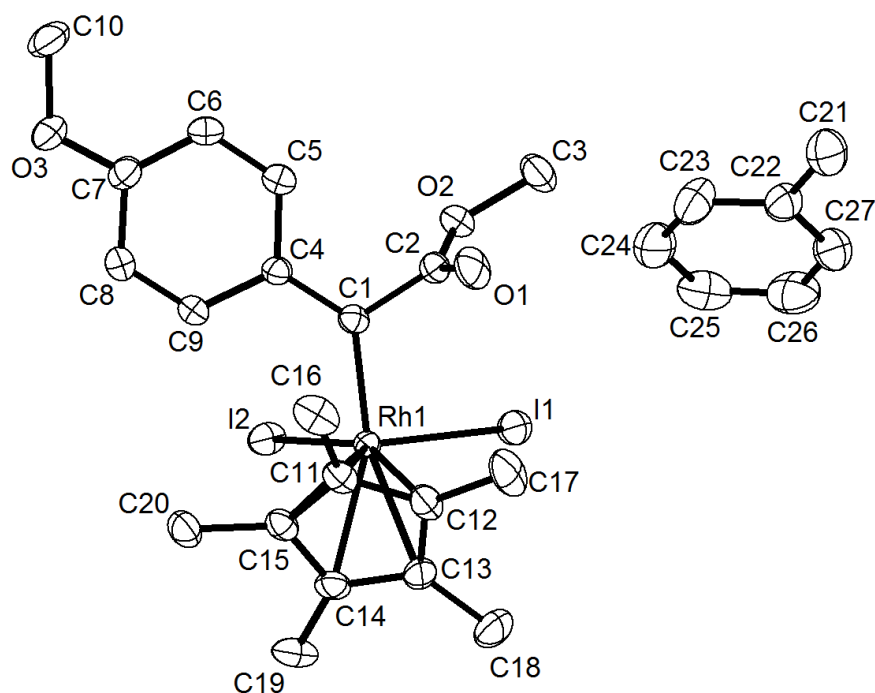


Figure S8. Molecular structure of **19c**. The crystal contains solute toluene.

X-ray Crystal Structure Analysis of 19c: (C₂₀H₂₅I₂O₃Rh) · (C₇H₈), $M_r = 762.24 \text{ g} \cdot \text{mol}^{-1}$, red-brown needle, crystal size 0.020 x 0.050 x 0.200 mm³, monoclinic, space group $P2_1/c$, $a = 7.5273(6) \text{ \AA}$, $b = 16.5760(15) \text{ \AA}$, $c = 22.501(3) \text{ \AA}$, $\beta = 99.185(7)^\circ$, $V = 2771.5(5) \text{ \AA}^3$, $T = 160(2) \text{ K}$, $Z = 4$, $D_{\text{calc}} = 1.827 \text{ g} \cdot \text{cm}^3$, $\lambda = 0.71073 \text{ \AA}$, $\mu(\text{Mo-K}\alpha) = 2.869 \text{ mm}^{-1}$, multi-scan absorption correction ($T_{\text{min}} = 0.5841$, $T_{\text{max}} = 0.6670$), Bruker AXS Enraf-Nonius KappaCCD diffractometer, $3.870 < \theta < 33.144^\circ$, 49011 measured reflections, 10484 independent reflections, 7717 reflections with $I > 2\sigma(I)$, $R_{\text{int}} = 0.044$. The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.037$ [$I > 2\sigma(I)$], $wR_2 = 0.073$, 304 parameters. Several low angle reflections were shadowed by the beamstop and removed from the data for refinement. H atoms riding, $S = 1.097$, residual electron density 0.79 (0.70 Å from I1)/ -1.70 (0.70 Å from I1) e Å⁻³. CCDC-1443597.

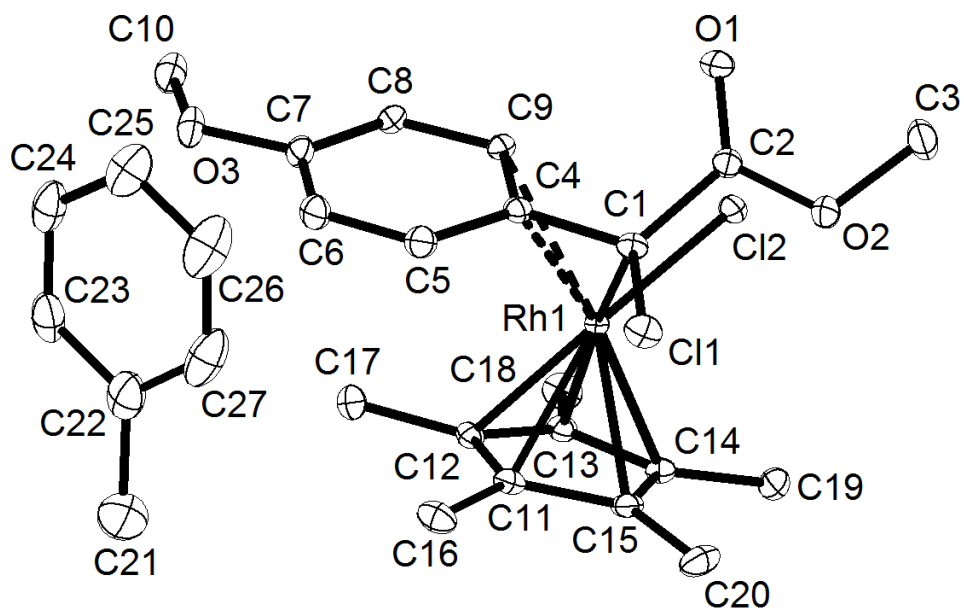


Figure S9. Molecular structure of **20**. The crystal contains solute toluene.

X-ray Crystal Structure Analysis of 20: $(C_{20}H_{25}Cl_2O_3Rh_2) \cdot (C_7H_8)$, $M_r = 579.34 \text{ g} \cdot \text{mol}^{-1}$, orange plate, crystal size $0.060 \times 0.240 \times 0.421 \text{ mm}^3$, monoclinic, space group $P2_1/c$, $a = 8.0295(15) \text{ \AA}$, $b = 24.801(5) \text{ \AA}$, $c = 13.004(9) \text{ \AA}$, $\beta = 98.970(4)^\circ$, $V = 2558.0(8) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 4$, $D_{calc} = 1.504 \text{ g} \cdot \text{cm}^{-3}$, $\lambda = 0.71073 \text{ \AA}$, $\mu(Mo-K\alpha) = 0.903 \text{ mm}^{-1}$, Gaussian absorption correction ($T_{min} = 0.78475$, $T_{max} = 0.95650$), Bruker AXS Enraf-Nonius KappaCCD diffractometer, $2.696 < \theta < 33.077^\circ$, 84543 measured reflections, 9670 independent reflections, 8735 reflections with $I > 2\sigma(I)$, $R_{int} = 0.035$. The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.024 [I > 2\sigma(I)]$, $wR_2 = 0.057$, 308 parameters. Several low angle reflections were shadowed by the beamstop and removed from the data for refinement. H9 attached to C9 was located on a difference Fourier synthesis and its position and isotropic atomic displacement parameter were refined. Otherwise, H atoms riding, $S = 1.072$, residual electron density $1.02 (0.68 \text{ \AA} \text{ from Rh1}) / -0.87 (1.65 \text{ \AA} \text{ from H3A}) \text{ e} \cdot \text{\AA}^{-3}$. CCDC-1443599.

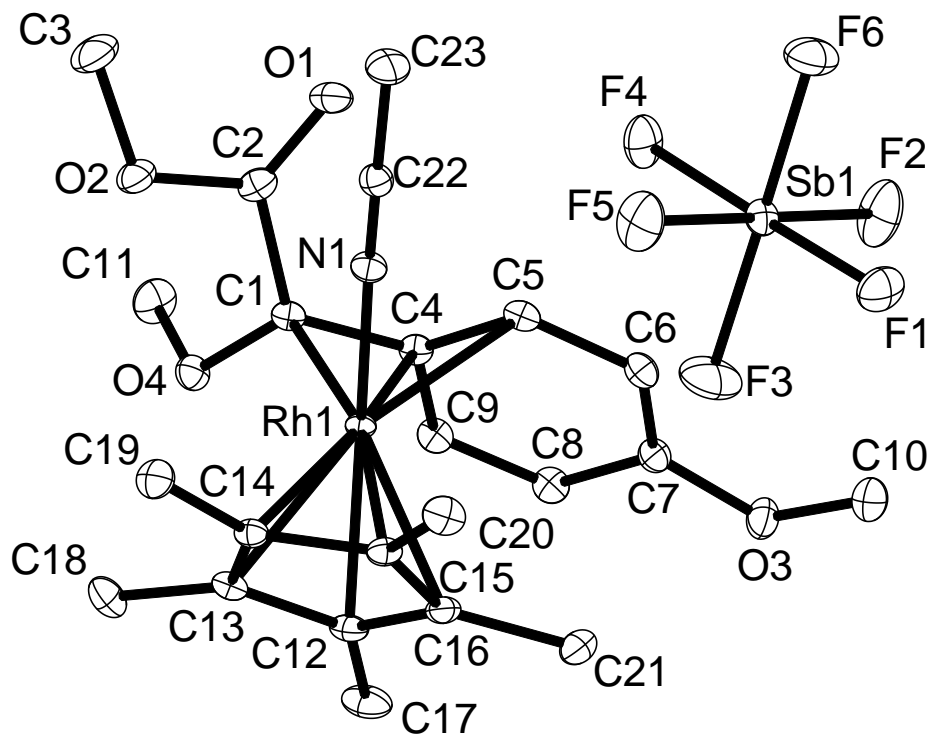


Figure S10. The ionic structure of **22**.

X-ray Crystal Structure Analysis of 22: $[\text{C}_{23}\text{H}_{31}\text{NO}_4\text{Rh}]^+ [\text{SbF}_6]^-$, $M_r = 724.15 \text{ g} \cdot \text{mol}^{-1}$, red prism, crystal size $0.089 \times 0.102 \times 0.205 \text{ mm}^3$, monoclinic, space group $P2_1/n$, $a = 11.149(2) \text{ \AA}$, $b = 14.664(3) \text{ \AA}$, $c = 16.182(3) \text{ \AA}$, $\beta = 92.199(3)^\circ$, $V = 2643.7(3) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 4$, $D_{\text{calc}} = 1.819 \text{ g} \cdot \text{cm}^3$, $\lambda = 0.71073 \text{ \AA}$, $\mu(\text{Mo-K}\alpha) = 1.718 \text{ mm}^{-1}$, Gaussian absorption correction ($T_{\text{min}} = 0.75812$, $T_{\text{max}} = 0.88264$), Bruker AXS Enraf-Nonius KappaCCD diffractometer, $2.778 < \theta < 31.433^\circ$, 78014 measured reflections, 8727 independent reflections, 7961 reflections with $I > 2\sigma(I)$, $R_{\text{int}} = 0.029$. The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.017 [I > 2\sigma(I)]$, $wR_2 = 0.040$, 338 parameters. Several low angle reflections were shadowed by the beamstop and removed from the data for refinement. H5 attached to C5 was located on a difference Fourier synthesis and its position and isotropic atomic displacement parameter were refined. Otherwise, H atoms riding, $S = 1.137$, residual electron density $0.56 (0.72 \text{ \AA} \text{ from C14}) / -0.49 (0.59 \text{ \AA} \text{ from Rh1}) \text{ e \AA}^{-3}$. CCDC-1443599.

General. All reactions were carried out under Argon in flame-dried glassware, ensuring rigorously inert conditions. The solvents were purified by distillation over the indicated drying agents and were stored and handled under Argon: CH₂Cl₂ (CaH₂), fluorobenzene (CaH₂), hexane (Na/K), methanol (Mg), pentane (Na/K), toluene (Na/K). NMR: Spectra were recorded on Bruker AV300, AV400, AV500 or AV600 spectrometers at the indicated temperatures with the chemical shifts (δ) given in ppm relative to TMS and the coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale (CD₂Cl₂: δ_{H} = 5.32 ppm, δ_{C} = 54.0 ppm; C₆D₆: δ_{H} = 7.16 ppm, δ_{C} = 128.06 ppm; MeOD: δ_{H} = 3.31 ppm, δ_{C} = 49.0 ppm). UV/VIS: UV-1650PC spectrophotometer (Shimadzu). HRMS (ESI): ESQ3000 (Bruker).

The different rhodium precursors were either purchased from Sigma Aldrich and were used as received, or were synthesized according to the literature.¹ The different diazoalkane derivatives were prepared from the corresponding ketones or imines, which were converted into the corresponding hydrazones that were then oxidized to the desired diazoalkane compounds according to literature procedures.²

General Procedures for the Preparation of the Rhodium Carbenoids

Method A: A solution of the corresponding diazoalkane compound in fluorobenzene (0.5 mL) was added dropwise to a solution of the rhodium precursor in fluorobenzene/CH₂Cl₂ (0.6/1.4 mL) at 0°C under rigorously inert conditions. A vigorous effervescence and concomitant color change were observed. Crystals of the resulting carbenoid suitable for X-ray diffraction were obtained by layering the solution with cold toluene (1 mL) and hexane (5 mL) at -20 °C.

Method B: A solution of the corresponding diazoalkane compound in fluorobenzene (0.5 mL) was quickly added under rigorously inert conditions to a solution of the rhodium precursor in CH₂Cl₂ (2 mL) at 0°C. A vigorous effervescence and concomitant color change to dark turquoise were observed. Crystals of the resulting carbenoid suitable for X-ray diffraction were obtained by layering the solution with cold toluene (1 mL) and hexane (5 mL) at -20 °C.

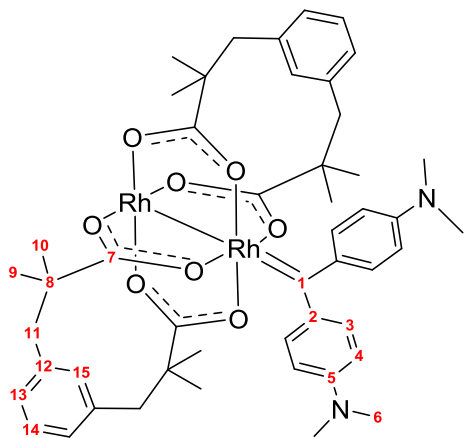
Method C: A solution of the corresponding diazoalkane compound in MeOH (0.5 mL) was added to a solution of rhodium precursor in MeOH (2 mL) at 0°C under rigorously inert conditions. A vigorous effervescence and concomitant color change to dark red were observed. Crystals of the resulting product suitable for X-ray diffraction were obtained by layering the solution with cold toluene (1 mL) and hexane (5 mL) at -20 °C.

Method D (for NMR characterization): A solution of the corresponding diazoalkane compound in CD₂Cl₂ [or C₆D₆ or MeOD] (1 mL) was added dropwise to a cold (8°C) solution of the rhodium precursor in CD₂Cl₂ [or C₆D₆ or MeOD] (1 mL) under rigorously inert conditions. A vigorous effervescence and concomitant color change were observed. The solution was stirred at 5°C for 5 min before being transferred into an NMR tube under inert conditions.

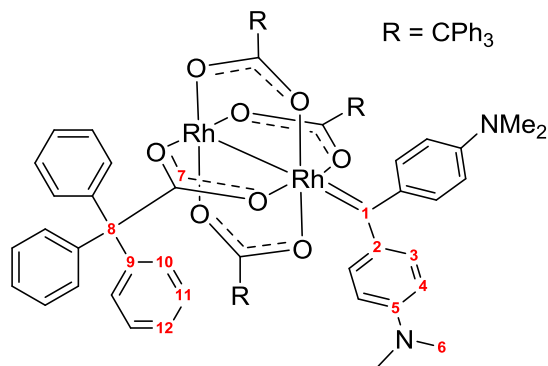
Method E (for NMR characterization): A solution of the corresponding diazoalkane compound in CD₂Cl₂ (1 mL) was quickly added to a cold (0°C) solution of the rhodium precursor in CD₂Cl₂ (1 mL) under rigorously inert conditions. A vigorous effervescence and concomitant color change were observed. The solution was stirred at 0°C for 5 min before being transferred into an NMR tube under inert conditions.

Method F (for NMR characterization): A solution of the corresponding diazoalkane compound in C₆D₆ (0.5 mL) was added dropwise to a cold (8°C) solution of the rhodium precursor in C₆D₆/CD₂Cl₂ (0.6/1.4 mL) under rigorously inert conditions. A vigorous effervescence and concomitant color change were observed. The solution was stirred at 5°C for 5 min before being transferred into an NMR tube under inert conditions.

The complete data set of complex **4a** is contained in the Supporting Information of our previous Communication.³



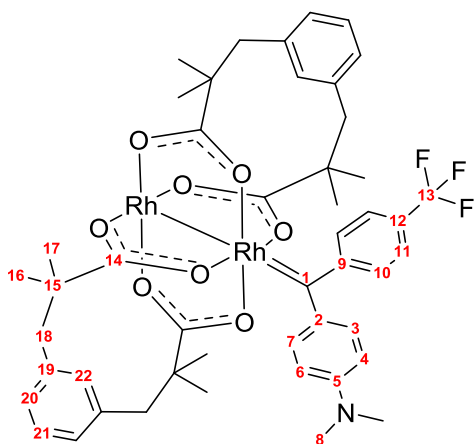
Complex 6b. Prepared according to method **A** from Rh₂(esp)₂ (20 mg, 0.03 mmol) and diazoalkane **3b** (7.39 mg, 0.03 mmol) as a dark green crystalline material suitable for X-ray diffraction. (characterized by NMR according to method **D** in C₆D₆). **¹H NMR** (500 MHz, C₆D₆, 283 K): δ 7.99 (d, *J* = 9.1 Hz, 4H, H₃), 7.41 (s, 2H, H₁₅), 7.16 (s, 2H, H₁₄), 6.90 (dd, *J* = 7.6, 1.6 Hz, 4H, H₁₃), 6.39 (d, *J* = 9.1 Hz, 4H, H₄), 3.04 (d, *J* = -12.3 Hz, 4H, H_{11a}), 2.36 (s, 12H, H₆), 2.28 (d, *J* = -12.3 Hz, 4H, H_{11b}), 1.12 (s, 12H, H₉), 0.96 (s, 12H, H₁₀); **¹³C{¹H} NMR** (126 MHz, C₆D₆, 283 K): δ 253.5 (br. s, C₁),⁴ 194.0 (C₇), 153.6 (C₅), 142.8 (C₂), 139.1 (C₁₂), 137.6 (C₃), 132.8 (C₁₅), 128.2 (C₁₃), 126.3 (C₁₄), 110.9 (C₄), 47.6 (C₁₁), 46.3 (C₈), 39.6 (C₆), 27.8 (C₉), 24.4 (C₁₀); **¹⁵N NMR** (51 MHz, C₆D₆, 283 K):⁵ δ = -317.1; **HRMS** (ESI+): calcd. for [C₄₉H₆₀N₂O₈Rh₂Na]⁺: 1033.23379; found 1033.23640; **UV/VIS**: λ_{max} [nm] = 587.



Complex 4b. Prepared according to method **A** from $[\text{Rh}(\text{tpa})_4] \cdot \text{CH}_2\text{Cl}_2$ (20 mg, 0.01 mmol) and diazoalkane **3b** (3.89 mg, 0.01 mmol) as a brown crystalline material suitable for X-ray diffraction (characterized by NMR according to method **D** in C_6D_6). $^1\text{H NMR}$ (500 MHz, C_6D_6 , 283 K): δ 7.90 (d, $J = 9.0$ Hz, 4H, H_3), 7.24 (t, $J = 7.2$ Hz, 12H, H_{12}), 7.15 (s, 24H, H_{10}), 7.09 (t, $J = 7.7$ Hz, 24H, H_{11}), 6.39 (d, $J = 9.0$ Hz, 4H, H_4), 2.65 (s, 12H, H_6); $^{13}\text{C}\{^1\text{H}\}$

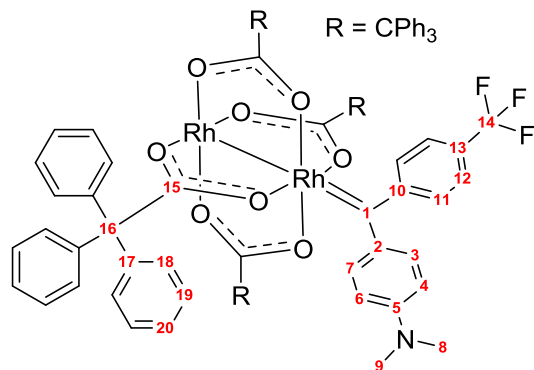
NMR (126 MHz, C_6D_6 , 283 K): δ 257.7 (br. s, C_1),⁴ 190.8 (C_7), 153.9 (C_5), 144.8 (C_9), 144.7 (C_2), 137.0 (C_3), 131.5 (C_{10}), 127.5 (C_{11}), 126.4 (C_{12}), 111.1 (C_4), 69.5 (C_8), 39.7 (C_6); $^{15}\text{N NMR}$ (51 MHz, C_6D_6 , 283 K):⁵ $\delta = -316.9$; **HRMS** (ESI+): calcd. for $[\text{C}_{97}\text{H}_{80}\text{N}_2\text{O}_8\text{Rh}_2]^+$: 1606.40193; found 1606.40112; **UV/VIS**: λ_{max} [nm] = 586.

Complex 6c. Prepared according to method **A** from $\text{Rh}_2(\text{esp})_2$ (20 mg, 0.03 mmol) and diazoalkane **3c**



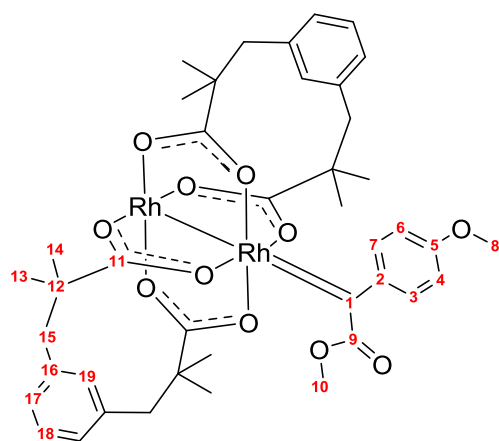
(8.05 mg, 0.03 mmol) as a dark green crystalline material suitable for X-ray diffraction (characterized by NMR according to method **D** in CD_2Cl_2). $^1\text{H NMR}$ (500 MHz, CD_2Cl_2 , 263 K): δ 8.27 (br. s, 1H, H_7), 8.00 (br. s, 1H, H_3), 7.66 – 7.63 (m, 2H, H_{11}), 7.62 – 7.59 (m, 2H, H_{10}), 7.01 (t, $J = 7.5$ Hz, 2H, H_{21}), 6.76 (dd, $J = 7.6, 1.7$ Hz, 4H, H_{20}), 6.72 (br. s, 2H, H_6, H_4), 6.46 – 6.34 (m, 2H, H_{22}), 3.28 (s, 6H, H_8), 2.51 (d, $J = 12.3$ Hz, 4H, H_{18a}), 2.27 (d, $J = 12.3$ Hz, 4H, H_{18b}), 0.85 (s, 12H, H_{17}), 0.80 (s, 12H, H_{16}); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 263 K): δ 250.2 (d, $J_{\text{C-Rh}} = 27.1$ Hz, C_1),⁶ 194.6 (C_{14}), 158.9 (C_5), 156.4 (C_9), 148.0 (br. s, C_7), 141.4

(C_2), 138.3 (C_{19}), 137.3 (br. s, C_3), 131.5 (C_{22}), 128.0 (C_{20}), 127.0 (q, $J_{\text{C-F}} = 32.1$ Hz, C_{12}), 126.8 (C_{21}), 125.4 (q, $J_{\text{C-F}} = 272.0$ Hz, C_{13}), 123.9 (C_{11}), 123.9 (C_{10}), 113.3 (br. s, C_6), 112.0 (br. s, C_4), 47.2 (C_{18}), 46.3 (C_{15}), 41.6 (C_8), 27.0 (C_{17}), 24.2 (C_{16}); $^{19}\text{F}\{^1\text{H}\}$ NMR (470 MHz, CD_2Cl_2 , 263 K): $\delta = -62.4$; $^{15}\text{N NMR}$ (51 MHz, CD_2Cl_2 , 263 K):⁵ $\delta = -283.2$; **HRMS** (ESI+): calcd. for $[\text{C}_{48}\text{H}_{54}\text{F}_3\text{N}_1\text{O}_8\text{Rh}_2]^+$: 1035.19061; found 1035.19173; **UV/VIS**: λ_{max} [nm] = 637.



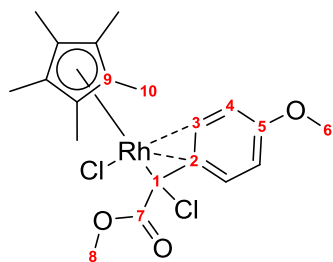
Complex 4c. Prepared according to method **A** from $[\text{Rh}(\text{tpa})_4] \bullet \text{CH}_2\text{Cl}_2$ (20 mg, 0.01 mmol) and diazoalkane **3c** (4.24 mg, 0.01 mmol) as a brown/red crystalline material suitable for X-ray diffraction (characterized by NMR according to method **D** in CD_2Cl_2). $^1\text{H NMR}$ (500 MHz, CD_2Cl_2 , 273 K): δ 7.75 (dd, $J = 9.6, 1.9$ Hz, 1H, H_7), 7.40 (dd, $J = 9.5, 1.9$ Hz, 1H, H_3), 7.04 (t, $J = 7.4$ Hz, 12H, H_{20}), 6.85 (t, $J = 7.9$ Hz, 24H, H_{19}), 6.62 (d, $J = 8.2$ Hz, 2H, H_{12}),

6.53 (d, $J = 7.5$ Hz, 24H, H_{18}), 6.47 (dd, $J = 9.6, 2.6$ Hz, 1H, H_4), 6.39 (d, $J = 8.0$ Hz, 2H, H_{11}), 5.55 (dd, $J = 9.7, 2.6$ Hz, 1H, H_6), 3.19 (s, 3H, H_8), 3.09 (s, 3H, H_9); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2 , 273 K): δ 250.4 (br. s, C_1),⁴ 190.9 (C_{15}), 159.1 (C_5), 155.7 (C_{10}), 147.2 (C_7), 144.0 (C_{17}), 141.6 (C_2), 137.0 (C_3), 131.0 (C_{18}), 127.4 (C_{19}), 126.7 (C_{20}), 125.8 (q, $J_{\text{C-F}} = 31.9$ Hz, C_{13}), 125.2 (q, $J_{\text{C-F}} = 270.3$ Hz, C_{14}), 123.4 (q, $J_{\text{C-F}} = 3.8$ Hz, C_{12}), 123.1 (C_{11}), 113.6 (C_6), 111.6 (C_4), 69.5 (C_{16}), 41.5 (C_8), 41.3 (C_9); $^{19}\text{F}\{^1\text{H}\}$ NMR (470 MHz, CD_2Cl_2 , 273 K): $\delta = -62.5$; $^{15}\text{N NMR}$ (51 MHz, CD_2Cl_2 , 273 K):⁵ $\delta = -281.5$; **HRMS** (ESI+): calcd. for $[\text{C}_{96}\text{H}_{74}\text{N}_1\text{O}_8\text{F}_3\text{Rh}_2]^+$: 1631.34711; found 1631.34580; **UV/VIS**: λ_{max} [nm] = 602.

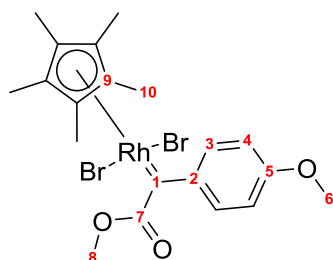


Complex 10. Prepared according to method **B** from $\text{Rh}_2(\text{esp})_2$ (20 mg, 0.03 mmol) and diazoalkane **9** (5.44 mg, 0.03 mmol) as a red/orange crystalline material suitable for X-ray diffraction (characterized by NMR according to method **E**). $^1\text{H NMR}$ (500 MHz, CD_2Cl_2 , 223 K): δ 8.49 (d, $J = 8.9$ Hz, 1H, H_3), 8.13 (d, $J = 5.8$ Hz, 1H, H_7), 7.09 (t, $J = 7.3$ Hz, 2H, H_{18}), 7.03 (d, $J = 7.8$ Hz, 1H, H_4), 6.83 (d, $J = 6.0$ Hz, 4H, H_{17}), 6.76 (d, $J = 9.0$ Hz, 1H, H_6), 6.65 (s, 2H, H_{19}), 4.02 (s, 3H, H_8), 3.89 (s, 3H, H_{10}), 2.55 (d, $J = 12.5$ Hz, 4H, H_{15a}), 2.46 (d, $J = 12.2$ Hz,

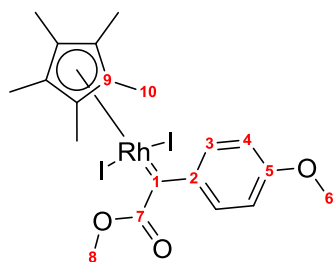
4H, H_{15b}), 0.87 (s, 12H, H_{13}), 0.85 (s, 12H, H_{14}); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2 , 223 K): δ 237.2 (br. s, C_1),⁶ 195.7 (C_{11}), 175.0 (br. s, C_9), 172.2 (C_5), 149.7 (C_7), 144.0 (C_2), 139.8 (C_3), 137.9 (C_{16}), 130.9 (C_{19}), 127.9 (C_{17}), 126.6 (C_{18}), 117.5 (C_6), 116.0 (C_4), 57.5 (C_{10}), 51.8 (C_8), 46.7 (C_{15}), 46.4 (C_{12}), 25.3 (br. s, C_{13}), 25.2 (br. s, C_{14}); **HRMS** (ESI+): calcd. for $[\text{C}_{42}\text{H}_{50}\text{O}_{11}\text{Rh}_2]^+$: 936.14577; found 936.14535. **UV/VIS**: λ_{max} [nm] = 756.



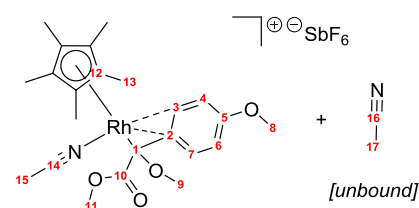
Complex 20. Prepared according to method **A** from $[\text{Cp}^*\text{RhCl}_2]_2$ (20 mg, 0.03 mmol) and diazoalkane **9** (13.34 mg, 0.06 mmol) as a brown/orange crystalline material suitable for X-ray diffraction (characterized by NMR according to method **D** in C_6D_6); $^1\text{H NMR}$ (500 MHz, C_6D_6 , 283 K): δ 7.24 (br. d, $J = 8.8$ Hz, 2H, H_3), 6.42 (br. d, $J = 8.3$ Hz, 2H, H_4), 3.70 (s, 3H, H_8), 3.12 (s, 3H, H_6), 0.99 (s, 15H, H_{10}); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 283 K): δ 169.7 (C_7), 160.9 (C_5), 116.6 (v. br. s, C_3),⁷ 115.6 (br. s, C_4), 96.7 (d, $J_{\text{C-Rh}} = 7.2$ Hz, C_9), 96.2 (br. s, C_2), 70.6 (br. s, C_1),⁸ 55.0 (C_6), 51.9 (C_8), 7.8 (C_{10}); **HRMS** (ESI⁺): calcd. for $[\text{C}_{20}\text{H}_{25}\text{O}_3\text{Cl}_1\text{Rh}_1]^+$: 451.05418; found 451.05393. **UV/VIS**: λ_{max} [nm] = 418.



Complex 19b. Prepared according to method **A** from $[\text{Cp}^*\text{RhBr}_2]_2$ (20 mg, 0.03 mmol) and diazoalkane **9** (10.36 mg, 0.05 mmol) as a brown/red crystalline material suitable for X-ray diffraction (characterized by NMR according to method **D** in C_6D_6). $^1\text{H NMR}$ (600 MHz, C_6D_6 , 281 K): δ 8.32 (br. s, 2H, H_3), 6.43 (d, $J = 8.9$ Hz, 2H, H_4), 3.84 (s, 3H, H_8), 3.19 (s, 3H, H_6), 1.41 (s, 15H, H_{10}); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6 , 281 K): δ 313.9 (br. s, C_1),⁴ 177.1 (C_7), 171.0 (C_5), 144.3 (br. s, C_2), 142.6 (br. s, C_3), 115.6 (C_4), 101.8 (d, $J_{\text{C-Rh}} = 5.3$ Hz, C_9), 56.8 (C_6), 51.2 (C_8), 9.5 (C_{10}); **UV/VIS**: λ_{max} [nm] = 428.



Complex 19c. Prepared according to method **A** from $[\text{Cp}^*\text{RhI}_2]_2$ (20 mg, 0.02 mmol) and diazoalkane **9** (8.38 mg, 0.04 mmol) as a brown/red crystalline material suitable for X-ray diffraction (characterized by NMR according to method **D** in C_6D_6). $^1\text{H NMR}$ (600 MHz, C_6D_6 , 281 K): δ 8.40 (br. s, 2H, H_3), 6.24 (d, $J = 8.6$ Hz, 2H, H_4), 3.81 (s, 3H, H_8), 2.97 (s, 3H, H_6), 1.66 (s, 15H, H_{10}); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6 , 281 K): δ 316.4 (d, $J_{\text{C-Rh}} = 35.0$ Hz, C_1), 179.1 (C_7), 170.6 (C_5), 147.4 (C_2), 140.9 (br. s, C_3), 115.1 (C_4), 102.7 (d, $J_{\text{C-Rh}} = 4.7$ Hz, C_9), 56.2 (C_6), 51.1 (C_8), 10.7 (C_{10}); **UV/VIS**: λ_{max} [nm] = 482.



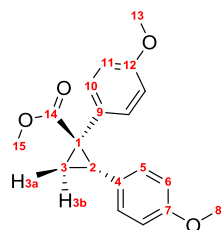
Complex 22. Prepared according to method **C** from $[\text{Cp}^*\text{Rh}(\text{MeCN})_2][\text{SbF}_6]_2$ (20 mg, 0.02 mmol) and diazoalkane **9** (4.95 mg, 0.02 mmol) as a red crystalline material suitable for X-ray diffraction (Characterized by NMR according to method **D** in MeOD). $^1\text{H NMR}$ (500 MHz, CD_3OD , 233K):⁹ δ 7.41 (br. s, 2H, H_6 , H_7), 6.80 (d, $J = 8.0$ Hz, 1H, H_4), 5.95 (d, $J = 7.9$ Hz, 1H, H_3), 3.91 (s, 3H, H_8), 3.70 (s, 3H, H_{11}), 2.59 (s, 3H, H_{15}),

2.06 (s, 6H, H₁₇), 1.36 (s, 15H, H₁₃); ¹³C{¹H} NMR (126 MHz, CD₃OD, 233K): δ 171.5 (C₁₀), 163.7 (C₅), 131.8 (C₇), 126.3 (d, J_{C-Rh} = 7.6 Hz, C₁₄), 126.2 (C₆), 118.3 (C₁₆), 107.7 (C₄), 100.4 (C₃), 100.1 (d, J_{C-Rh} = 7.0 Hz, C₁₂), 97.0 (d, J_{C-Rh} = 14.5 Hz, C₁), 94.0 (d, J_{C-Rh} = 3.5 Hz, C₂), 56.4 (C₈), 52.3 (C₁₁), 48.8 (C₉),¹⁰ 8.0 (C₁₃), 3.0 (C₁₅), 0.9 (C₁₇); **HRMS** (ESI+): calcd. for [C₂₁H₂₈O₄Rh₁]⁺: 447.10371; found 447.10404; **UV/VIS**: λ_{max} [nm] = 395.

Cyclopropanation reactions

General Procedure: A solution of the corresponding diazoalkane compound in pentane (5.0 mL) was added dropwise over 3 h to a solution of Rh₂(esp)₂ and 4-methoxystyrene in pentane (3 mL) at room temperature. The resulting mixture was stirred for 1 h before the solvent was removed under reduced pressure.

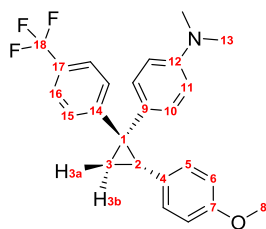
Methyl (1*R,2*R**)-1,2-bis(4-methoxyphenyl)cyclopropane-1-carboxylate (17).** Prepared from methyl 2-



diazo-2-(4-methoxyphenyl)acetate (100 mg, 0.49 mmol), Rh₂(esp)₂ (3.68 mg, 1 mol%) and 4-methoxystyrene (0.64 mL, 4.85 mmol) as a white solid after purification by flash chromatography on silica gel (10% EtOAc in hexane) (114 mg, 75%).

¹H NMR (400 MHz, C₆D₆, 300 K): δ 6.99 (d, J = 8.8 Hz, 2H, H₁₀), 6.62 (d, J = 8.9 Hz, 2H, H₅), 6.61 (d, J = 8.8 Hz, 2H, H₁₁), 6.53 (d, J = 8.8 Hz, 2H, H₆), 3.32 (s, 3H, H₁₅), 3.26 (dd, J = 9.3, 7.2 Hz, 1H, H_{2a}), 3.16 (s, 3H, H₁₃), 3.15 (s, 3H, H₈), 2.18 (dd, J = 9.4, 4.7 Hz, 1H, H_{3a}), 1.62 (dd, J = 7.2, 4.7 Hz, 1H, H_{3b}); ¹³C{¹H} NMR (101 MHz, C₆D₆, 300 K): δ 174.4 (C₁₄), 159.0 (C₁₂), 158.7 (C₇), 133.5 (C₁₀), 129.5 (C₅), 128.9 (C₄), 127.6 (C₉), 113.6 (C₆), 113.6 (C₁₁), 54.5 (C₈, C₁₃), 52.1 (C₁₅), 36.8 (C₁), 33.1 (C₂), 21.1 (C₃); **HRMS** (ESI+): calcd. for [C₁₉H₂₀O₄Na]⁺: 335.12538; found 335.12535.

4-((1*S,2*R**)-2-(4-methoxyphenyl)-1-(4-(trifluoromethyl)phenyl)cyclopropyl)-*N,N*-dimethylaniline (5c).**



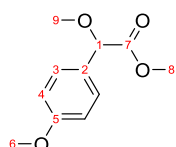
Prepared from 4-(diazo(4-(trifluoromethyl)phenyl)methyl)-*N,N*-dimethylaniline (20 mg, 0.07 mmol), Rh₂(esp)₂ (0.50 mg, 1 mol%) and 4-methoxystyrene (87 μL, 0.66 mmol) as a white solid after purification by flash chromatography on neutral alumina (5% EtOAc in hexane) (16 mg, 59 %).

¹H NMR (400 MHz, C₆D₆, 300 K): δ 7.33 (d, J = 8.2 Hz, 2H, H₁₆), 7.07 (d, J = 8.1 Hz, 2H, H₁₅), 6.99 (d, J = 8.8 Hz, 2H, H₁₀), 6.80 (d, J = 8.7 Hz, 2H, H₅), 6.65 (d, J = 8.7 Hz, 2H, H₆), 6.43 (d, J = 8.8 Hz, 2H, H₁₁), 3.20 (s, 3H, H₈), 2.62 (dd, J = 9.1, 6.8 Hz, 1H, H_{2a}), 2.40 (s, 6H, H₁₃), 1.84 (dd, J = 6.7, 5.4 Hz, 1H, H_{3b}), 1.55 (dd, J = 9.1, 5.3 Hz, 1H, H_{3a}); ¹³C{¹H} NMR (101 MHz, C₆D₆, 300 K): δ 158.5 (C₇), 152.6 (C₁₄), 149.5 (C₁₂), 132.5 (C₁₀), 130.8 (C₄), 129.3 (C₅), 129.0 (q, J_{C-F} = 34.7 Hz, C₁₇), 127.4 (C₁₅), 127.0 (C₉), 126.7 (q, J_{C-F} = 272.1 Hz, C₁₈),

125.4 (q, $J_{C-F} = 3.8$ Hz, C₁₆), 113.7 (C₆), 112.5 (C₁₁), 54.6 (C₈), 40.0 (C₁₃), 38.0 (C₁), 33.7 (C₂), 22.4 (C₃); ¹⁹F{¹H} NMR (282 MHz, C₆D₆, 303 K): $\delta = -61.9$; HRMS (ESI+): calcd. for [C₂₅H₂₅N₁O₁F₃]⁺: 412.18827; found 412.18828.

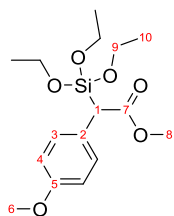
Cp*Rh(III)-Catalysis

Methyl 2-methoxy-2-(4-methoxyphenyl)acetate (15). A solution of 2-diazo-2-(4-methoxyphenyl)acetate

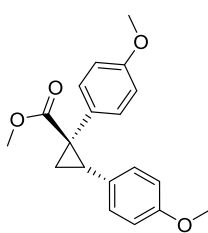


(20 mg, 0.097 mmol) in CH₂Cl₂ (2.0 mL) was added over 3 h to a solution of [Cp*RhI₂]₂ (1.0 mg, 1 mol%) and methanol (79 μ L, 1.94 mmol) in CH₂Cl₂ (1 mL) at room temperature. The resulting mixture was stirred for 2 h before the solvent was removed under reduced pressure. The residue was extracted with pentane and the combined extracts were filtered through a pad of Celite. Evaporation of the filtrate afforded the title compound in pure form (18 mg, 88%). ¹H NMR (300 MHz, C₆D₆, 303 K) δ 7.45 (d, $J = 8.7$ Hz, 2H, H₃), 6.74 (d, $J = 8.8$ Hz, 2H, H₄), 4.65 (s, 1H, H₁), 3.26 (s, 3H, H₉), 3.23 (s, 3H, H₆), 3.19 (s, 3H, H₈). ¹³C NMR (75 MHz, C₆D₆, 303 K) δ 171.2 (C₇), 160.5 (C₅), 129.5 (C₂), 129.0 (C₃), 114.3 (C₄), 82.7 (C₁), 57.0 (C₉), 54.8 (C₆), 51.4 (C₈). HRMS (ESI+): calcd. for [C₁₁H₁₄O₄Na]⁺: 233.07843; found 233.07850.

Methyl 2-(4-methoxyphenyl)-2-(triethoxysilyl)acetate (16). A solution of 2-diazo-2-(4-methoxy-



phenyl)acetate (20 mg, 0.097 mmol) in CH₂Cl₂ (2.0 mL) was added over 1 h to a solution of [Cp*RhI₂]₂ (1.0 mg, 1 mol%) and triethoxysilane (0.13 mL, 0.97 mmol) in CH₂Cl₂ (1 mL) at room temperature. The mixture was stirred for 1 h before the solvent was removed under reduced pressure. The residue was extracted with pentane and the combined extracts were filtered through a pad of Celite. Evaporation of the filtrate under reduced pressure gave the title compound in pure form (27 mg, 81%). ¹H NMR (300 MHz, C₆D₆, 303 K) δ 7.30 (d, $J = 8.8$ Hz, 2H, H₃), 6.83 (d, $J = 8.9$ Hz, 2H, H₄), 3.78 (s, 3H, H₈), 3.76 (q, $J = 7.0$ Hz, 6H, H₉), 3.66 (s, 3H, H₆), 3.50 (s, 1H, H₁), 1.15 (t, $J = 7.0$ Hz, 9H, H₁₀). ¹³C NMR (75 MHz, C₆D₆, 303 K) δ 172.9 (C₇), 158.8 (C₅), 131.0 (C₃), 127.7 (C₂), 114.1 (C₄), 59.9 (C₉), 55.8 (C₆), 52.2 (C₈), 41.8 (C₁), 18.5 (C₁₀). HRMS (ESI+): calcd. for [C₁₆H₂₆O₆SiNa]⁺: 365.13909; found 365.13919.

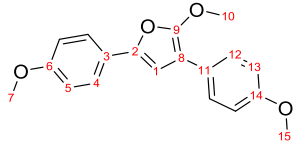


Methyl (1R,2R)-1,2-bis(4-methoxyphenyl)cyclopropane-1-carboxylate (17). A

solution of methyl 2-diazo-2-(4-methoxyphenyl)acetate (20 mg, 0.097 mmol) in pentane (2.0 mL) was added over 3 h to a solution of [Cp*RhI₂]₂ (1.0 mg, 1 mol%) and 4-methoxystyrene in pentane (1 mL) at room temperature. The mixture was stirred for 2 h before the solvent was removed under reduced pressure. Purification of the

residue flash chromatography on silica gel (5% EtOAc in hexane) gave the title compound as a white solid (21 mg, 69%). The analytical and spectral data were identical to those outlined above. The yield was only 46% when $[\text{Cp}^*\text{RhCl}_2]_2$ (0.6 mg, 1 mol%) was used as the catalyst.

2-Methoxy-3,5-bis(4-methoxyphenyl)furan (18). A solution of 2-diazo-2-(4-methoxyphenyl)acetate (20 mg, 0.097 mmol) in CH_2Cl_2 (2.0 mL) was added over 3 h to a solution of $[\text{Cp}^*\text{RhI}_2]_2$ (1.0 mg, 1 mol%) and 1-ethynyl-4-methoxybenzene (0.13 mL, 0.97 mmol) in CH_2Cl_2 (1 mL) at room temperature. The mixture was stirred overnight before the solvent was removed under reduced pressure.



Purification of the residue by flash chromatography on silica gel (5% EtOAc in hexane) led to the title compound as a colorless syrup that is sensitive to hydrolysis (17 mg, 56%). $^1\text{H NMR}$ (600 MHz, CD_2Cl_2 , 298 K) δ 7.55 (d, $J = 8.9$ Hz, 2H, H_4), 7.54 (d, $J = 8.9$ Hz, 2H, H_{12}), 6.93 (d, $J = 8.7$ Hz, 2H, H_5), 6.92 (d, $J = 8.9$ Hz, 2H, H_{13}), 6.73 (s, 1H, H_1), 4.08 (s, 3H, H_{10}), 3.82 (s, 3H, H_7), 3.81 (s, 3H, H_{15}). $^{13}\text{C NMR}$ (151 MHz, CD_2Cl_2 , 298 K) δ 159.2 (C_6), 158.3 (C_{14}), 155.3 (C_9), 144.6 (C_2), 127.3 (C_{12}), 125.5 (C_{11}), 124.6 (C_4), 124.3 (C_3), 114.7 (C_{13}), 114.5 (C_5), 104.2 (C_1), 101.6 (C_8), 59.5 (C_{10}), 55.9 (C_7), 55.8 (C_{15}). **HRMS** (ESI⁺): calcd. for $[\text{C}_{19}\text{H}_{18}\text{O}_4\text{Na}_1]^+$: 333.10973; found 333.10976.

References

- (a) Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970. (b) Jones, W. D.; Feher, F. J. *Inorg. Chem.* **1984**, *23*, 2376.
- (a) Chan, W.-W.; Yeung, S.-H.; Zhou, Z.; Chan, A. S. C.; Yu, W.-Y. *Org. Lett.* **2010**, *12*, 604. (b) Hu, M.; He, Z.; Gao, B.; Li, L.; Ni, C.; Hu, J. *J. Am. Chem. Soc.* **2013**, *135*, 17302. (c) Miller, J. B. *J. Org. Chem.* **1959**, *24*, 560. (d) Kumar, S.; Murray, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 1040. (e) For the synthesis of the starting imines see: Fergus, S.; Eustace, S. J.; Hegarty, A. F. *J. Org. Chem.* **2004**, *69*, 4663; (f) Pickard, P. L.; Tolbert, T. L. *J. Org. Chem.* **1961**, *26*, 4886.
- Werlé, C.; Goddard, R.; Fürstner, A. *Angew. Chem. Int. Ed.* **2015**, *54*, 15452
- The $^{13}\text{C NMR}$ signal of the carbene was observed and assigned by $^1\text{H}-^{13}\text{C}$ HMBC.
- Observed and assigned by $^1\text{H}-^{15}\text{N}$ HMBC.
- The signal was directly observed in the $^{13}\text{C NMR}$ spectrum and assigned by $^1\text{H}-^{13}\text{C}$ HMBC.
- The assignment was confirmed by $^1\text{H}-^{13}\text{C}$ HSQC.
- Observed only in the $^1\text{H}-^{13}\text{C}$ HMBC spectra as a weak crosspeak.
- The $^1\text{H NMR}$ signal of H_9 could not be observed by $^1\text{H NMR}$ spectroscopy because deuterated CD_3OD (99.8%) was used for the in-situ preparation of the complex.
- Observed only as a weak signal in the $^1\text{H}-^{13}\text{C}$ HMBC spectra.

