Advanced Synthesis & Catalysis

Supporting Information

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Probing of the Ligand Anatomy: Effects of the Chelating Alkoxy Ligand Modifications on the Structure and Catalytic Activity of Ruthenium Carbene Complexes

Supplementary Information
Advanced Synthesis & Catalysis

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1 General

Unless otherwise noted, all reactions were carried out under Ar in pre-dried glassware using Schlenk techniques. The solvents were dried by distillation over the following drying agents and were transferred under argon: THF (K/benzophenone), toluene (Na), *n*-pentane, *n*-hexane, CH_2Cl_2 (CaH_2), Et_2O ($LiAlH_4$), MeOH (Mg). Flash column chromatography: Merck silica gel 60 (230–400 mesh). NMR: Spectra were recorded on Bruker AVANCE 500, Varian Gemini 200 and 400 spectrometers in $CDCl_3$; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. IR: Perkin-Elmer Spectrum 2000 FT-IR, wavenumbers in cm^{-1}. MS (EI, LSIMS): AMD 604 Intectra GmbH. MS (ESI): Mariner Perseptive Biosystems, Inc. GC: HP 6890 with HP 5 column. GC/MS: HP 5890 with HP 5 column. Micro-analyses were provided by Institute of Organic Chemistry, PAS, Warsaw. All commercially available chemicals were used as received.

2 Synthesis of Ligand Precursors

2.1 Wittig reaction of aldehydes 8B,D–F, (scheme 4, top)

2.1.1 General procedure for Wittig reaction

Solid $Ph_3P{=}CH_2$ (0.693 g, 2.5 mmol, Aldrich) and THF (20 mL) were placed in a Schlenk tube under argon atmosphere. A solution of an aldehyde (1.1 mmol) in THF (5 ml) at -78 °C was added to the reaction mixture. The mixture was stirred at the same temperature for 1h, then warmed to r.t. and treated with saturated solution of NH_4Cl, extracted with MTBE (4 x 20 mL) and dried over anhydrous magnesium sulfate. The solvent was evaporated and the product was purified by column chromatography.

2.1.2 Characterization data of styrenes 7B,D–F

1-(Benzyloxy)-2-vinylbenzene (7B): IR (film): ν 3065, 3033, 2928, 1625, 1597, 1486, 1451, 1380, 1292, 1239, 1108, 1016, 910, 749 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.16 (s, 2H), 5.34 (dd, 1H, J = 11.1, 1.5 Hz), 5.84 (dd, 1H, J = 17.7, 1.5 Hz), 6.97–7.06 (m, 2H), 7.22 (dd, 1H, J = 17.7, 11.1 Hz), 7.26–7.42 (m, 2H), 7.43–7.48 (m, 2H), 7.50–7.54 (m, 2H), 7.57–7.62 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.0, 137.2, 131.7, 128.8, 128.6, 128.2, 127.9, 127.5, 127.3, 127.2, 126.6, 121.0, 114.5, 112.6, 70.4. MS (EI) *m/z* (rel intensity) 210 (21, M$^{+\cdot}$), 209 (5), 195 (2), 119 (6), 116 (3), 92 (9), 91 (100), 89 (2), 65 (19), 63 (4), 51 (3), 39 (6).

1-(Trifluoromethoxy)-2-vinylbenzene (7D) was prepared according to the literature method.

7-Vinyl-2,3-dihydrobenzofurane (7E): white solid, (70%) IR (film): ν 3319, 3019, 2934, 2833, 1609, 1514, 1464, 1449, 1356, 1325, 1258, 1222, 1135, 1050, 857, 757 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.19 (t, 2H, J = 8.7 Hz), 4.60 (t, 2H, J = 8.7 Hz), 5.30 (dd, 1H, J = 11.3, 1.6 Hz), 5.90 (dd, 1H, J = 17.7, 1.6 Hz), 6.74 (dd, 1H, J = 17.7, 11.3 Hz), 6.78–6.83 (m, 1H), 7.06–7.09 (m, 1H), 7.14–7.17 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.8, 132.0, 127.4, 126.0, 123.9, 120.5, 120.4, 115.4, 71.1, 29.6 MS (EI) *m/z* (rel intensity) 149 (16), 148 (76), 147 (100, M$^{+\cdot}$), 146 (27), 145 (49), 136 (81), 120 (20), 119 (26), 118 (38), 117 (19), 107 (19), 91 (57), 90 (22), 89 (32), 79 (23), 77 (22), 65 (25), 63 (24), 43 (59), 39 (25). Anal. calcd for $C_{10}H_{10}O$ (146.19): C 82.16, H 6.89; found C 82.20, H 7.07.

8-Vinyl-3,4-dihydro-2*H*-1-benzopyran (7F): white solid, (76%) IR (film): ν 3084, 2938, 2873, 1624, 1590, 1472, 1453, 1413, 1307, 1262, 1238, 1220, 1189, 1098, 1064, 1023, 906, 748 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.00–2.06 (m, 2H), 2.81 (t, 2H, J = 6.5 Hz), 4.26 (t, 2H, J = 5.2 Hz), 6.32 (dt, 1H, J = 15.1, 1.5 Hz), 5.26 (dd, 1H, J = 11.1, 1.6 Hz), 5.73 (dd, 1H, J = 17.7, 1.6 Hz), 6.80–6.85 (m, 1H), 6.94–6.99 (m, 1H), 7.03 (dd, 1H, J = 17.7, 11.1 Hz), 7.29–7.32 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.2, 131.7, 129.3, 126.1, 124.3, 122.3, 119.7, 114.2, 66.6, 25.1, 22.2. MS (EI) *m/z* (rel intensity) 160 (100, M$^{+\cdot}$), 159 (14), 145 (28), 133 (7), 132 (39), 131 (35), 128 (5), 117 (13), 115 (11), 104 (13), 103 (8), 91 (9), 78 (6), 77 (8), 65 (4), 63 (3), 52 (5), 51 (6), 39 (4). HRMS (ESI) calcd for [M+Na]$^+$ ($C_{11}H_{12}O$): 160.0888; found: 160.0894 Anal. calcd for $C_{11}H_{12}O$ (160.22): C 82.46, H 7.55; found C 82.63, H 7.47.

2.2 Alkylation of 2-propenylphenole, (scheme 4, middle)

2.2.1 Alkylation of 2-propenylphenol

To a suspension of $Bu_4N^+HSO_4^-$ (0.070 g; 0.2 mmol) and K_2CO_3 (2.2 g; 16.0 mmol) in CH_3CN (20 mL), 2-propenylphenol (1.03 g; 8.0 mmol) was added. After stirring for 30 min at room temperature, 4-nitrobenzyl chloride (1.37 g, 8.0 mmol) was added and the reaction mixture was stirred 1 day at 40 °C . Then the reaction mixture was poured into 40 mL water and extracted three times with diethyl ether. The combined extracts were washed with brine, water and dried over magnesium sulfate. The solvent was evaporated and crude product was purified by column chromatography in cyclohexane. The product **7C′** (0.8 g; 74%) was obtained as a yellow solid.

1-(4-Nitrobenzyloxy)-2-vinylbenzene (7C′): yellow crystals, (74 %) 5:4 (E/Z) mixture of isomers. Mp: 69–71 °C . IR (KBr): ν 2916, 2858, 1608, 1598, 1579, 1525, 1487, 1449, 1420, 1377, 1348, 1322, 1300, 1239, 1223, 1162, 1110, 1053, 1089, 1053, 1038, 1015, 973, 944, 857, 843, 796, 581 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.84 (dd, 3H, J = 7.1, 1.8 Hz), 5.18–5.21 (m, 2H), 5.88 (m, 1H), 5.91 (m, 1H), 6.62 (m, 1H), 6.78–7.24 (m, 2H), 7.45 (dd, 2H, J = 7.7, 1.65 Hz), 7.58-7.63 (m, 2H), 8.22-8.27.11 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.9, 68.9, 112.0, 121.0, 123.8, 124.9, 126.6, 127.0, 127.3, 127.5, 130.5, 144.7, 154.6. MS (EI) *m/z* (rel intensity) 269 (26, M$^{+\cdot}$), 136 (6), 134 (12), 134 (25), 133 (100), 131 (8), 115 (5), 107 (5), 106 (14), 105 (87), 103 (10), 91 (6), 90 (13), 89 (13), 79 (15), 78 (12), 77 (15), 51 (5), 39 (6). HRMS (EI) calcd for M$^{+\cdot}$ ($C_{13}H_{16}O_3$): 269.30994; found: 269.31005 Anal. calcd for $C_{16}H_{15}NO_3$ (269.30): C 70.30, H 5.51, N 5.47; found C 70.40, H 5.59, N 5.15.

2.3 Synthesis of intermediates 9E,F, (scheme 4, bottom)

2.3.1 Alkylation of 2,6-dibromophenol with 1-bromo-2-chloroethane

A suspension of K_2CO_3 (5.56g, 40 mmol) in solution of 2,6-dibromophenol (2.53g, 10 mmol) and 1-bromo-2-chloroethane (2.15g, 15 mmol) in DMF (35 mL) was vigorously stirred at 65°C for 4h. Then mixture was poured into water, extracted with CH_2Cl_2, washed with water and dried with anhydrous magnesium sulfate. Column chromatography gave product **9E** as colorless oil (2.9g, 97%).

(2,6-Dibromophenyl)(2-chloethyl)ether 9E: colorless oil, IR (film): ν 3688, 3601, 2965, 2871, 1932, 1863, 1794, 1671, 1605, 1557, 1456, 1441, 1379, 1300, 1242, 1199, 1149, 1073, 1021, 994, 972, 888, 842, 794, 772, 670, 612, 542, 517 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ 3.91 (t, 2H, $J = 6.3$ Hz), 4.27 (t, 2H, $J = 6.3$ Hz), 6.89 (t, 1H, $J = 8.1$ Hz), 7.51 (d, 2H, $J = 8.1$ Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 152.6, 132.8, 126.7, 118.3, 72.5, 42.0. MS (EI) *m/z* (rel intensity) 318 (4) 316 (18), 314 (27, $M^{+\cdot}$), 312 (12), 254 (49), 252 (100), 250 (52), 223 (7), 172 (6), 170 (5), 145 (6), 144 (4), 143 (7), 75 (8), 74 (4), 65 (11), 63 (42), 62 (8). Anal. calcd for $C_8H_7OClBr_2$ (314.41): C 30.89, H 2.30; found C 30.60, H 2.24.

2.3.2 Alkylation of 2,6-dibromophenol with 1,3-dichloropropane

A suspension of K_2CO_3 (4.43g, 32 mmol) in solution of 2,6-dibromophenol (2.01g, 7.98 mmol), 1,3-dichloropropane (4.52g, 40 mmol) and Bu_4NHSO_4 (0.137g, 0.4 mmol) in acetonitrile (15 mL) was vigorously stirred at 45°C for 20h. Then mixture was concentrated *in vacuo*, poured into water, extracted with CH_2Cl_2, washed with water, brine and dried with anhydrous magnesium sulfate. Column chromatography gave product **9F** as colorless oil (1.28g, 49%).

2,6-Dibromophenyl)(2-chlopropyl)ether 9F: colorless oil, IR (film): ν 3687, 3620, 2957, 2890, 2507, 1931, 1861, 1795, 1673, 1605, 1555, 1469, 1441, 1380, 1359, 1301, 1246, 1198, 1170, 1148, 1088, 1070, 1028, 1013, 930, 893, 833, 773, 657, 613, 544, 519 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ 2.32 (tt, 2H, $J = 6.7$, 6.5 Hz) 3.88 (t, 2H, $J = 6.5$ Hz), 4.15 (t, 2H, $J = 6.7$ Hz), 6.87 (t, 1H, $J = 8.1$ Hz), 7.51 (d, 2H, $J = 8.1$ Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 153.0, 132.7, 126.4, 118.4, 69.7, 41.6, 33.3. MS (EI) *m/z* (rel intensity) 330 (11), 328 (15, $M^{+\cdot}$), 326 (7), 255 (3), 254 (48), 253 (7), 252 (100), 251 (4), 250 (51), 223 (4), 172 (4), 170 (3), 145 (4), 143 (5), 65 (11), 63 (42), 62 (4), 49 (3), 41 (22), 39 (7), Anal. calcd for $C_9H_9OClBr_2$ (328.43): C 32.91, H 2.76; found C 32.73, H 2.75.

2.4 Synthesis of cyclic aldehydes 8E,F, (scheme 4, bottom)

2.4.1 Metallation–cyclization–DMF quenching sequence

To a vigorously stirred solution of *n*-BuLi (8.5 mL, 13.6 mmol, 1.6M in hexanes) in THF (12 mL) at -40 °C was added slowly *via* syringe immersed deeply solution of **9E** (1.37g, 4.35 mmol) in THF (5 mL). After few minutes solution of DMF (0.7 mL) in THF (1 mL) was added slowly in the same manner. Cooling bath was removed and mixture was left at RT for 1h. Then $HCl_{aq.}$ (20 mL, 1M) was added with vigorous stirring, brine was added and mixture was extracted with ethyl acetate, washed with brine and dried with magnesium sulfate. After column chromatography (hexanes:ethyl acetate 20:1) product **8E** was obtained as an oil (0.54, 84%), that solidified on prolonged storage in refrigerator.

The same produre was applied for the reaction of **9F**, with the exception, that after addition of **9F** to the solution of *n*-BuLi, mixture was kept for 1h at -40 °C before addition of DMF. Yield 76% of **8F**.

2.4.2 Characterization data of cyclic aldehydes 8E,F

7-Formyl-2,3-dihydrobenzofurane (8E): white solid, m.p.=53–54 °C , IR (film): ν 3347, 2980, 2927, 2927, 2905, 2859, 2772, 2733, 1681, 1610, 1581, 1454, 1442, 1397, 1363, 1340, 1278, 1228, 1207, 1189, 1159, 1068, 1055, 1021, 998, 972, 962, 931, 838, 666, 606, 575, 525, cm^{-1}. ^1H NMR (200

MHz, $CDCl_3$) δ 3.18-3.30 (m, 2H), 4.67-4.79 (m, 2H), 6.92 (t, 1H, $J = 7.9$ Hz), 7.35-7.44 (m, 1H), 7.53-7.61 (d, 1H), 10.18 (d, 1H, $J = 0.5$ Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 188.9, 162.1, 130.8, 129.4, 127.3, 120.5, 119.7, 72.7, 28.6. MS (EI) *m/z* (rel intensity) 148 (100, $M^{+\cdot}$), 147 (92), 120 (25), 119 (11), 105 (5), 102 (18), 92 (6), 91 (50), 90 (4), 89 (10), 77 (3), 65 (20), 64 (4), 63 (13), 62 (5), 53 (3), 51 (8), 50 (4), 39 (14), 38 (3). Anal. calcd for $C_9H_8O_2$ (148.16): C 72.96, H 5.44; found C 72.73, H 5.47.

8-Formyl-3,4-dihydro-2*H*-1-benzopyran (8F): white solid, m.p.=34–39 °C , IR (film): ν 3601, 3346, 2983, 2958, 2881, 2785, 2416, 1936, 1681, 1591, 1476, 1455, 1434, 1399, 1380, 1331, 13200, 1240, 1229, 1192, 1162, 1092, 1077, 1021, 962, 908, 877, 856, 809, 780, 667, 636, 572, 541 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ 1.98-2.21 (m, 2H), 2.76-2.87 (m, 2H), 4.24-4.34 (m, 2H), 6.83-6.93 (m, 1H), 7.20-7.29 (m, 1H), 7.58-7.66 (m, 1H), 10.40 (d, 1H, $J = 0.8$ Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 189.9, 157.6, 136.0, 126.4, 124.2, 123.5, 119.7, 66.9, 24.6, 21.7. MS (EI) *m/z* (rel intensity) 163 (11), 162 (100, $M^{+\cdot}$), 161 (72), 134 (13), 133 (22), 118 (6), 116 (5), 115 (12), 106 (32), 105 (14), 103 (4), 91 (6), 79 (5), 78 (9), 77 (14), 63 (4), 52 (4), 51 (11), 50 (4), 39 (6). Anal. calcd for $C_{10}H_{10}O_2$ (162.22): C 74.06, H 6.21; found C 74.15, H 6.21.

3 X-Ray data collection and structure refinement of complexes 3b, 6A, 6C, and 6F

3.1 Experimetal

The structures of 3b, 6A, 6C and 6F complexes were determined in single-crystal X-ray diffraction experiments. The measurements were performed on a Kuma KM4CCD κ-axis diffractometer with graphite-monochromated Mo Kα radiation (50.0 kV, 40.0 m$\mathring{A}$) at liquid nitrogen temperature. The crystals were positioned at 62 mm from the KM4CCD camera. The frames were measured at 1.0° intervals, except for the **6C**, where 1.25° interval was chosen and **6F**, where 0.75° interval was applied. The multi-scan absorption correction was applied to all the collected datasets, and the transmittance maximal and minimal values are reported in the Table 1. Data reduction and analysis for both crystals were carried out with CrysAlisCCD and CrysAlisRED Kuma Diffraction programs. The crystals of **6A** proved to be twins, and a twinning was by a 180° rotation along the [001] direction. The orientation matrices for twin components were determined, and several datasets, containing fully separated reflections and accordingly all the reflections were produced in each case. Due to the twin separation procedures no merging of symmetry equivalents was possible to apply for these datasets and since the values of the final data completeness are low and meaningless. The crystals of **6F**, on the other hand, grew small and scattered very weakly, which influenced the obtained structural results. All the structures were solved by direct methods approach using the SHELXS-97 program.[1,2] Then refinement was carried out with the SHELXL-97. The refinement was based on F^2 for all reflections except those with negative intensities. Weighted R factors wR and all goodness-of-fit S values were based on F^2, whereas conventional R factors were based on the amplitudes, with F set to zero for negative F^2. The $F_0^2 > 2\sigma(F_0^2)$ criterion was applied only for R factors calculation was not relevant to the choice of reflections for the refinement. The R factors based on F^2 are for both structures about twice as large as those based on F. All of the hydrogen atoms for all of the crystal structures were located in idealized geometrical positions and their thermal displacement parameters were constrained on the basis of thermal displacement parameters of the neighboring atoms. Also there were some special constraints applied to the bond lengths and anisotropic displacement parameters of some atoms in the case of **6C**, that were necessary due to the twinning effects and the data quality. Due to the poor scattering and data number as well as the disorders present in the **6F** structure it was necessary to apply constraints to several interatomic distances in this structure, and for some of the non-hydrogen atoms only isotropic thermal displacements were refined. Scattering factors were taken from Tables 4.2.6.8 and 6.1.1.4 from the International Crystallographic Tables Vol.C.[3]

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[1] G. M. Sheldrick, Acta Crystallogr. **1990**, *A46*, 467–473.

[2] G. M. Sheldrick, SHELXL93. *Program for the Refinement of Crystal Structures*, Univ. of Göttingen, Germany.

[3] *International Tables for Crystallography*, Ed. A. J. C. Wilson, Kluwer, Dordrecht, **1992**, Vol.C.

Crystalographic data (excluding structural factors) for the structures reported in this paper has been deposited with the Cambridge Crystallographic Data Center and allocated the deposition numbers: CCDC 620588 (**3b**), CCDC 620589 (**6A**), CCDC 620590 (**6C**), and CCDC 620591 (**6F**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EW, UK (Fax: Int code + (1223)336-033; E-mail: deposit@ccdc.cam.ac.uk).

3.2 Crystalographic data

Identification code	**3b** (C00101)	**6A** (C019801)	**6C** (C019901)	**6F** (C020101)
Empirical formula	$C_{32}H_{40}Cl_4N_2ORu$	$C_{32}H_{41}Cl_2N_2ORu$	$C_{37.50}H_{42}Cl_2N_3O_3Ru$	$C_{31.33}H_{36.67}Cl_{2.67}N_2ORu$
Formula weight	711.53	641.64	754.71	652.90
Temperature [K]	103(2)	100(2)	103(2)	103(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	P2(1)/n	P2(1)/c	P-1	P-1
a [Å]	13.6381(16)	23.924(5)	12.6278(9)	8.4174(6)
b [Å]	10.3510(9)	8.4752(17)	15.9601(12)	21.603(2)
c [Å]	22.8399(19)	15.766(3)	19.3775(15)	24.754(2)
α [°]	90	90	75.662(7)	79.486(8)
β [°]	95.298(8)	102.31(3)	87.673(6)	89.401(7)
γ [°]	90	90	70.730(7)	89.204(7)
Volume [Å^3]	3210.5(5)	3123.1(11)	3568.1(5)	4425.3(7)
Z	4	4	4	6
Calculated density [Mg/m^3]	1.472	1.365	1.405	1.470
Absorption coefficient [mm^{-1}]	0.849	0.699	0.629	0.800
F(000)	1464	1332	1560	2016
Crystal size [mm]	0.39/0.35/0.1	0.38/0.18/0.09	0.35/0.26/0.08	0.27/0.08/0.02
θ range for data collection[$\circ$]	2.66–27.50	3.49–27.50	2.59–27.50	2.55–25.00
Limiting indices	$-17 \leqslant h \leqslant 17$	$-30 \leqslant h \leqslant 31$	$-16 \leqslant h \leqslant 16$	$-10 \leqslant h \leqslant 7$
	$-13 \leqslant k \leqslant 13$	$-11 \leqslant k \leqslant 11$	$-20 \leqslant k \leqslant 20$	$-25 \leqslant k \leqslant 25$
	$-29 \leqslant l \leqslant 29$	$-19 \leqslant l \leqslant 19$	$-25 \leqslant l \leqslant 25$	$-29 \leqslant l \leqslant 29$
Reflections collected/unique	58541/7365	6746/6746	65677/16353	34674/15486
R_{int}	0.0181	0.0000	0.0550	0.1522
Completeness to θ = 27.50°	99.9%	28.9%	99.6%	99.5%
Max. and min. transmission	0.88, 0.73	0.88, 0.75	0.91, 0.80	0.98, 0.85
Data/restraints/parameters	7365/0/367	6746/246/344	16353/71/920	15486/42/808
Goodness-of-fit on F^2	1.057	1.018	0.883	0.675
R1 [I>2sigma(I)]	0.0210	0.0626	0.0424	0.0546
wR2	0.0530	0.1559	0.1090	0.0594
R1 [all data]	0.0265	0.0826	0.0945	0.2309
wR2	0.0541	0.1750	0.1187	0.0773
Max. diff. peak and hole [e/A^{-3}]	1.236, -0.763	0.717, -0.467	1.677, -0.611	0.909, -0.653

Table 1: Crystalographic Data

3.3 ORTEP drawings of complexes 3b, 6A and 6C

3.3.1 Complex 3b

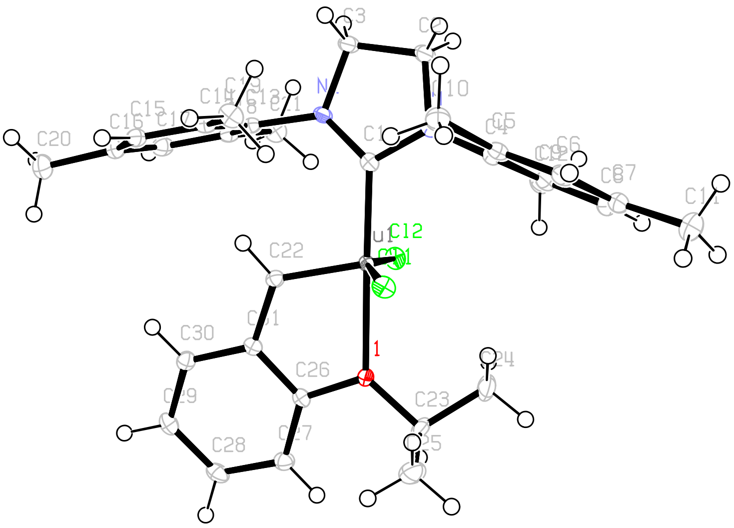

Figure 1: ORTEP drawing of complex **3b** (complex **3b**$\cdot CH_2Cl_2$, cocrystallized solvent molecule has been omitted for clarity).

3.3.2 Complex 6A

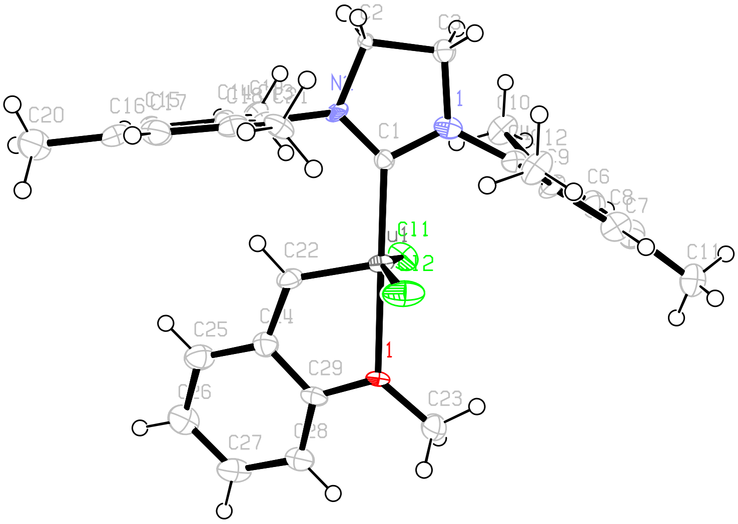

Figure 2: ORTEP drawing of complex **6A** (complex **6A**$\cdot n-C_6H_{14}$, cocrystallized solvent molecule has been omitted for clarity).

3.3.3 Complex 6C-I

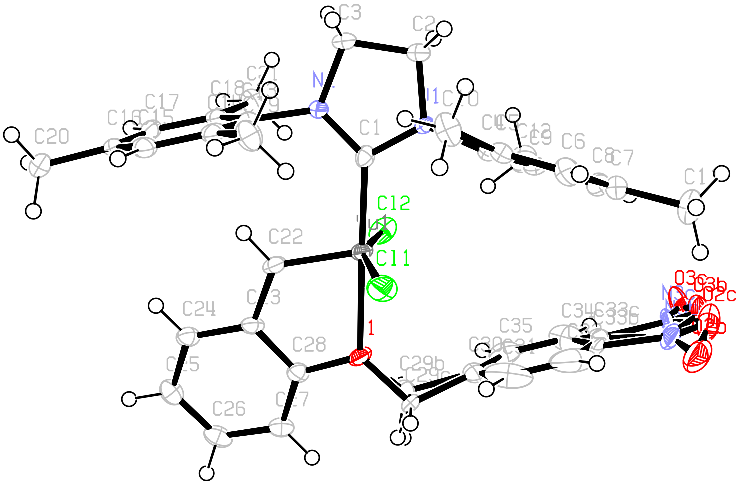

Figure 3: ORTEP drawing of complex **6C-I** (first molecule in asymmetric unit; complex **6C-I**·**6C-II**·$n\text{−}C_5H_{12}$, cocrystallized solvent and second molecule **6C-II** have been omitted for clarity).

3.3.4 Complex 6C-II

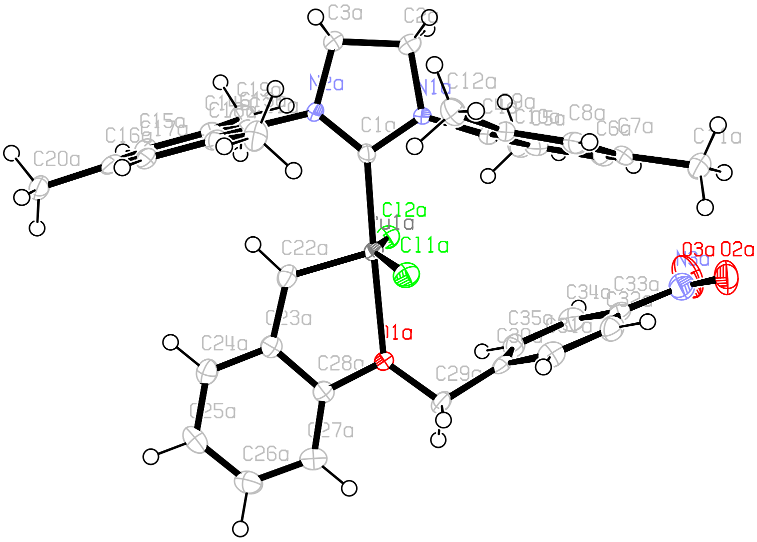

Figure 4: ORTEP drawing of complex **6C-II** (second molecule in asymmetric unit; complex **6C-I**·**6C-II**·$n\text{−}C_5H_{12}$, cocrystallized solvent and first molecule **6C-I** have been omitted for clarity).

3.4 Selected structural parameters of complexes 3b, 6A, 6C and 6F

Bonds [Å]	**3b**	**6A**	**6C-I**	**6C-II**	**6F-I**	**6F-II**	**6F-III**
Ru(1)-C(22)	1.8286(15)	1.802(9)	1.818(4)	1.819(4)	1.827(7)	1.771(7)	1.831(7)
Ru(1)-C(1)	1.9791(15)	2.016(7)	1.967(4)	1.981(4)	2.005(7)	2.013(8)	2.016(8)
Ru(1)-O(1)	2.2562(10)	2.263(5)	2.277(3)	2.273(2)	2.256(5)	2.277(5)	2.205(6)
Ru(1)-Cl(1)	2.3279(4)	2.322(2)	2.3320(12)	2.3264(11)	2.318(2)	2.340(3)	2.312(3)
Ru(1)-Cl(2)	2.3380(4)	2.329(2)	2.3331(12)	2.3330(11)	2.324(2)	2.347(3)	2.372(2)
O(1)-C(26)	1.3701(18)	1.352(10)	1.347(10)	1.385(4)	1.351(9)	1.392(9)	1.428(10)
O(1)-C(23)	1.4694(18)	1.440(10)	1.380(5),1.438(10)	1.448(4)	1.420(12),1.411(18)	1.416(16),1,410(13)	1.433(15),1.449(15)
Angles [deg]							
C(22)-Ru(1)-C(1)	101.33(6)	101.9(3)	101.39(16)	102.11(16)	102.0(3)	100.1(4)	98.8(3)
C(22)-Ru(1)-O(1)	79.43(5)	78.6(3)	79.51(14)	79.39(14)	78.4(3)	79.9(3)	80.2(3)
C(1)-Ru(1)-O(1)	176.06(5)	179.1(2)	174.46(14)	177.49(13)	176.9(3)	177.6(3)	96.1(3)
C(22)-Ru(1)-Cl(1)	100.19(5)	102.9(3)	100.17(14)	100.35(13)	102.3(2)	96.9(3)	105.2(2)
C(1)-Ru(1)-Cl(1)	96.76(4)	94.47(19)	96.24(12)	96.47(12)	97.0(2)	93.7(3)	155.9(3)
O(1)-Ru(1)-Cl(1)	86.88(3)	84.62(14)	88.96(8)	85.20(7)	85.95(15)	83.95(17)	85.64(17)
C(22)-Ru(1)-Cl(2)	100.39(5)	96.4(3)	99.26(14)	100.75(12)	100.7(2)	103.3(3)	94.4(3)
C(1)-Ru(1)-Cl(2)	90.69(4)	95.06(19)	89.91(11)	89.43(12)	93.4(2)	96.1(3)	89.6(3)
O(1)-Ru(1)-Cl(2)	85.37(3)	85.71(16)	84.55(8)	88.30(7)	83.46(15)	86.18(18)	172.69(16)
Cl(1)-Ru(1)-Cl(2)	156.251(15)	156.13(10)	158.01(4)	156.35(4)	152.14(8)	155.60(9)	91.01(10)
C(26)-O(1)-C(23)	119.93(12)	119.9(6)	114.7(5),122.8(5)	116.1(3)	118.2(13)	124.6(8),111.0(10)	111.2(11),119.4(11)
C(26)-O(1)-Ru(1)	110.10(9)	109.3(4)	109.2(2)	109.7(2)	109.6(5)	108.7(5)	109.9(6)
C(23)-O(1)-Ru(1)	129.79(9)	129.7(5)	126.3(5),131.0(5)	127.8(2)	131.2(14)	125.6(6),138.5(10)	133.9(9),117.0(8)

Table 2: Selected structural parameters of complexes 3b, 6A, 6C and 6F