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Note

Synthesis of cyclopentadienyl ruthenium complexes bearing pendant chelating picolinates through an electrophilic precursor

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Abstract

This note reports the facile synthesis of two ruthenium cyclopentadienyl half-sandwich complexes functionalized with coordinating α-picolinates. The synthetic approach involves the (η^5-chloromethylcyclopentadienyl)(η^6-benzene)ruthenium(II) cation as a useful common building block for cyclopentadienyl complexes bearing anchored ligands.
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1. Introduction

The cyclopentadienyl group is one of the most ubiquitous and most important ligands in organometallic chemistry [1]. We are especially interested in η^5-cyclopentadienyl ruthenium half-sandwich complexes because of their structure and reactivity. For example, we recently reported ruthenium cyclopentadienyl complexes as substitutionally inert protein kinase inhibitors but also as reactive compounds which can induce the cleavage of protection groups in a biological environment [2,3].

To expand our ability to control structure and reactivity, we are aiming for cyclopentadienyl ruthenium complexes with additional intramolecularly tethered coordinating groups [4–7]. For ruthenium, synthetic approaches to such complexes typically fall into one of two categories: (1) The synthesis of functionalized cyclopentadienes followed by coordination to the metal, or (2) the anchoring of an additional donor ligand to an already formed cyclopentadienyl complex [4–8]. We feel that the latter approach is more versatile albeit less explored [8]. To this end, we herein describe the exemplary synthesis of two ruthenium cyclopentadienyl half-sandwich complexes functionalized with coordinating α-picolinates, both accessible through a common electrophilic ruthenium sandwich building block **1**.

2. Results and discussion

2.1. Synthesis of the (η^5-chloromethylcyclopentadienyl)(η^6-benzene)ruthenium(II) cation *1*

Complex **1** was synthesized starting with sodium cyclopentadienyl carbaldehyde **2** [9]. Its reaction with commercially available $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ afforded sandwich complex **3** which was carried on crude due to purification problems and reduced to the alcohol **4** with $NaBH_4$. Silica gel chromatography, followed by precipitation with KPF_6, and extraction into CH_2Cl_2, provided the clean compound **4** in 28% yield over two steps. Next, **4** was chlorinated by the reaction with $SOCl_2$ (3.1 equiv.) in acetonitrile to afford the complex **1** in 88% yield (Scheme 1).

2.2. Utility of *1* as an electrophilic building block

2.2.1. Synthesis of picolinate complex rac-*8*

The (η^5-chloromethylcyclopentadienyl)(η^6-benzene)-ruthenium(II) cation **1** is a useful precursor for ruthenium

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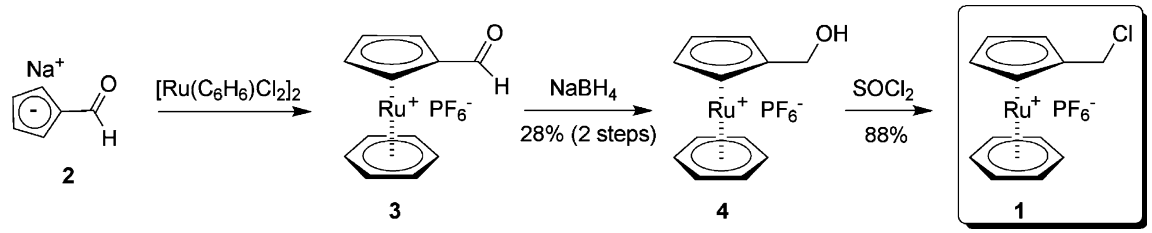


Scheme 1. Synthesis of precursor complex **1**.

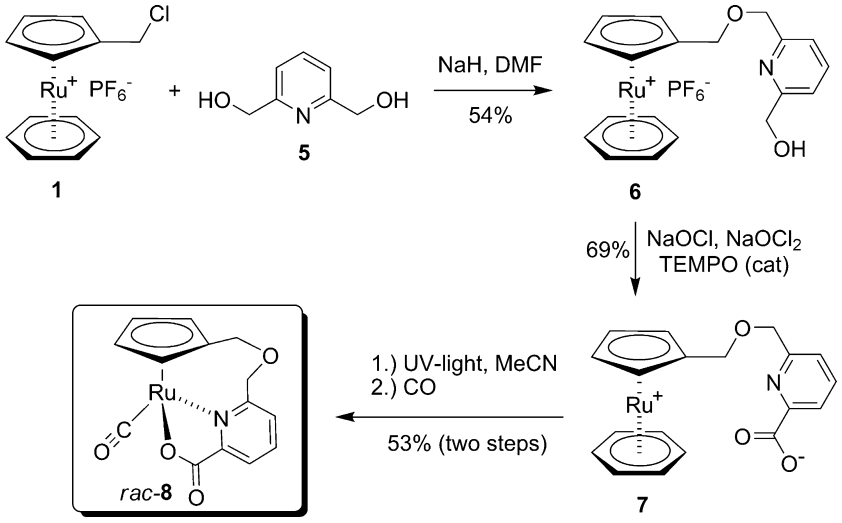
half-sandwich complexes with anchored coordinating ligands. The nucleophilic substitution of the chloride serves as a convenient way to introduce functionality into the cyclopentadienyl ring, while the sandwich scaffold itself is quite robust and withstands many typical reaction conditions without any decomposition. After derivatization of the cyclopentadienyl moiety, the benzene substituent can then conveniently be replaced by three labile acetonitrile ligands upon UV irradiation, giving access to additional coordination sites on the ruthenium center [8,10]. As representative examples, we here discuss the syntheses of two picolinate-anchored ruthenium cyclopentadienyl complexes.

The chloride in precursor **1** can be replaced by oxygen nucleophiles as shown in Scheme 2. Accordingly, the deprotonation of 2,6-pyridinedimethanol with NaH, followed by the reaction with **1**, afforded ether **6**. As representative for such cationic complexes, we purified **6** by flash silica gel chromatography with a mixture of MeCN, H_2O, and saturated aqueous KNO_3, and extracted the eluted compound as a PF_6 salt in 54% yield. Next, the alcohol was oxidized in one step to the carboxylic acid with a mixture of NaOCl and $NaOCl_2$ under TEMPO catalysis to provide complex **7** in 69% yield [11]. Finally, UV-irradiation to remove the benzene [8,10], followed by purging with CO, enabled us to isolate the half-sandwich complex *rac*-**8**, having a bidentate α-picolinate tethered to the cyclopentadienyl moiety through an ether linkage.

2.2.2. Synthesis and structure of picolinate complex *rac*-13

The chloride in precursor complex **1** can also be replaced by carbon nucleophiles. For example, α-methyl pyridine **9** was deprotonated with PhLi in THF and reacted with precursor **1** to form a C–C bond, providing complex **10** in 46% yield [12]. Subsequently, the acetal was cleaved by heating **10** in 4 M HCl at 65 °C overnight to afford aldehyde **11** in 93%. The latter was next oxidized to the carboxylic acid **12** with H_2O_2 in formic acid before removing the benzene with UV-light, followed by purging with CO to provide the picolinate half-sandwich complex *rac*-**13** in 43% over three steps.

Complex *rac*-**13** was crystallized by slow diffusion of pentane into chloroform. Its crystal structure is shown in Fig. 1 and it demonstrates that the picolinate indeed coordinates intramolecularly as a bidentate ligand to the cyclopentadienyl ruthenium fragment and that the remaining coordination site is filled with a CO ligand. Apparently, the intramolecular tether produces a certain degree of strain in the complex, indicated by a slight tilt of the cyclopentadienyl group towards the tethered picolinate. For example, the distances between ruthenium and the cyclopentadiene carbons increase as the distance from the tether



Scheme 2. Synthesis of picolinate complex *rac*-**8**.

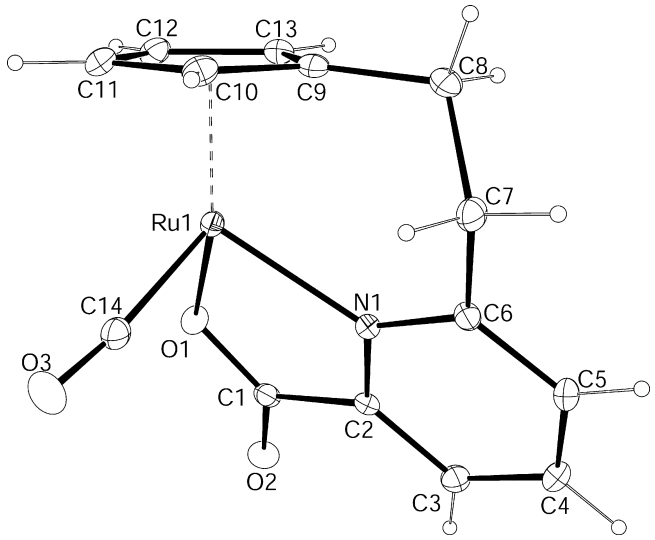


Fig. 1. Crystal structure of half-sandwich complex *rac*-**13** with 30% probability ellipsoids. Selected molecular parameters (bonds in Å, angles in °): Ru(1)–N(1) 2.086(2), Ru(1)–O(1) 2.119(2), Ru(1)–C(14) 1.874(2), and N(1)–Ru(1)–O(1) 77.39(6), N(1)–Ru(1)–C(14) 96.63(8), O(1)–Ru(1)–C(14) 94.00(8).

increases (Fig. 1, Ru(1)–C(9): 2.160 Å vs. Ru(1)–C(12): 2.213 Å) (Scheme 3).

3. Conclusion

We here disclosed the building block **1** as a common and versatile precursor for the synthesis of cyclopentadienyl ruthenium half-sandwich complexes with tethered picolinate ligands. This strategy should be applicable to the synthesis of related complexes with a large variety of anchored coordinating ligands. In the future, this methodology will hopefully result in the design of cyclopentadienyl complexes with tailored catalytic and structural properties.

4. Experimental

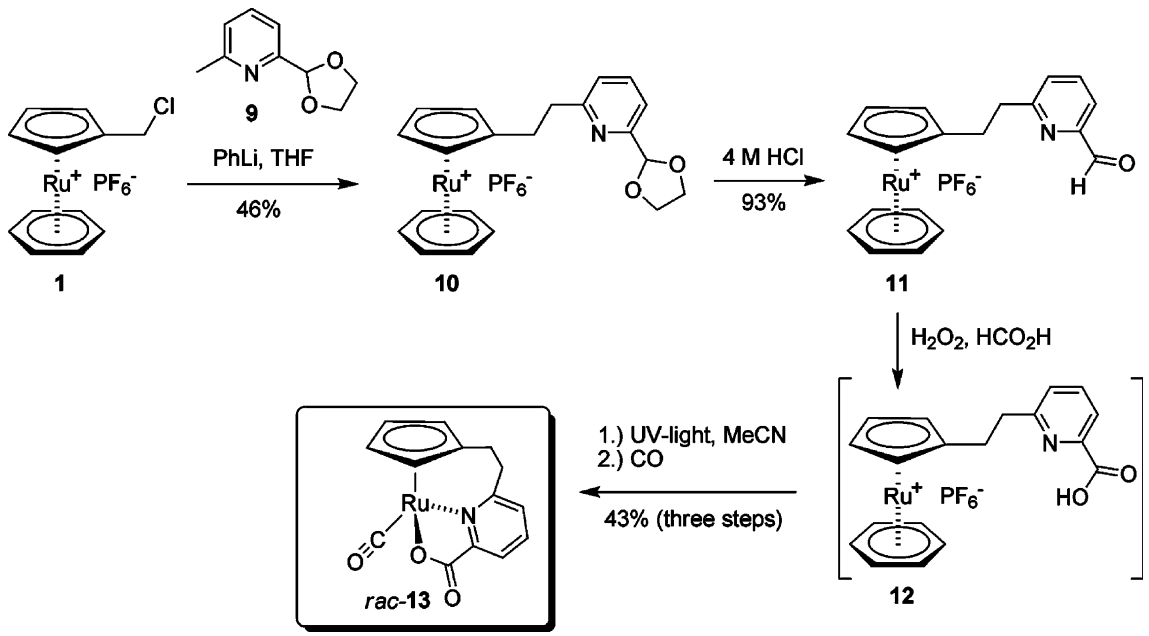
4.1. General remarks

Reactions were carried out using oven-dried glassware and were conducted under a positive pressure of argon unless otherwise specified. NMR spectra were recorded on a DMX-360 or Bruker AM-500 spectrometer. Infrared spectra were recorded on a Perkin–Elmer 1600 series FTIR spectrometer. Low-resolution mass spectra were obtained on an LC platform from Micromass using ESI technique. High-resolution mass spectra were obtained with a Micromass AutoSpec instrument using either CI or ES ionization. Sodium cyclopentadienyl carbaldehyde **2** and α-picoline **9** were synthesized according to the literature [9,12].

4.2. Synthesis of complex 3

$[Ru(C_6H_6)Cl_2]_2$ (2.0 g, 4.0 mmol) was added to a 1 L round bottomed flask and dissolved in 400 mL of acetonitrile. To the brick red solution was added sodium cyclopentadienide **2** (928 mg, 8.0 mmol). After stirring overnight at room temperature, the reaction was filtered through Celite and concentrated. The crude chloride salt was carried on directly to the next step. However, for characterization purposes, the PF_6 salt was isolated as an off-white solid by evaporating the crude reaction mixture and redissolving in the minimum volume of methanol from which the aldehyde **3** could be precipitated with 0.1 M aqueous KPF_6.

^{1}H NMR (360 MHz, CD_3CN): δ (ppm) 9.81 (s, 1H), 6.18 (s, 6H), 5.83 (t, $J = 1.8$, 2H), 5.55 (dd, $J = 1.8$, 1.7,



Scheme 3. Synthesis of picolinate complex *rac*-**13**.

2H). ^{13}C NMR (90 MHz, CD_3CN): δ (ppm) 190.2, 88.5, 83.9, 80.9 (missing one). IR (film): ν (cm^{-1}) 3388, 3103, 2861, 1898, 1707, 1445, 1393, 1367, 1241, 1153, 1038, 923, 829, 736. HRMS calc. for $C_{12}H_{11}ORu$ $(M)^+$ 272.9853, found $(M)^+$ 272.9866.

4.3. Synthesis of complex 4

To a 500 mL round bottomed flask containing the crude aldehyde **3** (see previous step) was added 250 mL of ethanol. After purging with argon, the reaction was cooled to 0 °C and $NaBH_4$ (334 mg, 8.8 mmol) was added portionwise over 30 min. In the course of the addition, much bubbling occurred and the reaction quickly turned black. After stirring for 6 h, while warming up to room temperature, the reaction was neutralized with 10% HCl and concentrated. Flash-chromatography was performed over silica gel with a 50:3:1 CH_3CN/H_2O/saturated aqueous KNO_3 mobile phase and the product was eluted as a light yellow band which was concentrated and taken up in the minimum volume of water. To this solution was added saturated aqueous KPF_6 and the product was then vigorously extracted into methylene chloride. The organic phase was evaporated to give a pale yellow solid of **4** (930 mg, 28% over two steps).

^{1}H NMR (500 MHz, CD_3CN): δ (ppm) 6.09 (s, 6H), 5.41 (t, $J = 1.8$, 2H), 5.27 (dd, $J = 1.8$, 1.7, 2H), 4.19 (d, $J = 4.6$, 2H), 3.44 (br s, OH, 1H). ^{13}C NMR (125 MHz, CD_3CN): δ (ppm) 105.0, 87.4, 81.0, 80.4, 58.0. IR (film): ν (cm^{-1}) 3605, 3374, 3103, 2933, 2875, 1646, 1445, 1414, 1391, 1236, 1184, 1054, 1026, 973, 921, 831. HRMS calc. for $C_{12}H_{13}ORu$ $(M)^+$ 275.0010, found $(M)^+$ 275.0012.

4.4. Synthesis of complex 1

To a 100 mL round bottomed flask containing alcohol **4** (923 mg, 2.2 mmol) was added 25 mL of CH_3CN. After cooling the reaction to 0 °C, $SOCl_2$ (0.50 mL, 6.9 mmol) was added over 10 min. Once addition of the $SOCl_2$ was completed, the ice bath was removed and the reaction allowed to warm to room temperature. After 2 h, the reaction was concentrated, taken up in the minimum volume of acetone, and pipetted slowly into 30 mL of saturated aqueous KPF_6. The solution was cooled to 4 °C for several hours before collecting the chalky white powder by vacuum filtration (845 mg, 88%).

^{1}H NMR (360 MHz, acetone-d_6): δ (ppm) 6.37 (s, 6H), 5.71 (dd, $J = 1.9$, 1.8, 2H), 5.53 (dd, $J = 1.9$, 1.8, 2H), 4.51 (s, 2H). ^{13}C NMR (90 MHz, acetone-d_6): δ (ppm) 101.7, 89.4, 83.1, 83.0, 41.2. IR (film): ν (cm^{-1}) 3098, 1696, 1644, 1442, 1402, 1277, 1239, 1147, 1066, 1034, 978, 919, 822, 741, 684. HRMS calc. for $C_{12}H_{12}ClRu$ $(M)^+$ 292.9671, found $(M)^+$ 292.9677.

4.5. Synthesis of complex 6

To a 25 mL round bottomed flask was added 2,6-pyridinedimethanol (**5**) (143 mg, 1.0 mmol) and a 60% NaH suspension in mineral oil (41 mg, 1.0 mmol) before cooling the flask to 0 °C. These solids were then suspended in 5 mL of dry DMF and allowed to stir for 1 h at 0 °C before dropwise addition of **1** (250 mg, 0.57 mmol) dissolved in 5 mL of DMF. The reaction was then allowed to slowly warm to room temperature overnight before being concentrated and subjected to flash chromatography over silica gel with a 100:3:1 CH_3CN/H_2O/saturated aqueous KNO_3 mobile phase. The product was concentrated and taken up in the minimum volume of water. To this solution was added saturated aqueous KPF_6 and the product was then extracted into methylene chloride. The organic phase was evaporated to give a clear oil of **6** (167 mg, 54%).

^{1}H NMR (500 MHz, CD_3CN): δ (ppm) 7.82 (t, $J = 7.7$, 1H), 7.38 (d, $J = 7.8$, 1H), 7.33 (d, $J = 7.6$, 1H), 6.09 (s, 6H), 5.46 (t, $J = 1.8$, 2H), 5.30 (t, $J = 1.8$, 2H), 4.67 (s, 2H), 4.65 (s, 2H), 4.24 (s, 2H), 2.7–2.1 (br s, 1H). ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 159.2, 156.1, 138.0, 121.2, 120.1, 100.9, 86.7, 80.5, 80.2, 74.3, 65.2, 64.3. IR (film): ν (cm^{-1}) 3707, 3594, 3370, 3107, 2920, 2845, 1723, 1586, 1449, 1399, 1261, 1149, 1099, 831. HRMS calc. for $C_{19}H_{20}NO_2Ru$ $(M)^+$ 396.0538, found $(M)^+$ 396.0527.

4.6. Synthesis of complex 7

To a 5 mL round bottomed flask was added **6** (131 mg, 0.242 mmol) which was dissolved in 910 μL of pH 6.7 phosphate buffer and 1.17 mL of acetonitrile. To this solution was added TEMPO (5.5 mg, 0.035 mmol) at room temperature and the solution was warmed to 35 °C. At this temperature, $NaClO_2$ (113 mg, 1.25 mmol) dissolved in 5% NaOCl (1.34 mL, 0.90 mmol) was added dropwise to the reaction under stirring, changing it from red to a pale yellow color. After stirring at 35 °C for 2 h, the reaction was concentrated and purified over a Fisher PrepSep C_{18} column by eluting with acetonitrile to give a pale yellow oil of **7** (68 mg, 69%).

^{1}H NMR (360 MHz, CD_3OD): δ (ppm) 7.92 (d, $J = 7.6$, 1H), 7.88 (t, $J = 7.6$, 1H), 7.51 (br d, $J = 7.7$, 1H), 6.21 (s, 6H), 5.60 (t, $J = 1.8$, 2H), 5.40 (t, $J = 1.8$, 2H), 4.78 (s, 2H), 4.30 (s, 2H). ^{13}C NMR (90 MHz, CD_3OD): δ (ppm) 173.1, 158.3, 156.6, 139.0, 124.2, 124.0, 101.7, 87.9, 81.3, 81.3, 74.9, 66.5. IR (film): ν (cm^{-1}) 3390, 3068, 2919, 1614, 1579, 1438, 1377, 1262, 1236, 1095, 1029, 994, 835, 778. HRMS calc. for $C_{19}H_{18}NO_3Ru$ $(M+H)^+$ 410.0330, found $(M+H)^+$ 410.0342.

4.7. Synthesis of complex rac-8

A clear solution of **7** (28 mg, 0.068 mmol) in acetonitrile (250 mL) was irradiated with a medium pressure Hg lamp using an uranium filter (50% transmission at 350 nm) for 3 h at 0 °C with constant argon flow through the solution. The resulting yellow solution was then stirred with a slow CO purge for 12 h. The solution was concentrated to dryness *in vacuo* and subjected to silica gel chromatography with acetonitrile to provide *rac*-**8** (13 mg, 53%) as an orange/yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.13 (dd, $J = 7.8$, 1.4, 1H), 7.93 (t, $J = 7.7$, 1H), 7.53 (dd, $J = 7.6$, 1.5, 1H), 5.74 (m, 1H), 5.28 (m, 1H), 5.02 (d, $J = 12.4$, 1H), 4.84 (d, $J = 13.4$, 1H), 4.76 (m, 1H), 4.66 (m, 1H), 4.35 (d, $J = 12.4$, 1H), 3.71 (d, $J = 13.4$, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 198.4, 172.6, 162.7, 153.6, 139.1, 127.7, 126.6, 104.4, 86.7, 85.7, 80.2, 73.8, 70.8, 64.8. IR (film): ν (cm^{-1}) 3421, 3081, 2914, 2865, 1942, 1645, 1602, 1459, 1348, 1238, 1145, 1072, 919, 899, 842, 772. HRMS calc. for $C_{14}H_{11}NNaO_4Ru$ $(M+Na)^+$ 381.9629, found $(M+Na)^+$ 381.9625.

4.8. Synthesis of complex **10**

To a 50 mL round bottomed flask was added α-picoline **9** (188 mg, 1.14 mmol) which was dissolved in 2 mL of dry THF and cooled to −20 °C. To this was added dropwise a 2.0 M solution of phenyl lithium in dibutylether (560 μL, 1.12 mmol). The reaction was allowed to stir at −20 °C for 15 min before a pre-cooled solution of precursor **1** (78 mg, 0.178 mmol) in THF (13 mL) was added at once. The reaction was allowed to warm slowly to room temperature overnight. The reaction was neutralized with saturated aqueous NH_4OAc before being concentrated and subjected to flash chromatography over silica gel with a 100:3:1 CH_3CN/H_2O/saturated aqueous KNO_3 mobile phase. The product was concentrated and taken up in the minimum volume of water. To this solution was added saturated aqueous KPF_6 and the product was then extracted into methylene chloride. The organic phase was evaporated to give an orange solid of **10** (46 mg, 46%).

^{1}H NMR (360 MHz, CD_3CN): δ (ppm) 7.73 (t, $J = 7.7$, 1H), 7.38 (d, $J = 7.7$, 1H), 7.22 (d, $J = 7.7$, 1H), 6.06 (s, 6H), 5.71 (s, 1H), 5.30 (dd, $J = 1.9$, 1.8, 2H), 5.20 (t, $J = 1.8$, 2H), 4.15-3.97 (m, 4H), 2.96 (m, 2H), 2.74 (m, 2H). ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 159.3, 156.8, 137.8, 123.8, 118.6, 104.2, 103.8, 86.3, 81.0, 80.1, 65.7, 38.4, 27.5. IR (film): ν (cm^{-1}) 3100, 2958, 2916, 2852, 1595, 1578, 1459, 1443, 1402, 1366, 1105, 1026, 965, 839. HRMS calc. for $C_{21}H_{22}NO_2Ru$ $(M)^+$ 422.0694, found $(M)^+$ 422.0713.

4.9. Synthesis of complex **11**

To a 25 mL round bottomed flask was added **10** (133 mg, 0.24 mmol) which was dissolved in 15 mL of 4 M HCl and heated to 65 °C overnight. The reaction was neutralized with saturated $NaHCO_3$ and the product was extracted from the aqueous layer with methylene chloride. The organic layer was dried with $MgSO_4$ and evaporated to give a pale yellow solid of **11** (114 mg, 93%).

^{1}H NMR (360 MHz, CD_3CN): δ (ppm) 10.0 (s, 1H), 7.90 (t, $J = 7.7$, 1H), 7.81 (dd, $J = 7.7$, 1.1, 1H), 7.48 (dd, $J = 7.6$, 1.0, 1H), 6.09 (s, 6H), 5.32 (t, $J = 1.8$, 2H), 5.22 (t, $J = 1.8$, 2H), 3.08 (m, 2H), 2.81 (m, 2H). ^{13}C NMR (90 MHz, CD_3CN): δ (ppm) 194.6, 162.1, 153.6, 138.9, 128.6, 120.8, 104.7, 87.3, 81.8, 80.6, 38.9, 28.0. IR (film): ν (cm^{-1}) 3097, 2918, 2849, 1711, 1592, 1463, 1443, 1403, 1212, 1152, 920, 839. HRMS calc. for $C_{19}H_{18}NORu$ $(M)^+$ 378.0432, found $(M)^+$ 378.0434.

4.10. Synthesis of complex *rac*-**13**

To a 50 mL round bottomed flask was added complex **11** (114 mg, 0.218 mmol), which was dissolved in 25 mL of formic acid and cooled to 0 °C. After cooling with an ice bath, 35% aqueous H_2O_2 (64 μL, 0.654 mmol) was added and the reaction was allowed to stir at 0 °C. After 2.5 h the reaction mixture was concentrated to give crude complex **12** (117 mg) as a white solid. A clear solution of **12** (33 mg, 0.061 mmol) in acetonitrile (250 mL) was irradiated with a medium pressure Hg lamp using an uranium filter (50% transmission at 350 nm) for 3 h at 0 °C with constant argon flow through the solution. The resulting yellow solution was stirred with a slow CO purge for 12 h. The solution was then concentrated to dryness *in vacuo* and subjected to silica gel chromatography with neat acetone to provide *rac*-**13** (9.0 mg, 43% over three steps) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.01 (d, $J = 7.8$, 1H), 7.89 (dd, $J = 7.7$, 7.6, 1H), 7.52 (d, $J = 7.8$, 1H), 5.62 (m, 1H), 4.82 (m, $J = 1.7$, 1H), 4.77 (m, $J = 2.0$, 1H), 4.07 (m, 1H), 3.39–3.35 (m, 1H), 2.66–2.58 (m, 2H), 1.86 (ddd, $J = 13.8$, 13.7, 2.8, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 198.2, 172.4, 160.1, 153.0, 138.7, 126.1, 124.4, 102.4, 92.7, 83.0, 73.4, 63.9, 42.3, 22.8. IR (film): ν (cm^{-1}) 3088, 2926, 2854, 1940, 1639, 1603, 1463, 1436, 1409, 1355, 1332, 1265, 1152, 1085, 837, 774, 729. HRMS calc. for $C_{14}H_{12}NO_3Ru$ $(M+H)^+$ 343.9860, found $(M+H)^+$ 343.9862.

4.11. Crystal structure determination of complex *rac*-**13**

Crystals of *rac*-**13** suitable for X-ray crystal structure determination were obtained by slow diffusion of pentane into chloroform. X-ray intensity data were collected on a Rigaku Mercury CCD area detector employing graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) at a temperature of 143 K. Table 1 lists cell information, data collection parameters, and refinement data. Rotation images were processed using CrystalClear, producing a listing of unaveraged F^2 and $\sigma(F^2)$ values which were then passed to the CRYSTALSTRUCTURE program package for further processing and structure solution. The intensity data were corrected for Lorentz and polarization effects and for absorption using REQAB (minimum and maximum transmission 0.787, 1.000). The structure was solved by direct methods (SIR97) [13]. Refinement was done by full-matrix least squares based on F^2 using SHELXL-97 [14]. All reflections were used during refinement (F^2 values that were experimentally negative were replaced by $F^2 = 0$). The weighting scheme used was $w = 1/[\sigma^2(F_o^2) + 0.0306P^2 + 0.4645P]$, where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms

Table 1
Crystal data and structure refinement for complex *rac*-**13**

Chemical formula	$C_{14}H_{11}NO_3Ru \cdot CHCl_3$
Formula weight	461.68
Temperature (K)	143
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	7.0349(8)
b (Å)	9.7815(13)
c (Å)	11.9494(14)
α (°)	88.492(7)
β (°)	84.078(6)
γ (°)	83.031(5)
Volume (Å^3)	811.8(2)
Z	2
μ (cm^{-1})	14.71
Crystal size (mm)	$0.38 \times 0.33 \times 0.10$
D_{calc} (g/cm^3)	1.889
$F(000)$	456
Radiation	Mo Kα ($\lambda = 0.71073$Å)
2θ range (°)	5.38–54.92
hkl collected	$-8 \leqslant h \leqslant 9$; $-12 \leqslant k \leqslant 10$; $-15 \leqslant l \leqslant 12$
Reflections measured	9631
Unique reflections	3676 ($R_{int} = 0.0192$)
Observed reflections	3458 ($F > 4\sigma$)
Reflections used in refinement	3676
Parameters	209
R indices ($F > 4\sigma$)	$R_1 = 0.0259$
	$wR_2 = 0.0601$
R indices (all data)	$R_1 = 0.0279$
	$wR_2 = 0.0616$
GOF	1.086
Final difference peaks (e/Å^3)	+0.751, −1.084

were refined anisotropically and hydrogen atoms were refined using a riding model.

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