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η^6-Arene complexes of ruthenium and osmium with pendant donor functionalities

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ABSTRACT

Conversion of 4′-(2,5-dihydrophenyl)butanol or N-trifluoroacetyl-2,5-dihydrobenzylamine with $MCl_3 \cdot n H_2O$ (M = Ru, Os) affords the corresponding dimeric η^6-arene complexes in good to excellent yields. Under similar reaction conditions, the amine functionalized arene precursor 2,5-dihydrobenzylamine yields the corresponding Ru(II) complex. For osmium, HCl induced oxidation leads to formation of $[OsCl_6]^{2-}$ salts. However, under optimized reaction conditions, conversion of the precursor 2,5-dihydrobenzylamine chloride results in clean formation of η^6-arene Os(II) complex. X-ray structures of [(η^6-benzyl ammonium)(dmso)$RuCl_2$] and (2,5-dihydrobenzyl ammonium)$_4[OsCl_6]_2$confirm the spectroscopic data. High stability towards air and acid as well as enhanced solubility in water is observed for all η^6-arene complexes.

1. Introduction

Halide bridged half sandwich complexes of ruthenium and osmium have been investigated for several decades [1,2]. They have attracted considerable attention due to a wide range of applications including building blocks for supramolecular structures [3], catalysts for transfer hydrogenations [4], hydrogenations [5], C–C couplings [6] as well as biomarkers [7] and bio-active compounds [8]. In particular the *in vivo* and *in vitro* cytotoxicity of η^6-arene M(II) complexes (M = Ru, Os) has recently triggered intense research activity targeting the design of organometallic anti cancer agents [9]. Hence, η^6-arene complexes exhibiting reactive functionalization have raised major interest, since they may be conjugated to proteins [10], enzymes [11] or allow to tune the hydrophobicity and bioavailability for *in vivo* applications [12]. Some reports about functionalized η^6-arene ruthenium(II) complexes exist in literature [13]. For example, η^6-arenes with pendant carboxylate groups [14,15], alcohols [16], or even amino acids [17–20] have been synthesized (**A**, Fig. 1). Several examples of η^6:η^1-arenes which include an additional tether at the metal centre are known, comprising functional groups such as alcohols [21], amides [22,15] or carbenes [23–25].

Solubility in aqueous solutions is crucial for bioavailability of organometallic systems, hence studies were reported targeting improved uptake, biomolecular interactions and efficacy of η^6-arene ruthenium(II) systems via side chain functionalization of the arene ligand [12]. Recently, several reports have emphasized the antiproliferate activity of η^6-arene complexes of osmium and their potential to serve as chemotherapeutics (**B**) [26,27]. Esteruelas et al. published η^5-cyclopentadiene half-sandwich complexes of osmium (II) with pendant amino group, which were generated from Os(IV) hydride precursors (**C**) [28]. However, to the best of our knowledge, no example of η^6-arene osmium(II) species comprising a reactive side-chain functionalization has been described, yet.

Hence, we became interested in exploring synthetic routes to η^6-arene ruthenium and osmium half-sandwich complexes providing pendant reactive functionalities. While the half-sandwich architecture of such complexes is particularly important to generate the desired reactivity profile, the labile coordination sphere at the metal center may complicate synthetic access due to additional coordination of the side chain [15]. We herein report the synthesis of three new μ-chloro-bridged η^6-arene ruthenium(II) complexes as well as the first examples of functionalized η^6-arene osmium(II) species providing a pendant reactive donor moiety. Our approach utilizes dehydrogenative coordination of cyclohexadiene derivatives utilizing ruthenium(III) chloride or osmium(III) chloride [1,2].

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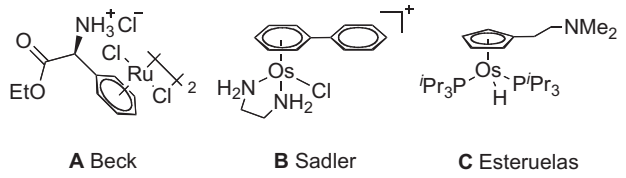


Fig. 1. Various η^6-arene Ru(II) and Os(II) complexes, presented by Beck (**A**) [18], Sadler (**B**) [27], and Esteruelas (**C**) [28].

2. Results and discussion

Dimeric μ-chloro-bridged complexes **2** and **3** are readily formed upon conversion of 4′-(2,5-dihydrophenyl)butanol with the respective M(III) chlorides (M = Ru, Os) in refluxing ethanol (Scheme 1). The products are obtained as brown powders in good yields and excellent purity, if the reaction is carried out under an atmosphere of argon. For the osmium complex **3**, use of dry ethanol is mandatory to achieve satisfactory product formation. Complexes **2** and **3** are moderately soluble in alcohols yet dissolve readily in donor solvents such as water and DMSO. Both were characterized by elemental analysis, ^{1}H-NMR, ^{13}C-NMR and IR spectroscopy. Resonances for the η^6-arene moieties show a typical upfield shift compared to non-coordinated arenes.

^{13}C-NMR resonances for the arene carbons of monomeric $\mathbf{2}^{DMSO}$ and $\mathbf{3}^{DMSO}$ in DMSO-d_6 are observed between 109 ppm and 75 ppm. For the osmium(II) complex **3**, signals are shifted 7 to 8 ppm upfield, compared to the analogous ruthenium(II) complex **2** (Fig. 2). This indicates a weaker ring current for the Os(II) compound, which might be explained by an increased transfer of electron density from the ligand π-system to metal centered orbitals, since the interacting 6s and 5d orbitals (osmium) are lower in energy than the respective 5s and 4d orbitals (ruthenium) [29].

There are no spectroscopic indications of an interaction between the alcohol functionality and the metal centre. For the Ru (II) complex **2**, the O*H*-resonance observed by ^{1}H-NMR in DMSO-d_6 is nearly identical to that of 4′-phenylbutanol with a triplet around $\delta = 4.4$ ppm and a $^3J_{HH}$ coupling constant of the expected 5 Hz [30]. The corresponding signal for Os(II) derivative **3** appears slightly broadened and is shifted upfield to $\delta = 3.8$ ppm. They are stable under aerobic conditions for several months without any apparent signs of decomposition. Even in a combination of 1 M of hydrochloric acid in water and DMSO, no change of the arene resonances was detected over a period of several days.

To introduce a tether with an amine based functionality, M(III) chlorides (M = Ru, Os) were reacted with N-trifluoroacetyl-dihydrobenzylamide **5** (Scheme 2). The dihydro precursor was obtained from dihydrobenzylamine **4** and trifluoroacetic acid anhydride using standard acetylation protocols [31]. For both, Ru(II) and Os(II) respective η^6-arene complexes were obtained. Similar to complex **3**, dry ethanol was necessary to obtain osmium compound **7**. ^{1}H-NMR spectra indicate that the amide nitrogen does not coordinate to the metal centre ($\mathbf{6}^{DMSO}$: 9.95 ppm, N*H*; $\mathbf{7}^{DMSO}$: 9.91 ppm, N*H*). ^{19}F-NMR spectra show a pronounced singlet with an almost identical shift for **6** and **7** ($\mathbf{6}^{DMSO}$: −75.72 ppm; $\mathbf{7}^{DMSO}$: −74.19 ppm). ^{13}C-NMR

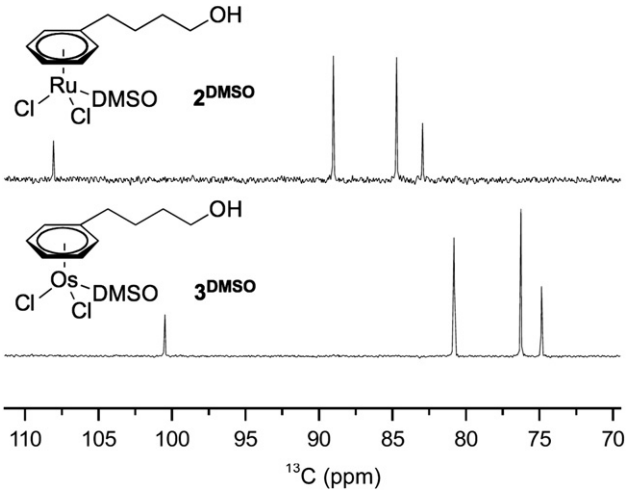
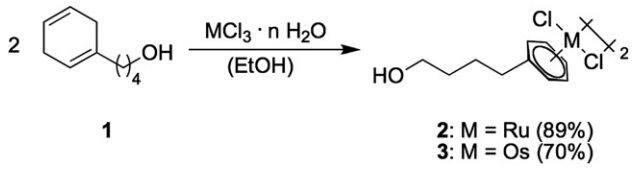


Fig. 2. Aromatic ^{13}C NMR resonances of complexes $\mathbf{2}^{DMSO}$ and $\mathbf{3}^{DMSO}$ (100.5 MHz, 300 K, DMSO-d_6).

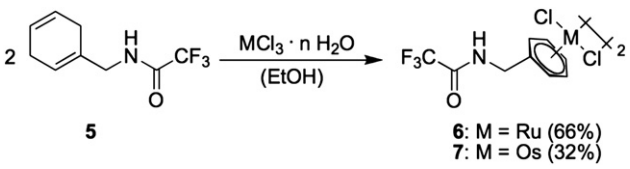
resonances for the arene carbons of monomeric $\mathbf{6}^{DMSO}$ in DMSO-d_6 are observed between 100 ppm and 86 ppm. As observed for osmium(II) complex **3**, signals of **7** appear significantly more upfield (90 ppm to 78 ppm), compared to the analogous ruthenium(II) complex **6** (Fig. 2).

While synthesis of alcohol and trifluoracetamide functionalized η^6-arene complexes is straight forward, conversion of ω-(2,5-dihydrophenyl)alkyl amines with M(III) chlorides (M = Ru, Os) under similar conditions does not afford any identifiable product. This may be attributed to the high affinity of the amine tethers towards electrophilic cationic d^6 metal centres impairing arene coordination. Hence, to prevent coordination of the amino functionality, 2,5-dihydrobenzyl amine **4** was protonated by dissolving it in a 2 M solution of HCl in ethyl acetate prior to addition of the metal chloride (Scheme 3) [17]. Under the acidic reaction conditions, Ru(II) complex **8** formed in good yields as an ochre powder. It is virtually insoluble in aprotic media like dichloromethane and acetone and only slightly soluble in alcohols yet dissolves readily in donor solvents such as water and DMSO. According to ^{1}H and ^{13}C NMR spectrometry as well as elemental analysis and IR, complex **8** was obtained as its hydrochloride salt. The ammonium protons give rise to a distinct singlet at $\delta = 8.80$ ppm in ^{1}H NMR. Resonances corresponding to aromatic carbons appear between 93.4 ppm and 86.9 ppm in ^{13}C NMR, which again represents a typical upfield shift in comparison to non-coordinated arenes. Complex $\mathbf{8}^{DMSO}$ crystallized from a concentrated solution in DMSO-d_6 within several days at room temperature (Fig. 3, Table 1). The molecular structure was derived by single crystal X-ray diffraction and solved in the centrosymmetric space group $P2_1/c$. It reveals a η^6-arene Ru(II) dichloride motive, which is electronically saturated by an DMSO ligand featuring typical S-coordination [32].

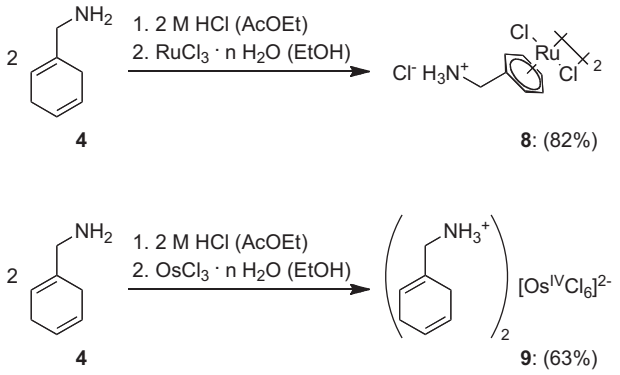
In solid state, each ammonium hydrogen is part of a N—H—Cl hydrogen bond. An intramolecular interaction with Cl(2) is evident



Scheme 1. Synthesis of compounds **2** and **3**.



Scheme 2. Synthesis of compounds **6** and **7**.



Scheme 3. Synthesis of Ru(II) complexes **8** and Os(IV) salt **9**.

from distance ($R_{H\text{-}Cl(2)} = 2.73(1)$ Å) and angle ($\angle_{N\text{-}H\text{-}Cl(2)} = 162.2(1)^\circ$) criteria [33]. Two additional short intermolecular hydrogen bonds connect the ammonium moieties and the chloride counter ions by a two-dimensional zig-zag motive ($d_{H\text{-}Cl} = 2.28(1)/2.25(1)$ Å). Hydrogen bonding between the ammonium moiety and the DMSO-O can be excluded due to a minimal O—H distance of 2.674 Å and a respective N—H—O angle of 100.6(4)°.

In contrast to synthesis of Os(II) complex **3**, reaction of 2,5-dihydrobenzyl ammonium chloride with Os(III) chloride under acidic conditions (HCl) reproducibly yields the Os(IV) salt **9** as deep red crystals in good yields (Scheme 3). The crystalline reaction product consists of the well known, stable osmate(IV) dianion $[OsCl_6]^{2-}$, counterbalanced by two 2,5-dihydrobenzylammonium cations. ^1H and ^{13}C NMR spectra of the reaction mixture only exhibit signals corresponding to the 2,5-dihydrobenzyl ammonium cation. Absence of aromatic or η^6-arene signals clearly indicates that oxidation of the ligand precursor by Os(III) chloride does not take place under these conditions.

Complex **9** was crystallized from the reaction mixture (Fig. 4, Table 1). The structure, which was solved in space group $P2_1/c$, features the octahedral $[OsCl_6]^{2-}$ dianion surrounded by two hydrogen bonded 2,5-dihydrobenzylammonium cations ($R_{H\text{-}Cl} = 2.48(1)$ Å). Os-Cl bond lengths are significantly elongated for the two chloride ligands Cl(1) ($R_{Os\text{-}Cl(1)} = 2.3588(5)$Å) and Cl(2) ($R_{Os\text{-}Cl(2)} = 2.3427(6)$ Å) which are participating in hydrogen bonding, if compared to the average of the other four Os-Cl bonds ($R = 2.3284$ Å). In agreement with NMR, alternating C—C bond lengths indicate the cations to be 2,5-dihydrobenzyl ammonium and not benzyl ammonium. Formation of Os(IV) complex **9** under acidic conditions, which are well suited for the synthesis of η^6-arene Ru(II) complexes may be attributed to the well established tendency of 5d vs. 4d transition metals to prefer higher oxidation states [34].

Table 1
Crystallographic data for complexes $\mathbf{8}^{DMSO}$ and **9**.

	$\mathbf{8}^{DMSO}$	**9**
Formula	$C_9H_{16}Cl_3N_1O_1Ru_1S_1$	$C_{28}H_{48}Cl_{12}N_4Os_2$
Formula wt	393.71	1246.50
Space group	$P2_1/c$	$P2_1/c$
a (Å)	7.660(5)	12.228(2)
b (Å)	21.030(5)	13.715(3)
c (Å)	8.260(5)	24.472(5)
α (deg)	90	90
β (deg)	91.264(5)	97.69(3)
γ (deg)	90	90
V (Å^3)	1330.3(12)	4067.3(14)
Z	4	4
D_{calc} (g cm^{-3})	1.966	2.036
No. of indep rflns	2465	7420
No. of params	147	410
$R1$ ($I > 2\sigma(I)$)	0.0494	0.0327
w$R2$ (all data)	0.0868	0.0708
Goodness of fit	0.690	0.992

Since rigorous exclusion of oxygen did not change the outcome of the reaction the most likely oxidant is the added hydrochloric acid. Direct conversion of the 2,5-dihydrobenzyl amine with osmium(III) chloride only resulted in formation of a black tar, which showed a plethora of signals in the aromatic region in ^1H- and ^{13}C-NMR when dissolved in DMSO. However, if the hydrochloride salt of 2,5-dihydrobenzyl amine $\mathbf{4}^{HCl}$ is used, the ammonium salt's small dissociation constant ensures a proton concentration low enough to restrict oxidative formation of Os(IV) salts, while efficiently preventing coordination of the amino function to the Os-center. Additionally, the low chloride concentration limits formation of the stable $[OsCl_6]^{2-}$

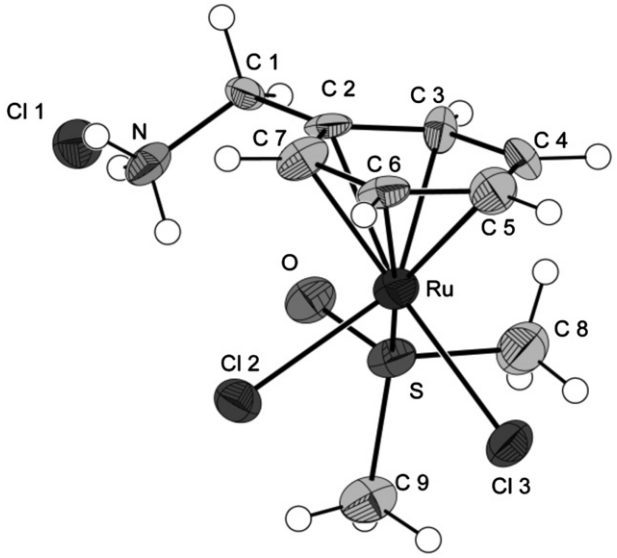


Fig. 3. ORTEP drawing of complex $\mathbf{8}^{DMSO}$ (50% thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Ru-C(2) 2.204(8), Ru-C(3) 2.184(9), Ru-C(4) 2.219(8), Ru-C(5) 2.191(10), Ru-C(6) 2.162(9), Ru-C(7) 2.144(8), Ru-S 2.331(3), Ru-O 3.201(6),C(2)-C(1)-N 112.6(7), Cl(2)-Ru-Cl(3) 88.57(9), Cl(2)-Ru-S 85.49(9), Cl(3)-Ru-S 84.80(9).

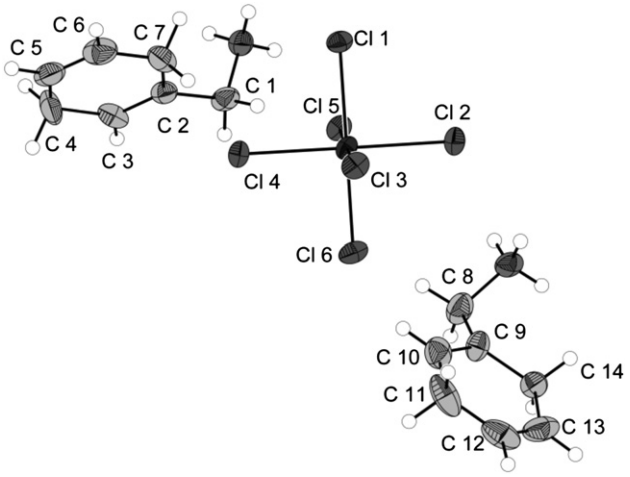
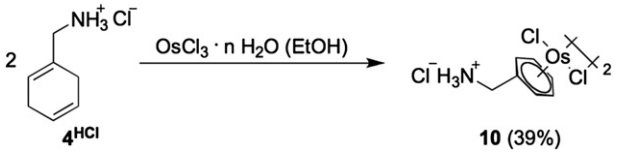


Fig. 4. ORTEP drawing of **9** (50% thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Os-Cl(1) 2.3588(5), Os-Cl(2) 2.3427(6), Os-Cl(3) 2.3110(4), Os-Cl(4) 2.3386(6), Os-Cl(5) 2.3391(4), Os-Cl(6) 2.3249(5), C(2)-C(3) 1.3298(2), C(3)-C(4) 1.4751(3), C(4)-C(5) 1.4490(3), C(5)-C(6) 1.3309(2), C(6)-C(7) 1.4699(3), C(7)-C(2) 1.4696(3).



Scheme 4. Synthesis of compound **10**.

dianion. Correspondingly, reaction with $OsCl_3 \cdot n\ H_2O$ in dry ethanol yields the respective η^6-arene complex **10** (Scheme 4).

In ^{1}H-NMR, the ammonium protons are observed as a singlet at $\delta = 8.52$ ppm. ^{13}C-NMR resonances corresponding to aromatic carbons appear between 85 ppm and 78 ppm, again shifted upwards compared to the analogue ruthenium complex (**8**: 93.4 ppm to 86.9 ppm). The synthesis of complex **10** with 2,5-dihydrobenzyl ammonium chloride $\mathbf{4}^{HCl}$ and $OsCl_3 \cdot n\ H_2O$ was also carried out successfully in the presence of trifluoroacetic acid (EtOH/TFA = 9/1), confirming excess of HCl to be the reason for the oxidation observed, presumably due to the reduced oxidation potential resulting from formation of the very stable $[OsCl_6]^{2-}$ anion.

3. Conclusion

This study reports the synthesis of η^6-arene complexes of Os(II) and Ru(II) with alcohol, trifluoroacetamide and ammonium pendant functional groups. Furthermore, it reveals distinct reactivity differences for ruthenium and osmium during the conversion of the respective metal(III) chlorides with 2,5-dihydro arenes comprising amine-functionalized side chains. In contrast to clean formation of the Ru(II) η^6-benzyl ammonium complex **8** in the presence of excess hydrochloric acid, the corresponding Os(II) compound did not form due to predominant oxidation to [Os(IV)$Cl_6]^{2-}$ **9**. However, the successful formation of the analogue η^6-benzyl ammonium chloride Os(II) complex **10** was achieved when using the hydrochloride salt of 2,5-dihydrobenzyl amine $\mathbf{4}^{HCl}$. Complexes **3**, **7** and **10** are the first examples of η^6-arene complexes of osmium(II) with pendant functional groups. Stability against air, moisture, water and acid in combination with an enhanced solubility in aqueous media qualify such compounds as potential precursors for biological probes in drug development.

4. Experimental

4.1. General remarks

Commercially available solvents and reagents were purified according to literature procedures. All reactions were carried out in degassed solvents under an argon atmosphere. $RuCl_3 \cdot n\ H_2O$ and $OsCl_3 \cdot n\ H_2O$ were obtained from Sigma–Aldrich and used without further purification. Cyclohexadiene derivatives 4′-(2,5-dihydrophenyl)butanol **1** and 2,5-dihydro-benzylamine **4** were prepared as previously reported [10,35]. Elemental analyses were obtained from the Microanalytical Laboratory of Technische Universität München. Spectroscopic data were recorded on the following instruments: IR spectra: Jasco FT/IR-460 PLUS (KBr pellets); NMR spectra: JEOL JNM-GX 400 (^{1}H NMR 400.13 MHz, ^{13}C NMR 100.53 MHz, ^{19}F NMR 376.2), $T = 300$ K. Signals were calibrated to the residual proton resonance respectively the natural abundance ^{13}C resonance of the solvent (DMSO-d_6, $\delta_H = 2.50$ and $\delta_C = 39.52$ ppm; $CDCl_3$, $\delta_H = 7.26$ and $\delta_C = 77.16$ ppm; CD_3OD $\delta_H = 3.31$ and $\delta_C = 49.00$ ppm). Signal multiplicities are abbreviated as: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), br (broad).

4.2. Preparation of [(η^6-4′-phenylbutanol)$RuCl_2$]$_2$ (**2**)

A solution of 4′-(2,5-dihydrophenyl)butanol **1** (1.17 g, 7.65 mmol) in ethanol (60 mL) was added to $RuCl_3 \cdot n\ H_2O$ (400 mg, 1.53 mmol). The reaction mixture was heated to reflux for 16 h and subsequently cooled to −18 °C. The precipitate was filtered off, washed with cold ethanol and pentane (each 2 × 5 mL) and the brown precipitate was dried *in vacuo*. Yield: 89% (438 mg, 0.68 mmol). – $C_{20}H_{28}Cl_4O_2Ru_2$ (644.4): calcd. C 37.28, H 4.38; found C 37.08, H 4.24. – IR (KBr): $\tilde{\nu} = 2930$ vs, 2874 s, 1456 w, 1442 s, 1406 s, 1379 w, 1186 w, 1145 w, 1076 vs, 1029 w, 981 s, 868 s, 858 s cm^{-1}. – ^{1}H-NMR (400 MHz, DMSO-d_6): $\delta = 5.98$ (t, $^3J = 5.6$, 4 H, $C_{meta}H$), 5.75–5.71 (m, 6 H, $C_{ortho}H$, $C_{para}H$), 4.42 (t, $^3J = 5.0$, 2 H, –O*H*), 3.41 (q, $^3J = 5.7$, 4 H, $C_{(1)}H_2$), 2.44 (t, $^3J = 7.7$, 4 H, $C_{(4)}H_2$), 1.61 (quint, $^3J = 6.8$, 4 H, $C_{(3)}H_2$), 1.47 (quint, $^3J = 6.4$, 4 H, $C_{(2)}H_2$). – ^{13}C-NMR (100.5 MHz, DMSO-d_6): $\delta = 108.1$, 89.0, 84.7, 83.0 (C_{arom}), 60.3 ($C_{(1)}H_2$), 32.4/32.0/25.6 ($C_{(2)}H_2$/$C_{(3)}H_2$/$C_{(4)}H_2$).

4.3. Preparation [(η^6-4′-phenylbutanol)$OsCl_2$]$_2$ (**3**)

4′-(2,5-dihydrophenyl)butanol **1** (282 mg, 1.85 mmol) was added to a suspension of $OsCl_3 \cdot n\ H_2O$ (109 mg, 0.37 mmol) dry ethanol (20 mL). The resulting slurry was heated to reflux for 16 h and subsequently cooled to −18 °C. The precipitate was filtered off, washed with cold ethanol and pentane (each 2 × 2.5 mL) and the brown product was dried *in vacuo*. Yield: 70% (107 mg, 0.13 mmol). – $C_{20}H_{28}Cl_4O_2Os_2$ (822.7): calcd. C 29.20, H 3.43; found C 28.66, H 3.52. – IR (KBr): $\tilde{\nu} = 2930$ vs, 2875 vs, 1455 s, 1433 s, 1399 s, 1184 w, 1137 w, 1074 vs, 1026 w, 980 s, 950 w, 874 s cm^{-1}. – ^{1}H-NMR (400 MHz, DMSO-d_6): $\delta = 6.19$ (t, $^3J = 5.4$, 4 H, $C_{meta}H$), 6.02 (t, $^3J = 5.2$, 4 H, $C_{ortho}H$), 5.95 (d, $^3J = 5.8$, 2 H, $C_{para}H$), 3.80 (br, 2 H, O*H*), 3.41 (t, $^3J = 6.4$, 4 H, $C_{(1)}H_2$), 2.37 (t, $^3J = 7.7$, 4 H, $C_{(4)}H_2$) , 1.61 (quint, $^3J = 7.2$, $^3J = 7.6$, 4 H, $C_{(3)}H_2$), 1.47 (quint, $^3J = 7.6$, $^3J = 6.8$, 4 H, $C_{(2)}H_2$). – ^{13}C-NMR (100.5 MHz, DMSO-d_6): $\delta = 100.5$, 80.8, 76.3, 74.9 (C_{arom}), 60.3 ($C_{(1)}H_2$), 32.2/32.1/25.9 ($C_{(2)}H_2$/$C_{(3)}H_2$/$C_{(4)}H_2$).

4.4. Preparation of N-trifluoroacetyl-1′,4′-cyclohexadiene-1-benzyl amine (**5**)

To a stirred, cooled solution (0 °C) of 2,5-dihydrobenzyl amine **4** (543 mg, 3.74 mmol) in dichloromethane (4 mL) first pyridine (440 μL) and then slowly a solution of trifluoroacetic acid anhydride (510 μL) in dichloromethane (1 mL) was added. The reaction mixture was stirred for 2 h at 0 °C and over night at room temperature. Then, water was slowly added (4 mL) and the reaction mixture extracted with dichloromethane (3 × 5 mL). The organic phase was dried over $MgSO_4$ and volatiles removed under reduced pressure, yielding an ivory powder. Yield: 84% (647 mg, 3.16 mmol). – $C_9H_{10}F_3NO$ (750.27): calcd. C 52.68, H 4.91, N 6.83; found C 52.28, H 4.89, N 6.56.– IR (KBr):$\tilde{\nu} = 3291$ s, 3098 w, 2887 m, 2862 w, 2828 m, 1699 vs (C=O), 1560 s, 1435 m, 1367 m, 1251 s, 1181 vs cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.44$ (m, 1 H, N*H*), 5.69 (m, 2 H, C(7)*H*/C (8)*H*), 5.65 (m, 1 H, C(5)*H*), 3.87 (d, $^3J_{(H,H)} = 6.2$, 2 H, $C(3)H_2$), 2.73–2.58 (m, 4 H, $C(6)H_2$; $C(9)H_2$). – ^{13}C-NMR (100.5 MHz, $CDCl_3$): $\delta = 157.4$ (q, $^2J_{FC} = 36.9$, *C*(1)), 130.1 (*C*(4)), 124.0/123.5/122.9 (*C*(5)/*C*(7)/*C*(8)), 116.0 (q, $^1J_{FC} = 287.5$, *C*(2)), 45.6 (*C*(3)), 27.2/26.6 (*C*(6)/*C*(9)). – ^{19}F-NMR (376.2 MHz, $CDCl_3$): $\delta = -75.72$.

4.5. Preparation of [(η^6-N-trifluoroacetyl-benzylamine)$RuCl_2$]$_2$ (**6**)

To a stirred, degassed solution of N-trifluoroacetyl-2,5-dihydrobenzyl amine **5** (288 mg, 1.51 mmol) in ethanol (10 mL) $RuCl_3 \cdot n\ H_2O$ (68 mg, 0.26 mmol) was added and the resulting solution heated for 16 h at 80 °C. The reaction mixture was cooled

to −10 °C for 24 h, filtered and the precipitate washed with a small amount of ethanol and dichloromethane. The reaction product was dried *in vacuo*, yielding an ochre powder. Yield: 66% (64.3 mg, 0.09 mmol). – $C_{18}H_{16}Cl_4F_6N_2O_2Ru_2$ (750.27): calcd. C 28.82, H 2.15, N 3.73; found C 28.71, H 2.24, N 3.72. – IR (KBr):$\tilde{\nu}$ = 3244 s, 3073 m, 1736 vs (C=O), 1555 m, 1449 m, 1423 m, 1227 vs, 1193 m, 1159 vs, 989 m cm^{-1}. – ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 9.95 (m, 2 H, N*H*), 6.08 (t, ^3J = 5.0, 4 H, $C_{meta}H$), 5.93 (d, ^3J = 5.0, 4 H, $C_{ortho}H$), 5.88 (d, ^3J = 5.0, 2 H, $C_{para}H$), 4.26 (d, ^3J = 4.6, 4 H, CH_2). – ^{13}C NMR (100.5 MHz, DMSO-d_6): δ = 157.3 (q, $^2J_{FC}$ = 36.6, *C*(1)), 116.3 (q, $^1J_{FC}$ = 287.5, *C*(2)), 99.7, 88.6, 87.4, 86.0 (C_{arom}), 41.5 (C_3). – ^{19}F NMR (376.2 MHz, DMSO-d_6): δ = −74.17.

4.6. Preparation of [(η^6-N-trifluoroacetyl-benzylamine)$OsCl_2$]$_2$ (**7**)

To a stirred solution of N-trifluoroacetyl-2,5-dihydrobenzyl amine **5** (288 mg, 1.51 mmol) in dry ethanol (10 mL) $OsCl_3 \cdot n\ H_2O$ (30 mg, 0.10 mmol) was added and the resulting solution heated for 16 h at 80 °C. The reaction mixture was allowed to cool down to room temperature, filtered and the precipitate subsequently washed with a small amount of ethanol. The reaction product was dried *in vacuo*, yielding a green powder. Yield: 32% (14.9 mg, 0.03 mmol). – $C_{18}H_{16}Cl_4F_6N_2O_2Os_2$ (928.59): calcd. C 23.28, H 1.74, N 3.02; found C 22.55, H 1.63, N 2.91. – IR (KBr): $\tilde{\nu}$ = 3269 s, 3075 m, 1738 vs (C=O), 1553, s, 1428 m, 1227 vs, 1193 s, 1158 vs, 990 m cm^{-1}. – ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.91 (m, 2 H, N*H*), 6.29 (t, ^3J = 5.2, 4 H, $C_{meta}H$), 6.15–6.14 (m, 6 H, $C_{ortho}H$, $C_{para}H$), 4.17 (d, ^3J = 5.4, 4 H, CH_2). – ^{13}C NMR (100.5 MHz, DMSO-d_6): δ = 156.6 (q, $^2J_{FC}$ = 36.9, *C*(1)), 115.8 (q, $^1J_{FC}$ = 287.6, *C*(2)), 90.4, 79.6, 79.1, 77.6 (C_{arom}), 41.2 (C_3). – ^{19}F NMR (376.2 MHz, DMSO-d_6): δ = −74.19.

4.7. Preparation of [(η^6-benzyl ammonium)$RuCl_2$]$_2Cl_2$ (**8**)

2,5-dihydrobenzyl amine **4** (1.11 g, 7.65 mmol) was stirred with a solution of 20 mL of HCl in ethyl acetate (approx. 2 M). To this solution, $RuCl_3 \cdot n\ H_2O$ (400 mg, 1.53 mmol) in 40 mL of ethanol was added and subsequently heated to reflux for 16 h. The resulting suspension was reduced to half the volume under reduced pressure, cooled to −10 °C for 48 h and filtered. The precipitate was washed with cold pentane and ethanol (each 3 × 5 mL) and the ochre powder was dried *in vacuo*. Yield: 82% (401 mg, 0.64 mmol). – $C_{14}H_{20}Cl_6N_2Ru_2$ (631.2): calcd. C 26.64, H 3.19, N 4.44; found C 26.90, H 3.40, N 4.27. – IR(KBr): $\tilde{\nu}$ = 3052 vs, 2912 vs, 1594 s, 1489 s, 1455 m, 1384 m, 1203 w, 1111 w, 1088 w, 876 s cm^{-1}. – ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.80 (s, 6 H, NH_3^+), 6.23 (d, ^3J = 5.8, 4 H, $C_{ortho}H$), 6.13 (t, ^3J = 5.8, 4 H, $C_{meta}H$), 5.98 (t, ^3J = 5.6, 2 H, $C_{para}H$), 3.81 (s, 4 H, CH_2). – ^{13}C NMR (100.5 MHz, DMSO-d_6): δ = 93.4, 89.3, 87.3, 86.9 (C_{arom}), 40.6 (CH_2).

4.8. Preparation of (2,5-dihydrobenzyl ammonium)$_4$[$OsCl_6$]$_2$ (**9**)

2,5-dihydrobenzyl amine **4** (280 mg, 1.93 mmol) was stirred with a solution of 20 mL of HCl in ethyl acetate (approx. 2 M). To this solution, $OsCl_3 \cdot n\ H_2O$ (150 mg, 0.51 mmol) in 20 mL of EtOH was added and subsequently heated to reflux for 16 h. The resulting suspension was reduced to half the volume under reduced pressure, cooled to −10 °C for 48 h and filtered. The precipitate was washed with cold pentane and ethanol (each 3 × 5 mL) and the red powder dried *in vacuo*. Yield: 63% (201 mg, 0.16 mmol).– $C_{28}H_{48}Cl_{12}N_4Os_2$ (1246.5): calcd. C 26.98, H 3.88, N 4.49; found C 27.07, H 3.96, N 4.49. – IR (KBr): $\tilde{\nu}$ = 2878 s, 2817 s, 1572 vs, 1469 vs, 1422 s, 1100 w, 1062 w, 960 s, 930 s, 669 s. – ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.76 (s, 12 H, NH_3^+), 5.75–5.66 (m, 12 H, $C_{(3)}H/C_{(5)}H/C_{(6)}H$), 3.36 (s, 8 H, $C_{(1)}H_2$), 2.70–2.60 (m, 16 H, $C_{(4)}H_2$ / $C_{(7)}H_2$). – ^{13}C NMR (100.5 MHz, CD_3OD): δ = 129.2/127.4/124.6/124.3 ($C_{(2)}/C_{(3)}H/C_{(5)}H/C_{(6)}H$), 51.0 ($C_{(1)}H_2$), 29.6/27.4 ($C_{(4)}H_2/C_{(7)}H_2$).

4.9. Preparation of [(η^6-benzyl ammonium)$OsCl_2$]$_2Cl_2$ (**10**)

To a stirred solution of 2,5-dihydrobenzyl ammonium chloride $\mathbf{4}^{HCl}$ (112 mg, 0.77 mmol) in dry ethanol (10 mL) $OsCl_3$. n H_2O (50 mg, 0.17 mmol) was added and the resulting solution heated for 16 h at 80 °C. The reaction mixture was allowed to cool down to room temperature, filtered and the precipitate subsequently washed with a small amount of ethanol, methanol and diethylether. The reaction product was dried in vacuo, yielding a brown powder. Yield: 39% (27.1 mg, 0.07 mmol). – $C_{14}H_{20}Cl_6N_2Os_2$ (809.5): calcd. C 20.67, H 2.97, N 3.44; found C 19.83, H 2.43, N 2.93. – IR(KBr): $\tilde{\nu}$ = 3056 vs, 1565 m, 1496 m, 1450 w, 1436 w, 1376 w, 1211 w, 875 w, 865 w cm^{-1}. – ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.52 (s, 6 H, NH_3^+), 6.39–6.33 (m, 6 H, $C_{ortho}H$, $C_{meta}H$), 6.22 (t, ^3J = 5.0 2 H, $C_{para}H$), 3.72 (s, 4 H, CH_2). – ^{13}C NMR (100.5 MHz, DMSO-d_6): δ = 84.4, 81.7, 79.3, 78.6 (C_{arom}), 41.3 (CH_2).

4.10. Crystallographic details

Crystals suitable for single-crystal X-ray analyses of complex $\mathbf{8}^{DMSO}$ were grown in a solution of DMSO-d_6 (approx 40 mg/mL) at room temperature within several days. Complex **9** was crystallized from the reaction solution at −18 °C within several weeks. Diffraction data were collected on an Oxford Xcalibur3 and Nonius Kappa CCD diffractometer using MoK_α radiation (λ = 0.71073 Å, graphite monochromator). A Cryojet Controller from Oxford Diffractions allowed measurements at 150 K. The absorption correction (empirical) of the Oxford Xcalibur3 data set was carried out using the program CrysAlis RED (Oxford Diffraction Ltd). The structures were solved by Direct Methods and refined by least-squares and difference Fourier analysis, using least-squares cycles based on F^2 with the SHELXTL software package [36]. All the hydrogen atoms were geometrically fixed and refined using a riding model.

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Appendix A. Supplementary material

CCDC-713129 (for $\mathbf{8}^{DMSO}$) and CCDC-713130 (for **9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB21EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk).

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