

Preliminary communication

# Osmium complexes containing either chelating or non-chelating 8-quinolyl ligands

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Received 6 June 1997

## Abstract

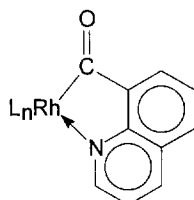
The reaction of  $\text{Qn}_2\text{Hg}$  ( $\text{Qn} = 8\text{-quinolyl}$ ) with  $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$  gives  $\text{Os}(\eta^2\text{-Qn})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (**1**), in which the 8-quinolyl ligand binds through both N and C-8 forming a 4-membered chelate ring. Reaction of **1** with  $\text{AgPF}_6$  to remove chloride, followed by addition of either  $\text{NaI}$  or  $\text{NaS}_2\text{CNMe}_2$ , gives the neutral compounds  $\text{Os}(\eta^2\text{-Qn})\text{I}(\text{CO})(\text{PPh}_3)_2$  (**2**) or  $\text{Os}(\eta^1\text{-Qn})(\eta^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$  (**3**), respectively, while reaction with  $\text{AgPF}_6$  followed by  $\text{CO}$  gives  $[\text{Os}(\eta^2\text{-Qn})(\text{CO})_2(\text{PPh}_3)_2]^+\text{PF}_6^-$  (**4**). Single crystal X-ray structures of **2** and **3** have been determined. In **2**, the 8-quinolyl ligand is chelated through C-8 and N, but in **3** it is coordinated only through C-8. © 1997 Elsevier Science S.A.

**Keywords:** Osmium; Quinoline; Quinolyl; Crystal structure

## 1. Introduction

We are interested in the synthesis of  $\sigma$ -aryl complexes of ruthenium and osmium in which the aryl ligands bear unusual functional groups. Of particular interest is the 8-quinolyl ligand because of the basic nitrogen function being located in a position capable of interacting with the metal centre.

Metal complexes bonded to quinoline through a substituent in the 8- position as well as at the heterocyclic nitrogen are known, e.g.,



Such complexes have been prepared by oxidative addition of 8-quinolinealdehyde to rhodium(I) complexes [1,2].

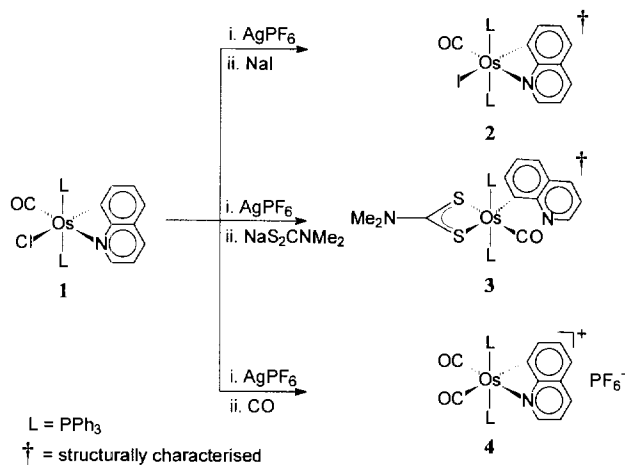
In this paper we report the synthesis of osmium complexes of the 8-quinolyl ligand, both with and without the nitrogen chelated to the metal to form a 4-membered ring. The synthetic method involves transmetalation from  $\text{Qn}_2\text{Hg}$  ( $\text{Qn} = 8\text{-quinolyl}$ ). We have reported previously a number of reactions between  $\text{MHCl}(\text{CO})(\text{PPh}_3)_3$  ( $\text{M} = \text{Ru}, \text{Os}$ ) and  $\text{Ar}_2\text{Hg}$  to form  $\text{MArCl}(\text{CO})(\text{PPh}_3)_2$ , where  $\text{Ar}$  can be a simple aromatic hydrocarbon fragment (e.g., phenyl, *ortho*- and *para*-tolyl), a heterocycle fragment (e.g., 2-pyrrolyl) or a fragment with a chelating pendant group (e.g., *N*-acetyl-2-pyrrolyl) [3–7].

## 2. Results and discussion

The transmetalation of  $\text{Qn}_2\text{Hg}$  with  $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$  follows the same stoichiometry as with simple diaryl mercury reagents, depositing elemental mercury, and forming  $\text{QnH}$ , free  $\text{PPh}_3$ , and  $\text{Os}(\eta^2\text{-Qn})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (**1**). Unlike complexes with simple aryl ligands, however, **1** is not a strongly coloured, coordinatively unsaturated complex of the form  $\text{OsArCl}(\text{CO})(\text{PPh}_3)_2$ . The 6-coordinate geometry and chelating nature of the 8-quinolyl ligand has been established for the closely related iodo-analogue  $\text{Os}(\eta^2\text{-Qn})\text{I}(\text{CO})(\text{PPh}_3)_2$  (**2**), by the crystal structure determi-

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nation of this derivative and undoubtedly **1** has the same basic structure.

Compound **1** is unreactive toward CO even under forcing conditions. Similarly it does not react with sodium dimethyldithiocarbamate, a reagent which rapidly forms derivatives with the coordinatively unsaturated compounds of the form  $\text{OsArCl}(\text{CO})(\text{PPh}_3)_2$ . This suggests that the 4-membered chelate ring is moderately robust.

Derivatives were prepared by first reacting **1** with  $\text{AgPF}_6$  to remove the coordinated chloride (see Scheme 1). Subsequent treatment with NaI then gave the halide metathesis product,  $\text{Os}(\eta^2\text{-Qn})\text{I}(\text{CO})(\text{PPh}_3)_2$  (**2**), while treatment with sodium dimethyldithiocarbamate gave  $\text{Os}(\eta^1\text{-Qn})(\eta^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$  (**3**). The dithio-

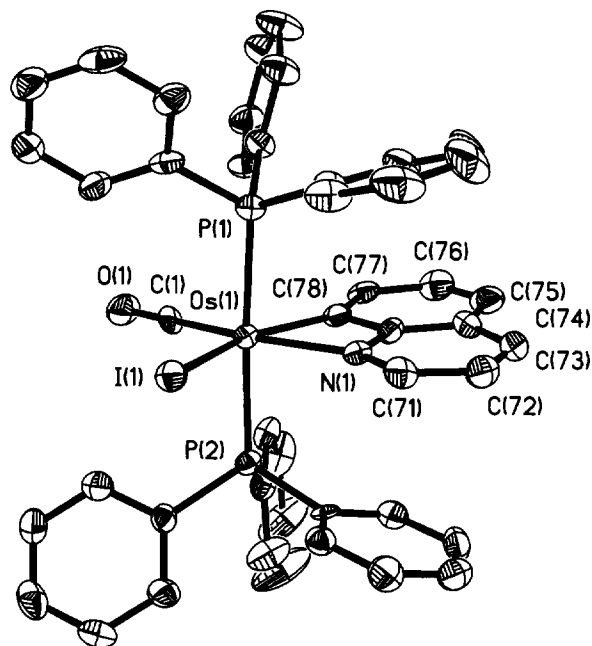


Fig. 1. The molecular structure of  $\text{Os}(\eta^2\text{-Qn})\text{I}(\text{CO})(\text{PPh}_3)_2$  (**2**).

Table 1  
Selected bond lengths [Å] for complexes **2** and **3**

	<b>2</b>	<b>3</b>	
Os(1)–C(1)	1.805 (9)	Os(1)–C(13)	1.858 (6)
Os(1)–C(78)	2.095 (10)	Os(1)–C(1)	2.127 (6)
Os(1)–N(1)	2.214 (8)	Os(1)–P(1)	2.3696 (14)
Os(1)–P(1)	2.381 (2)	Os(1)–P(2)	2.3753 (14)
Os(1)–P(2)	2.376 (2)	Os(1)–S(1)	2.479 (2)
Os(1)–I(1)	2.7916 (8)	Os(1)–S(2)	2.502 (2)

carbamate ligand is known to be a strongly chelating ligand, and in this case it displaces the coordinated nitrogen of the 8-quinolyl ligand. Reaction of **1** with  $\text{AgPF}_6$  followed by addition of carbon monoxide at room temperature and pressure gave the colourless salt  $[\text{Os}(\eta^2\text{-Qn})(\text{CO})_2(\text{PPh}_3)_2]^+ \text{PF}_6^-$  (**4**), which is thought to retain the dihapto coordination mode of the quinolyl ligand.

There are no previous reports of structural data for metal complexes containing 4-membered rings with an  $\eta^2$ -8-quinolyl ligand. The crystal structure of **2** (see Fig. 1) shows the basic nitrogen coordinated to osmium. The quinolyl ligand does not show any marked distortion of the fused aromatic rings. The Os–C distance (2.095(10) Å, see Table 1) for the quinolyl ligand is close to the average distance reported for Os–aryl bonds, whereas the Os–N distance (2.214(8) Å) is a little longer than the average reported distance between osmium and a coordinated heterocyclic nitrogen base. The crystal structure of **3** (see Fig. 2) clearly shows the effect of replacing the monodentate chloride ligand with the strongly chelating dimethyldithiocarbamate ligand. The nitrogen atom that was previously bound to the metal

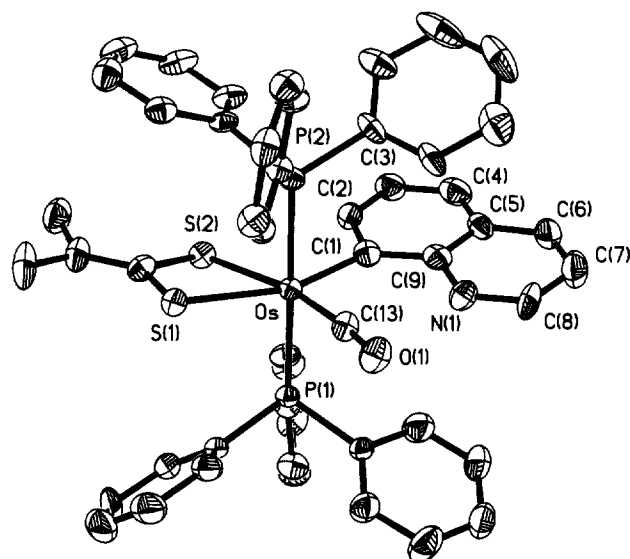


Fig. 2. The molecular structure of  $\text{Os}(\eta^1\text{-Qn})(\eta^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$  (**3**).

has been displaced. The Os–C bond of the quinolylligand (2.127(6) Å) is slightly longer than in **2**.

We are currently examining reactions of the heterocyclic nitrogen atom when it is not coordinated to the metal, functionalisation of the aromatic rings of the ligand, and the facilitation of migratory insertion reactions of the quinolylligand.

### 3. Experimental

All reactions were carried out with laboratory reagent grade solvents, used as purchased. Infrared spectra were run on a Perkin Elmer Spectrum 1000 as nujol mulls between KBr plates. NMR spectra were run on a Bruker DRX-400 at 25°C using TMS as an internal standard,  $\delta = 0.00$  ppm. OsHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> [**8**] was prepared by a literature method. Bis(8-quinolylligand)mercury was prepared either by the method of Cookson and Deacon [9] or more conveniently by direct mercuration of quinoline [10,11] followed by symmetrisation with sodium thiosulfate.

#### 3.1. Preparation of Os( $\eta^2$ -Qn)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub> (**1**)

OsHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> (400 mg) was combined with Qn<sub>2</sub>Hg (200 mg) in toluene (20 ml) and brought to reflux under an atmosphere of nitrogen. After 30 min, the solution was cooled, excess hexane added, and the solution filtered. The resulting yellow solid was recrystallised from dichloromethane/ethanol (265 mg, yield 76%). The analytical sample was purified by column chromatography on silica gel using dichloromethane as the eluent and crystallised with ethanol.

##### 3.1.1. Characterising data

IR:  $\nu(\text{CO}) = 1893 \text{ cm}^{-1}$ . NMR:  $\delta(\text{ppm, CDCl}_3)$  6.38–7.70 (multiple overlapping aromatic protons). Anal. Found: C, 59.34; H, 3.87; N, 1.38. C<sub>46</sub>H<sub>36</sub>ClNOOsP<sub>2</sub> · 1/2CH<sub>2</sub>Cl<sub>2</sub> Calc.: C, 58.84; H, 3.93; N, 1.48%.

#### 3.2. Preparation of Os( $\eta^2$ -Qn)I(CO)(PPh<sub>3</sub>)<sub>2</sub> (**2**)

**1** (100 mg) was dissolved in dichloromethane (20 ml). A solution of AgPF<sub>6</sub> (80 mg) in ethanol (5 ml) and water (5 ml) was added, and the solution was stirred for 10 min. Excess water was added, and the yellow organic phase was separated and filtered to remove AgCl.

An excess of NaI in a small volume of water was added, with enough ethanol to bring about miscibility of the solvents. The mixture was stirred for several minutes before excess water was added. The organic layer was again separated, and the product obtained by adding ethanol and reducing volume in vacuo to form yellow crystals, (106 mg, 96% yield).

#### 3.2.1. Characterising data

IR:  $\nu(\text{CO}) = 1891 \text{ cm}^{-1}$ . NMR:  $\delta(\text{ppm, CDCl}_3)$  6.24–7.48 (multiple overlapping aromatic protons). Anal. Found: C, 55.06; H, 3.61; N, 1.59. C<sub>46</sub>H<sub>36</sub>INOOsP<sub>2</sub> Calc.: C, 55.35; H, 3.64; N, 1.40%.

#### 3.3. Preparation of OS( $\eta^1$ -Qn)( $\eta^2$ -S<sub>2</sub>CNMe<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub> (**3**)

The intermediate cationic complex was prepared as in 3.2. A solution of NaS<sub>2</sub>CNMe<sub>2</sub> (50 mg) in water (5 ml) was added, with enough ethanol to bring about miscibility of the solvents. The mixture was stirred for several minutes before excess water was added. The organic layer was separated, and the product obtained by adding ethanol and reducing the volume in vacuo. (78 mg, 71% yield).

##### 3.3.1. Characterising data

IR:  $\nu(\text{CO}) = 1906 \text{ cm}^{-1}$ ;  $\nu(\text{S}_2\text{CNMe}_2) = 1518 \text{ cm}^{-1}$ . NMR:  $\delta(\text{ppm, CDCl}_3)$  6.40–8.78 (multiple overlapping aromatic protons, 36H); 2.58 (s, 3H, NCH<sub>3</sub>); 2.32 (s, 3H, NCH<sub>3</sub>). Anal. Found: C, 57.33; H, 4.25; N, 2.58. C<sub>49</sub>H<sub>42</sub>N<sub>2</sub>OOS<sub>2</sub>P<sub>2</sub> · 1/2CH<sub>2</sub>Cl<sub>2</sub> Calc.: C, 57.50; H, 4.20; N, 2.71%.

#### 3.4. Preparation of [OS( $\eta^2$ -Qn)(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>PF<sub>6</sub><sup>-</sup> (**4**)

The intermediate cationic complex was prepared as in 3.2. CO was bubbled through the stirred solution for several minutes, during which time the solution became colourless. Ethanol was added and reduction of the volume in vacuo yielded a colourless product, which was recrystallised from dichloromethane/ethanol (75 mg, 65% yield).

##### 3.4.1. Characterising data

IR:  $\nu(\text{CO}) = 2040, 1971 \text{ cm}^{-1}$ ;  $\nu(\text{PF}_6) = 839 \text{ cm}^{-1}$ . NMR:  $\delta(\text{ppm, CDCl}_3)$  6.94–8.03 (multiple overlapping aromatic protons). Anal. Found: C, 52.81; H, 3.28; N, 1.12. C<sub>47</sub>H<sub>36</sub>F<sub>6</sub>NO<sub>2</sub>OsP<sub>3</sub> · 1/2CH<sub>2</sub>Cl<sub>2</sub> Calc.: C, 52.49; H, 3.43; N, 1.29%.

#### 3.5. Crystallography

Data were collected on a Siemens SMART CCD area detector diffractometer using graphite monochromated Mo K $\alpha$  radiation. Data were collected using 0.3° frames and three-dimensional profile fitting. Absorption corrections were applied using the empirical method of Blessing [12]. 24 231 reflections (4715 unique,  $R_{\text{int}} = 0.051$ ) were collected for **2** and 23 923 reflections (7284 unique,  $R_{\text{int}} = 0.049$ ) for **3**. Cell parameters were refined by least squares fit using all reflections with  $I > 10\sigma(I)$ .

The structures were solved by Patterson and Fourier techniques and refined by full matrix least squares on

$F^2$ . All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using a riding model with  $U_{\text{iso}}$  20% greater than  $U_{\text{eq}}$  of the carrier atom. Weights were  $w = 1.0/[\sigma^2(F_o^2) + a * P^2 + b * P]$  ( $P = (F_o^2 + 2F_c^2)/3$ ) with  $a = 0.0302$  and  $b = 55.81$  for **2** and  $a = 0.0001$  and  $b = 3.41$  for **3**. Final  $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$  were 0.0715 for **2** and 0.0633 for **3**, and conventional  $R = 0.0343$  for **2** and 0.0424 for **3**, values quoted for 4113 observed reflections for **2** and 5219 observed reflections for **3** ( $I > 2\sigma(I)$ ). Programs: Siemens SMART and SAINT for data collection and reduction, SHELXTL for structure solution and refinement.

Atomic coordinates, bond lengths and angles, anisotropic thermal parameters and hydrogen coordinates have been deposited at the Cambridge Crystallographic Data Centre. Selected bond lengths are listed in Table 1.

### 3.5.1. Crystal data for **2**

$\text{C}_{46}\text{H}_{36}\text{INO}_2\text{P}_2$ , yellow needle  $0.64 \cdot 0.09 \cdot 0.04$  mm,  $M = 997.80$ , Orthorhombic, space group  $\text{Aba2}$ ,  $a = 19.8759(2)$ ,  $b = 24.6077(3)$ ,  $c = 16.0870(3)$  Å,  $U = 7868.2(2)$  Å<sup>3</sup>,  $Z = 8$ ,  $F(000) = 3888$ ,  $D_c = 1.685$  g cm<sup>-3</sup>,  $\mu(\text{Mo K}\alpha) = 4.14$  mm<sup>-1</sup>,  $\lambda = 0.71069$  Å,  $2\theta_{\text{max}} = 28.2^\circ$ ,  $T = 203$  K.

### 3.5.2. Crystal data for **3**

$\text{C}_{49}\text{H}_{42}\text{N}_2\text{O}_2\text{P}_2\text{S}_2$ , colourless tablet  $0.16 \times 0.16 \times 0.08$  mm,  $M = 991.11$ , Monoclinic, space group  $P2_1/c$ ,

$a = 10.3995(2)$ ,  $b = 18.1120(3)$ ,  $c = 22.1347(5)$  Å,  $\beta = 90.12(1)^\circ$ ,  $U = 4151.71(14)$  Å<sup>3</sup>,  $Z = 4$ ,  $F(000) = 1984$ ,  $D_c = 1.586$  g cm<sup>-3</sup>,  $\mu(\text{Mo K}\alpha) = 3.29$  mm<sup>-1</sup>,  $\lambda = 0.71069$  Å,  $2\theta_{\text{max}} = 25.0^\circ$ ,  $T = 203$  K.

## Acknowledgements

We thank the Marsden fund for supporting this work and for granting a Ph.D. scholarship to A.M.C.

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