

## Chemistry of a family of osmium(II) metallacycles incorporating isonitrile coordination

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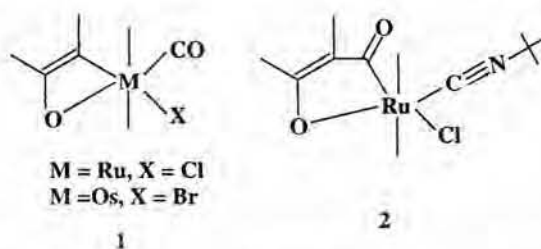
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The reaction of  $\text{Os}(\text{RL})(\text{PPh}_3)_2(\text{CO})\text{Br}$  (**3**) with  $\text{CNBu}^t$  in dichloromethane solution has furnished the cationic complex  $[\text{Os}(\text{RL})(\text{PPh}_3)_2(\text{CO})(\text{CNBu}^t)]^+$  isolated as  $\text{PF}_6^-$  salt, **4** which behaves as a 1:1 electrolyte in acetone solution (RL is  $\text{C}_6\text{H}_2\text{O}-2\text{-CHNHC}_6\text{H}_4\text{R}(p)$ -3-Me-5 and R is Me, OMe and Cl). The presence of significant Os-CN $\text{Bu}^t$  back-bonding in **4** is reflected in the blue shift of both the MLCT transition maximum ( $\sim 500$  nm) and C=O stretching frequency ( $\sim 1930$   $\text{cm}^{-1}$ ) compared to those in **3** ( $\sim 550$  nm and  $\sim 1870$   $\text{cm}^{-1}$ , respectively). For the same reason, the  $\text{Os}^{\text{III}}/\text{Os}^{\text{II}}$  reduction potential ( $\sim 0.8$  V vs. SCE) in **4** is  $\sim 100$  mV higher than those in **3**. The complex  $4\cdot 2\text{CH}_2\text{Cl}_2$  (R = Me) represents the first example of a structurally characterized cyclometallated osmium(II) isonitrile system. In the distorted octahedral  $\text{OsC}_3\text{OP}_2$  coordination sphere of  $4\cdot 2\text{CH}_2\text{Cl}_2$  (R = Me), the Os-P, Os-CO and Os-O bond lengths are closely similar to those in an analogue of **3**. Due to the *trans* influence of the  $\text{CNBu}^t$  ligand, the Os-C(aryl) bond is however lengthened by  $\sim 0.15$  Å in  $4\cdot 2\text{CH}_2\text{Cl}_2$  (R = Me). The type **3** complexes stand in strong contrast to the corresponding ruthenium system, which undergoes halide substitution as well as insertion into the Ru-O bond upon treatment with  $\text{CNBu}^t$ . This happens because the Os-O bond (2.166(6) Å) is stronger than the Ru-O bond (2.235(4) Å).

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The reactivity of the four-membered metallacycle **1**<sup>1-3</sup> generated via decarbonylative metallation has been of interest in this laboratory. It was recently demonstrated that the ruthenium system **1** (M = Ru, X = Cl) reacts smoothly with *tert* butyl isonitrile ( $\text{CNBu}^t$ )<sup>4</sup> which inserts into the Ru-O bond as well as displaces the chloride ligand furnishing imidic ester organometallics. The latter are themselves reactive and undergo spontaneous C-C bond formation via aryl migration leading to acylruthenium species of type **2**.



These findings have logically prompted us to explore the reactivity of the osmium system **1** (M = Os, X = Br) towards isonitrile and the results are reported here. In this case no insertion occurred. The

isonitrile however displaced the bromide ligand furnishing cationic isonitrile species, which have been isolated and characterized including structure determination of a representative complex — the first cyclometallated osmium(II) isonitrile system to be so examined. The origin of the contrasting behaviour of the ruthenium and osmium systems are scrutinized.

### Materials and Methods

The starting complexes  $\text{Os}(\text{PPh}_3)_3\text{Br}_2$ <sup>5</sup> and  $\text{Os}(\text{RL})(\text{PPh}_3)_2(\text{CO})\text{Br}$ <sup>1</sup> were prepared by reported methods. *Tert*-butyl isocyanide was obtained from Aldrich. The purification of dichloromethane for electrochemical work was done as described before<sup>6,7</sup>. All other chemicals and solvents were of analytical grade and were used as received.

### Physical measurements

Electronic and IR spectra were recorded with a Shimadzu UV-1601 PC spectrophotometer and a Nicolet Magna IR series II spectrometer, respectively. <sup>1</sup>H NMR spectra were obtained using a Bruker 300 MHz FT NMR spectrometer. The numbering scheme used for <sup>1</sup>H NMR is the same as in the

crystallography. Spin-spin structures are abbreviated as: s, singlet; d, doublet; t, triplet; m, multiplet. Microanalysis (C, H, N) was performed using a Perkin-Elmer 240C elemental analyzer. Solution electrical conductivity was measured in acetone with a Philips PR 9500 bridge by using a platinized electrode (cell constant 1.05). The electrochemical measurements were performed at a platinum electrode under a nitrogen atmosphere in dichloromethane solution using an electrochemical analyzer of CH Instruments (model 620A). The supporting electrolyte was tetraethylammonium perchlorate and potentials are referenced to the saturated calomel electrode (SCE).

#### Synthesis of the complexes

##### $[\text{Os}(\text{RL})(\text{PPh}_3)_2(\text{CO})(\text{CNBu}^t)](\text{PF}_6)$ , **4**

The three  $[\text{Os}(\text{RL})(\text{PPh}_3)_2(\text{CO})(\text{CNBu}^t)]\text{PF}_6$  complexes were synthesized in excellent yields by reacting  $\text{Os}(\text{RL})(\text{PPh}_3)_2(\text{CO})\text{Br}$  with *tert*-butyl isocyanide. Details of a representative case are given below.

##### $[\text{Os}(\text{MeL})(\text{PPh}_3)_2(\text{CO})(\text{CNBu}^t)]\text{PF}_6$ , **4(Me)**

To a vigorously stirred violet solution of  $\text{Os}(\text{MeL})(\text{PPh}_3)_2(\text{CO})\text{Br}$  (100 mg, 0.099 mmol) in dichloromethane (40 mL), *tert*-butyl isocyanide (40 mg, 0.48 mmol) was added dropwise. The whole mixture was then refluxed for 3 h when the colour of the solution changed to red. The solvent was then removed under reduced pressure leaving an oily residue, which was dissolved in methanol (40 mL) and 20 mg (0.122 mmol) of  $\text{NH}_4\text{PF}_6$  was added to it. After stirring for 1 h, solvent was evaporated and the red crystalline solid thus obtained was filtered, washed with water and dried *in vacuo*. Yield: 89%. Anal Calcd. for  $\text{C}_{57}\text{H}_{53}\text{N}_2\text{O}_2\text{P}_3\text{F}_6\text{Os}$ : C, 57.28; H, 4.47; N, 2.34. Found: C, 57.36; H, 4.50; N, 2.28.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 11.73 (s, 1H,  $=\text{N}^+-\text{H}$ ), 6.13 (s, 1H, H(3)), 0.95 (s, 9H,  $\text{Bu}^t$ ), 1.95 (s, 3H, 4- $\text{CH}_3$ ), 7.30-7.61 (m, 34H, 2 $\text{PPh}_3$ , H(5), H(7), H(16), H(20)), 6.94 (d, 2H, H(17), H(19),  $J = 9.0$ ), 2.40 (s, 3H, 18- $\text{CH}_3$ ).  $\Lambda_{\text{M}}$  ( $\text{Me}_2\text{CO}$ ) =  $124 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ .

##### $[\text{Os}(\text{MeOL})(\text{PPh}_3)_2(\text{CO})(\text{CNBu}^t)](\text{PF}_6)$ , **4(OMe)**

$\text{Os}(\text{MeOL})(\text{PPh}_3)_2(\text{CO})\text{Br}$  (100 mg, 0.098 mmol),  $\text{CNBu}^t$  (40 mg, 0.48 mmol) and  $\text{NH}_4\text{PF}_6$  (20 mg, 0.122 mmol) were employed. Yield: 85%. Anal Calcd. for  $\text{C}_{57}\text{H}_{53}\text{N}_2\text{O}_3\text{P}_3\text{F}_6\text{Os}$ : C, 56.52; H, 4.41; N, 2.31. Found: C, 56.58; H, 4.36; N, 2.23.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 11.86 (s, 1H,  $=\text{N}^+-\text{H}$ ), 6.11 (s, 1H, H(3)), 0.94 (s, 9H,  $\text{Bu}^t$ ), 1.95 (s, 3H, 4- $\text{Me}$ ), 7.30-7.50 (m, 34H, 2 $\text{PPh}_3$ , H(5), H(7), H(16), H(20)), 6.99 (d, 2H,

H(17), H(19),  $J = 9.0$ ), 3.89 (s, 3H, 18- $\text{OMe}$ ).  $\Lambda_{\text{M}}$  ( $\text{Me}_2\text{CO}$ ) =  $121 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ .

##### $[\text{Os}(\text{CIL})(\text{PPh}_3)_2(\text{CO})(\text{CNBu}^t)](\text{PF}_6)$ , **4(Cl)**

$\text{Os}(\text{CIL})(\text{PPh}_3)_2(\text{CO})\text{Br}$  (100 mg, 0.098 mmol),  $\text{CNBu}^t$  (40 mg, 0.48 mmol) and  $\text{NH}_4\text{PF}_6$  (20 mg, 0.122 mmol) were used. Yield: 87%. Anal Calcd. for  $\text{C}_{56}\text{H}_{50}\text{N}_2\text{O}_3\text{P}_3\text{F}_6\text{ClOs}$ : C, 55.33; H, 4.15; N, 2.30. Found: C, 55.39; H, 4.09; N, 2.41.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 11.88 (s, 1H,  $=\text{N}^+-\text{H}$ ), 6.17 (s, 1H, H(3)), 0.95 (s, 9H,  $\text{Bu}^t$ ), 1.94 (s, 3H, 4- $\text{Me}$ ), 7.26-7.49 (m, 34H, 2 $\text{PPh}_3$ , H(5), H(7), H(16), H(20)), 7.03 (d, 2H, H(17), H(19),  $J = 9.1$ ).  $\Lambda_{\text{M}}$  ( $\text{Me}_2\text{CO}$ ) =  $124 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ .

#### X-ray crystallography

Single crystals of  $[\text{Os}(\text{MeL})(\text{PPh}_3)_2(\text{CO})(\text{CNBu}^t)]\text{PF}_6 \cdot 2\text{CH}_2\text{Cl}_2$ , [**4(Me)**·2 $\text{CH}_2\text{Cl}_2$ ] ( $0.35 \times 0.30 \times 0.20 \text{ mm}^3$ ) were grown by slow diffusion of hexane into dichloromethane solutions at room temperature. Cell parameters were determined by a least-squares fit of 30 machine-centred reflections ( $2\theta = 14\text{--}28^\circ$ ). Data were collected by the  $\omega$ -scan technique on a Siemens R3m/V four-circle diffractometer with graphite-monochromated  $\text{Mo-K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Two check reflections measured after every 198 reflections showed no significant intensity reduction in any case. All data were corrected for Lorentz polarization effects and an empirical absorption correction<sup>8</sup> was done on the basis of azimuthal scan of six reflections for the crystals.

The metal atom was located from Patterson maps and the rest of the non-hydrogen atoms emerged from successive Fourier syntheses. The structure was refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were added at calculated positions. Calculations were performed using the SHELXTL version 5.03<sup>9</sup> programme package. Significant crystal data are listed in Table 1.

## Results and Discussion

#### Synthesis

The complexes **3**, incorporating motif **1** ( $\text{M} = \text{Os}$ ,  $\text{X} = \text{Br}$ ) are abbreviated as  $\text{Os}(\text{RL})(\text{PPh}_3)_2(\text{CO})\text{Br}$  where the R group is Me, OMe or Cl. Individual compounds are identified here by specifying the R group in parenthesis, e.g. **3(Me)**, etc. In dichloromethane solution, **3** reacts smoothly with *tert*-butyl isocyanide giving a red solution which upon work-up with addition of  $\text{NH}_4\text{PF}_6$  afforded the red crystalline salt  $[\text{Os}(\text{RL})(\text{PPh}_3)_2(\text{CO})(\text{CNBu}^t)](\text{PF}_6)$ , **4** in excellent yield. The synthetic reaction is stated in Eq.(1). In

effect, the bromide ligand in **3** is displaced by an isocyanide molecule furnishing the cationic complex. In acetone solution **4** acts as a 1:1 electrolyte with  $\Lambda_M$  in the range 120–140  $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ .

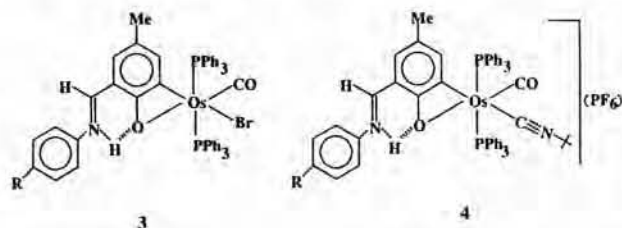
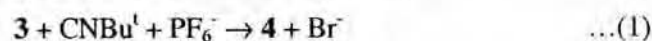


Table 1 — Crystal data for  $\text{Os}(\text{MeL})(\text{PPh}_3)_2(\text{CO})(\text{CNBu}^+)(\text{PF}_6^-) \cdot 2\text{CH}_2\text{Cl}_2$ , **4**(Me)·2CH<sub>2</sub>Cl<sub>2</sub>

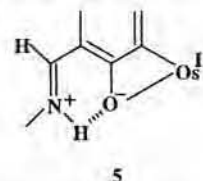
| Complex                                                                                               | <b>4</b> (Me)·2CH <sub>2</sub> Cl <sub>2</sub>                                                                 |
|-------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------|
| Empirical formula                                                                                     | C <sub>59</sub> H <sub>57</sub> N <sub>2</sub> O <sub>2</sub> P <sub>3</sub> F <sub>6</sub> Cl <sub>4</sub> Os |
| Formula weight                                                                                        | 1364.98                                                                                                        |
| Crystal system                                                                                        | Monoclinic                                                                                                     |
| Space group                                                                                           | <i>P</i> 2(1)/ <i>c</i>                                                                                        |
| <i>a</i> (Å)                                                                                          | 16.210(3)                                                                                                      |
| <i>b</i> (Å)                                                                                          | 18.529(4)                                                                                                      |
| <i>c</i> (Å)                                                                                          | 20.967(4)                                                                                                      |
| $\beta$ (°)                                                                                           | 100.48(3)                                                                                                      |
| <i>V</i> (Å <sup>3</sup> )                                                                            | 6192(2)                                                                                                        |
| <i>Z</i>                                                                                              | 4                                                                                                              |
| $\mu(\text{Mo-K}\alpha)(\text{mm}^{-1})$                                                              | 2.369                                                                                                          |
| <i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )                                                        | 1.464                                                                                                          |
| Total reflections                                                                                     | 8521                                                                                                           |
| Independent reflections ( <i>R</i> <sub>int</sub> )                                                   | 8089 (0.0463)                                                                                                  |
| <i>R</i> <sub>1</sub> <sup>a</sup> , <i>wR</i> <sub>2</sub> <sup>b</sup> [ <i>I</i> > 2σ( <i>I</i> )] | 5.60, 13.25                                                                                                    |

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|$$

$$^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$$

#### Spectra and electrochemistry

The UV-vis spectral data of the type **4** complexes in dichloromethane solution are listed in Table 2. The moderately intense band observed near 500 nm is assigned to  $t_{2g} \rightarrow \pi^*$  MLCT transition within the chelated zwitterionic iminium-phenolato function **5** which is present in **4**. The same function is also present in the parent system **3** wherein the band lies near 550 nm<sup>1</sup>. This is qualitatively consistent with the extra stabilization of the  $t_{2g}$  shell in **4** via osmium-isonitrile back-bonding (as shown below).



Selected IR stretching frequencies of **4** are listed in Table 2. There is a ~60 cm<sup>-1</sup> blue shift of the C≡O stretch in going from **3** (~1870 cm<sup>-1</sup>) to **4** signifying that Os-CN<sup>+</sup>Bu back-bonding reduces the demand on Os-CO back-bonding. In **3**, the bromide ligand is virtually ineffective for back-bonding. A broad band of medium intensity near 3440 cm<sup>-1</sup> in **4** is assigned to N<sup>+</sup>-H stretch. The observed frequency is consistent with weak hydrogen bonding<sup>10,12</sup> as in the case **3**<sup>1</sup>. The relatively high (~1630 cm<sup>-1</sup>) C=N stretching frequency is in agreement with nitrogen protonation<sup>10,13</sup> as in the iminium-phenolato function **5**.

The complexes display well-resolved <sup>1</sup>H NMR spectra, which are listed in the Materials and Methods section. The spectra are generally similar to those of **3**<sup>1</sup>. The 3-H signal occurs at relatively high field (~6.1 ppm) probably due to shielding by phosphine phenyl rings. The iminium =N<sup>+</sup>-H proton signal around 11.8 ppm is relatively broad<sup>1</sup>.

All the complexes of type **4** are electroactive in dichloromethane solution and display a quasi-reversible one-electron response assigned to the Os(III)/Os(II) couple in the range 0.7–0.9 V vs. SCE

Table 2 — UV-vis<sup>a</sup> and IR<sup>b</sup> spectral data

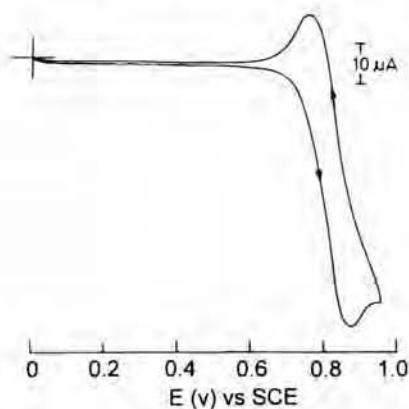
| Comp.          | $\lambda_{\text{max}}$ , nm ( $\epsilon^c$ , M <sup>-1</sup> cm <sup>-1</sup> ) | $\nu_{\text{C=O}}$ | $\nu_{\text{C=N}}$ | $\nu_{\text{C=N}}$ | $\nu_{\text{N}^+\text{-H}}$ |
|----------------|---------------------------------------------------------------------------------|--------------------|--------------------|--------------------|-----------------------------|
| <b>4</b> (Me)  | 392(10000), 505(6500)                                                           | 1927               | 1636               | 2161               | 3443                        |
| <b>4</b> (OMe) | 389(12360), 505(6721)                                                           | 1927               | 1638               | 2162               | 3437                        |
| <b>4</b> (Cl)  | 389(14646), 518(7109)                                                           | 1928               | 1633               | 2162               | 3423                        |

<sup>a</sup>Solvent: dichloromethane; <sup>b</sup>In KBr disk; <sup>c</sup>Extinction coefficient.

Table 3 — Cyclic voltammetric reduction potentials<sup>a</sup> of [Os(RL)(PPh<sub>3</sub>)<sub>2</sub>(CO)(CNBu<sup>t</sup>)](PF<sub>6</sub>), **4** at 298 K

| Comp.  | $E_{1/2}^b$ , Os(III)/Os(II) |
|--------|------------------------------|
|        | $V(\Delta E_p, \text{mV})$   |
| 4(Me)  | 0.74(90)                     |
| 4(OMe) | 0.73(90)                     |
| 4(Cl)  | 0.82(120)                    |

<sup>a</sup>Conditions: Solvent, dichloromethane; supporting electrolyte, TEAP (0.1 M); working electrode, platinum; reference electrode, SCE; solute concentration  $\sim 10^{-3}$  M; scan rate 50 mV/sec. <sup>b</sup> $E_{1/2} = 1/2(E_{pa} + E_{pc})$ ,  $\Delta E_p = E_{pa} - E_{pc}$  where  $E_{pa}$  and  $E_{pc}$  are anodic and cathodic peak potentials respectively.

Fig. 1 — Cyclic voltammogram (scan rate 50 mV s<sup>-1</sup>) of 10<sup>-3</sup> M solution of **4**(Cl).

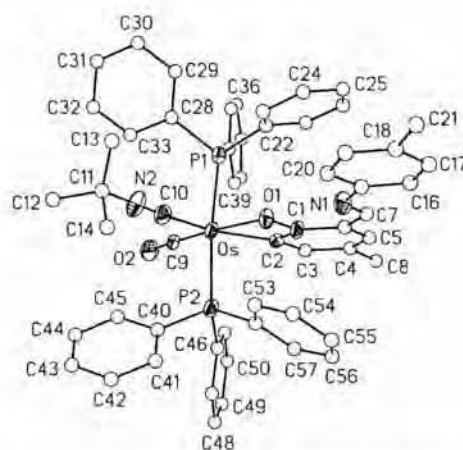
(Table 3). A representative voltammogram is shown in Fig. 1. The reduction potentials follow the expected order in R viz. OMe < Me < Cl. Significantly, the reduction potential of **4** is more than 100 mV higher than that of the precursor **3**<sup>1</sup>. Thus, the potentials of **3**(Me), and **4**(Me) are respectively 0.57V<sup>1</sup> and 0.74V. The extra stabilization of the  $t_{2g}$  shell due to Os-CNBU<sup>t</sup> back-bonding in **4** is consistent with this trend. Significantly, such bonding also increases the energy of the MLCT band in going from **3** to **4** (vide infra).

#### Structure

The X-ray structure of [Os(MeL)(PPh<sub>3</sub>)<sub>2</sub>(CO)(CNBu<sup>t</sup>)]PF<sub>6</sub>·2CH<sub>2</sub>Cl<sub>2</sub> has been determined. A view of the cation is shown in Fig. 2 and selected bond parameters are listed in Table 4. We note that structurally characterized species incorporating Os<sup>II</sup>-O(phenolato) and orthometallated Os<sup>II</sup>-C binding are relatively rare. The OsC<sub>3</sub>OP<sub>2</sub> coordination sphere in the cation constitutes a severely distorted octahedron in which the OsC<sub>3</sub>O fragment defines a virtually

Table 4 — Selected bond distances (Å) and bond angles (°) for [Os(MeL)(PPh<sub>3</sub>)<sub>2</sub>(CO)(CNBu<sup>t</sup>)](PF<sub>6</sub>)·2CH<sub>2</sub>Cl<sub>2</sub>, **4**(Me)·2CH<sub>2</sub>Cl<sub>2</sub>

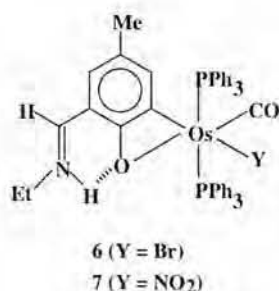
| Bond distances |           |           |           |
|----------------|-----------|-----------|-----------|
| Os-P1          | 2.374(3)  | C7-N1     | 1.296(14) |
| Os-P2          | 2.372(3)  | C9-O2     | 1.175(12) |
| Os-C2          | 2.126(10) | C1-O1     | 1.322(12) |
| Os-C9          | 1.829(12) | N2-C10    | 1.160(14) |
| Os-O1          | 2.166(6)  | N1-O1     | 2.658(10) |
| Os-C10         | 1.991(13) |           |           |
| Bond angles    |           |           |           |
| P1-Os-P2       | 174.69(9) | Os-C9-O2  | 178.1(9)  |
| P1-Os-C1       | 87.5(2)   | O1-Os-C1  | 30.7(3)   |
| P1-Os-O1       | 88.4(2)   | O1-Os-C10 | 92.8(4)   |
| P1-Os-C9       | 91.4(3)   | C2-Os-O1  | 63.4(3)   |
| P1-Os-C10      | 92.7(3)   | C9-Os-O1  | 172.6(4)  |
| P2-Os-C1       | 87.4(2)   | C9-Os-C2  | 109.2(4)  |
| P2-Os-O1       | 88.0(2)   | C9-Os-C10 | 94.6(4)   |
| P2-Os-C9       | 91.6(3)   | C7-N1-C15 | 128.0(11) |
| P2-Os-C10      | 91.5(3)   | C1-O1-Os  | 92.6(6)   |
| N2-C10-Os      | 173.8(10) |           |           |

Fig. 2 — Perspective view and atom-labelling scheme for the cation of **4**(Me)·2CH<sub>2</sub>Cl<sub>2</sub>

perfect equatorial plane (mean deviation, 0.02 Å), the P1-Os-P2 axis being approximately linear ( $\angle$ P1-Os-P2, 174.69(9)°). An interesting feature of the structure is that non-hydrogen atoms of the MeL ligand (excluding the pendant tolyl ring) along with Os, CO and CN(isonitrile) make an excellent plane with the mean deviation of 0.02 Å. The pendant tolyl ring is nearly coplanar with it, the dihedral angle being only 2.6°.

It is instructive to compare the metal-ligand bond lengths in **4**(Me) with those in the complex **6**<sup>1</sup> where

the  $C_6H_4R$  group of **3** is replaced by Et. The Os-P, Os-CO and Os-O bonds in the two compounds do not vary by more than 0.02 Å. In contrast in **4(Me)**, the CNBu<sup>l</sup> ligand exerts a remarkable *trans* influence and the Os-C(aryl) bond, 2.126(10) Å is ~0.15 Å longer than that in **6**. Interestingly, the bond parameters of the nitro complex **7**<sup>14</sup> are alike those of **4(Me)·2CH<sub>2</sub>Cl<sub>2</sub>**. In this case, the N-bonded NO<sub>2</sub><sup>-</sup> ligand is involved in back-bonding and the Os-C(aryl) length is 2.137(14) Å. The iminium-phenolato N...O distance in **4(Me)·2CH<sub>2</sub>Cl<sub>2</sub>**, 2.658(10) Å, can be compared with 2.665(12) and 2.729(20) Å in **6** and **7** respectively.



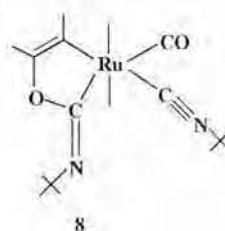
In the octahedral PF<sub>6</sub><sup>-</sup> anion in **4(Me)·2CH<sub>2</sub>Cl<sub>2</sub>**, the P-F distances lie within the range 1.440(13)-1.517(12) Å. The dichloromethane molecules occupy general positions and one of them (incorporating C59) displays two-fold disorder of a chlorine atom. There are a few F...C non-bonded contacts in the range 3.22-3.43 Å involving PF<sub>6</sub><sup>-</sup>, CH<sub>2</sub>Cl<sub>2</sub> and one PPh<sub>3</sub> phenyl ring.

Lastly, we refer to the literature on structurally characterized osmium complexes incorporating coordination of one or more isonitrile ligands. The number of such compounds is limited. The majority of the compounds are substituted carbonyl clusters<sup>15,16</sup> in which the Os-C(isonitrile) distance spans the range 1.92-2.05 Å. The structure of a mononuclear trivalent complex, viz. (η-Bu<sub>4</sub>N)[OsCl<sub>4</sub>(CNxyl)]<sup>17</sup> is known (Os<sup>III</sup>-C, 1.98 Å). The present complex **4(Me)·2CH<sub>2</sub>Cl<sub>2</sub>** represents a rare instance of structural characterization of an osmium(II) complex that incorporates isonitrile coordination. A number of mononuclear isonitrile complexes of osmium(II) have been reported<sup>18,19</sup> but structural characterization has been sparse: *trans*-[Os(CO)(PMe<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>11</sub>NC)(COMe)]<sup>20</sup>, *trans*-[OsH(CNH)L<sub>2</sub>][BF<sub>4</sub>]<sup>21</sup>, and [Os(COD)(CNCMe<sub>3</sub>)<sub>2</sub>(NH<sub>2</sub>N:CMe<sub>2</sub>)<sub>2</sub>](BPh<sub>4</sub>)<sub>2</sub><sup>22</sup>. The Os<sup>II</sup>-C(isonitrile) distances in these molecules span the range 2.00 ± 0.04 Å. To the best of our

knowledge, complex **4(Me)·2CH<sub>2</sub>Cl<sub>2</sub>** is the first example of a cyclometallated Os<sup>II</sup>-isonitrile complex whose structure has been determined. The Os<sup>II</sup>-CNBu<sup>l</sup> distance, 1.991(13) Å, lies within the above noted range.

#### Ruthenium-osmium contrast

Whereas **3** reacts with CNBu<sup>l</sup> furnishing [Os(RL)(PPh<sub>3</sub>)<sub>2</sub>(CO)(CNBu<sup>l</sup>)]<sup>+</sup> (cation of **4**) as the only stable product, in the case of the ruthenium analogue of **3** an isonitrile ligand displaces the chloride ligand and another inserts into the Ru-O bond affording an imidic ester complex incorporating motif **8** which is spontaneously reactive in solution leading to aryl migration resulting in the acyl complex incorporating motif **2**<sup>4</sup>. This contrast is consistent with bond length data. The Os-O(phenolato) distance in **6** is 2.151(10) Å<sup>1</sup> which does not change much upon going to **4(Me)·2CH<sub>2</sub>Cl<sub>2</sub>** (Os-O, 2.166(6) Å). On the other hand, in a ruthenium analogue of **3** the Ru-O(phenolato) length is significantly longer, 2.235(4) Å<sup>2</sup>. Thus M-O(phenolato) bond strength order is Os > Ru, the covalent radii of bivalent osmium and ruthenium being virtually equal<sup>23</sup>. The stronger Os-O bond is believed to be responsible for the lack of isonitrile insertion into it.



The second point of contrast is the lack of aryl migration in the osmium system. Comparison with ruthenium is not possible since the osmium analogue of **8** (which is the reactive ruthenium complex) is not formed. Why aryl migration does not occur in **4** itself? Indeed in **4(Me)·2CH<sub>2</sub>Cl<sub>2</sub>** the Os-C(aryl) bond (distance, 2.126(10) Å) appears to be weaker than the Ru-C(aryl) bond in a complex incorporating **8** (2.075(7) Å)<sup>4</sup>. The lack of reactivity of **4** seems to imply that isonitrile insertion into the M-O(phenolato) bond is a prerequisite for the aryl migration to occur.

#### Conclusions

It is demonstrated that Os(RL)(PPh<sub>3</sub>)<sub>2</sub>(CO)Br, **3**, undergoes a facile reaction with isonitrile furnishing [Os(RL)(PPh<sub>3</sub>)<sub>2</sub>(CO)(CNBu<sup>l</sup>)]<sup>+</sup> isolated in the form of PF<sub>6</sub><sup>-</sup> salt, **4**. No insertion of CNBu<sup>l</sup> into the Os-

O(phenolato) bond is observed and **4** fails to undergo aryl migration. Due to Os-CN<sup>+</sup>Bu<sup>+</sup> back-bonding, the  $t_{2g}$  shell in **4** is better stabilized than that in **3** and this is reflected in the shifts of the MLCT band, of C≡O stretch to higher frequency and of Os(III)/Os(II) reduction potential to more positive values. Structure determination of **4** (Me)-2CH<sub>2</sub>Cl<sub>2</sub> and its comparison with **6** has revealed that the Os-C(aryl) bond is significantly lengthened by the *trans* influence of the CN<sup>+</sup>Bu<sup>+</sup> ligand. The lack of isonitrile insertion into the Os-O(phenolato) bond is consistent with its shortness compared to the Ru-O(phenolato) bond.

### Supplementary Material

Crystallographic data for the structure analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 262998 corresponding to [Os(MeL)(PPh<sub>3</sub>)<sub>2</sub>(CO)(CN<sup>+</sup>Bu<sup>+</sup>)](PF<sub>6</sub>)-2CH<sub>2</sub>Cl<sub>2</sub>, [**4**(Me)-2CH<sub>2</sub>Cl<sub>2</sub>]. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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