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# Tris(*N*-pyrrolyl)phosphine complexes of osmium(II) and osmium(0)

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Dedicated to Professor François Mathey on the occasion of his 60th birthday and in recognition of his major contributions to phosphorus chemistry

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## Abstract

Reaction between $OsHCl(CO)(PPh_3)_3$ and the powerful π-accepting ligand tris(*N*-pyrrolyl)phosphine, $P(NC_4H_4)_3$, results in replacement of the $PPh_3$ ligand *trans* to hydride giving $OsHCl(CO)[P(NC_4H_4)_3](PPh_3)_2$ (**1**). The analogue of **1** with Cl replaced by *p*-tolyl, $OsH(p\text{-tolyl})(CO)[P(NC_4H_4)_3](PPh_3)_2$ (**3**), is accessible by thermal decarboxylation of $Os(p\text{-tolyl})(\eta^2\text{-}O_2CH)(CO)(PPh_3)_2$ (**2**) in the presence of $P(NC_4H_4)_3$. Complex **3**, despite having *cis*-hydride and *p*-tolyl ligands, is resistant to reductive elimination of toluene. Osmium(0) complexes containing $P(NC_4H_4)_3$ are conveniently prepared by replacement of one $PPh_3$ ligand from $Os(CO)(CE)(PPh_3)_3$ (E = O, S) to give $Os(CO)(CE)[P(NC_4H_4)_3](PPh_3)_2$ (**4**, E = O; **5**, E = S). Structure determination of **4** confirms a trigonal bipyramidal geometry with the $PPh_3$ ligands in the axial positions and the π-accepting $P(NC_4H_4)_3$ ligand in the expected equatorial site. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Tris(*N*-pyrrolyl)phosphine complex; Hydride complex; Osmium; X-ray crystal structure

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## 1. Introduction

Amongst $PR_3$ ligands, tris(*N*-pyrrolyl)phosphine has been shown to have strong π-accepting properties but to be a rather weak σ-donor [1]. This is because the *N*-pyrrolyl substituents are unusually effective electron-withdrawing groups as a result of aromatic delocalisation of the nitrogen lone pair into the pyrrole ring. *N*-pyrrolyl substituents when present on silyl ligands also exhibit the same electron-withdrawing properties and these effects have been studied both experimentally [2] and theoretically [3]. IR studies of ν(CO) for rhodium compounds containing both CO and $P(NC_4H_4)_3$ show the poor σ-donor and good π-acceptor properties of $P(NC_4H_4)_3$. Further evidence for the exceptional π-accepting properties is provided by the remarkable observation of complete substitution of CO in the electron-rich anion $[Rh(CO)_4]^-$ to give $[Rh\{P(NC_4H_4)_3\}_4]^-$ [1a]. To further consolidate this bonding picture of the tris(*N*-pyrrolyl)phosphine ligand, we describe in this paper the preparation and spectroscopic study of tris(*N*-pyrrolyl)phosphine complexes of osmium(II) and osmium(0). In addition, a structural study of an osmium(0) tris(*N*-pyrrolyl)phosphine complex has been completed.

## 2. Results and discussion

### 2.1. Introduction of tris(*N*-pyrrolyl)phosphine to $OsHCl(CO)(PPh_3)_3$

$OsHCl(CO)(PPh_3)_3$ has a labile phosphine ligand located *trans* to the hydride ligand. We have shown previously that a number of complexes of the type $OsHCl(CO)(PR_3)(PPh_3)_2$ are easily accessible from the reaction between the appropriate phosphine and $OsHCl(CO)(PPh_3)_3$ [4]. Following this approach, treatment of $OsHCl(CO)(PPh_3)_3$ with one equivalent of tris(*N*-pyrrolyl)phosphine gave $OsHCl(CO)[P(NC_4H_4)_3](PPh_3)_2$ (**1**) as a colourless product (see Scheme 1). The IR spectrum of **1** shows ν(OsH) at 2035 $cm^{-1}$, ν(CO) at 1936 $cm^{-1}$ and a strong band at 1178 $cm^{-1}$ associated with the tris(*N*-pyrrolyl)phosphine ligand. The

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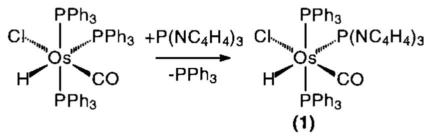
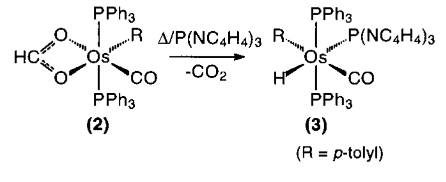


Scheme 1. Synthesis of an hydrido, tris(*N*-pyrrolyl)phosphine complex of osmium(II).

observed ν(CO) for **1** is 25 cm$^{-1}$ higher than that observed for $OsHCl(CO)(PPh_3)_3$. This indicates a significantly decreased donation of electron density from the osmium to the carbonyl ligand as a result of the increased π-acceptor and reduced σ-donor character of the tris(*N*-pyrrolyl)phosphine ligand relative to triphenylphosphine.

NMR studies confirmed the geometrical arrangement of the phosphine ligands as depicted in Scheme 1. In the $^1$H-NMR spectrum of **1**, the pyrrolyl protons are visible as multiplet resonances at 6.04 and 6.13 ppm. These chemical shifts are at slightly higher field values than those recorded for free tris(*N*-pyrrolyl)phosphine (6.43 and 6.88 ppm). A doublet of triplets at −4.92 ppm is assigned to the hydride ligand, and this collapses to a singlet in the $^1H\{^{31}P\}$-NMR spectrum. The splitting pattern of the hydride signal indicates the geometrical arrangement of the ligands about the osmium atom. The doublet coupling constant of 138.4 Hz is consistent with coupling to a single *trans* phosphine ligand, while the smaller triplet coupling constant (25.2 Hz) indicates *cis* coupling of the hydride to two equivalent, mutually *trans*, triphenylphosphine ligands. This fixes the geometry as depicted in Scheme 1.

The $^{13}$C-NMR spectrum of **1** shows two resonances for the tris(*N*-pyrrolyl)phosphine carbon atoms; a doublet at 111.32 ppm ($^2J_{CP} = 5.0$ Hz) and a second doublet at 123.98 ppm ($^3J_{CP} = 5.0$ Hz). The $^{31}$P-NMR spectrum shows a triplet at 68.74 ppm with a coupling constant $^2J_{PP}$ of 13.3 Hz, which is assigned to the tris(*N*-pyrrolyl)phosphine phosphorus atom. A second resonance at 3.71 ppm, which is split into a doublet with $^2J_{PP} = 13.4$ Hz, is assigned to the triphenylphosphine phosphorus nuclei. These observations also confirm the geometry depicted in Scheme 1.



Scheme 2. Synthesis of an hydrido, *p*-tolyl, tris(*N*-pyrrolyl)phosphine complex of osmium(II).

### 2.2. An osmium(II) complex containing hydride, p-tolyl and tris(N-pyrrolyl)phosphine ligands

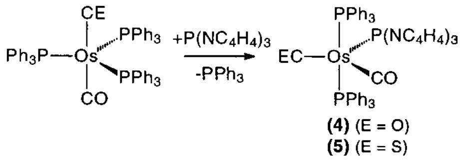
We have previously demonstrated that thermal decarboxylation of Os(Aryl)($\eta^2$-$O_2CH$)(CO)$(PPh_3)_2$ in the presence of excess triphenylphosphine produces OsH(Aryl)(CO)$(PPh_3)_3$ [5]. When Os(*p*-tolyl)($\eta^2$-$O_2CH$)(CO)$(PPh_3)_2$ (**2**) is heated in the presence of tris(*N*-pyrrolyl)phosphine, decarboxylation occurs and OsH(*p*-tolyl)(CO)$[P(NC_4H_4)_3](PPh_3)_2$ (**3**) is formed as a colourless solid in good yield (see Scheme 2). In the IR spectrum of **3**, ν(OsH) appears at 2137 cm$^{-1}$ and ν(CO) at 1935, 27 cm$^{-1}$ higher than that observed for OsH(*p*-tolyl)(CO)$(PPh)_3$ [5b].

The $^1$H-NMR spectrum of complex **3** reveals a doublet of triplets for the hydride resonance at −6.44 ppm, with coupling constants of $^2J_{HP\mathit{trans}} = 129.6$ Hz and $^2J_{HP\mathit{cis}} = 28.8$ Hz. These signals collapse to a singlet in the $^1H\{^{31}P\}$-NMR spectrum. The coupling pattern is consistent with the tris(*N*-pyrrolyl)phosphine ligand being *trans* to the hydride and the two mutually *trans* triphenylphosphine ligands *cis* to the hydride, as depicted in Scheme 2.

The $^{13}$C-NMR spectrum of complex **3** shows a resonance at 23.0 ppm assigned to the methyl group and doublet resonances at 111.35 ($^3J_{CP} = 5.0$ Hz) and 123.50 ppm ($^2J_{CP} = 6.0$ Hz) assigned to the pyrrolyl ring carbons. The $^{31}$P-NMR spectrum reveals a doublet resonance at −2.55 ppm ($^2J_{PP} = 13.2$ Hz), which is assigned to the two triphenylphosphine phosphorus atoms, and a triplet at 78.08 ppm ($^2J_{PP} = 13.6$ Hz) assigned to the single tris(*N*-pyrrolyl)phosphine phosphorus atom. Complex **3** exhibits remarkable thermal stability and when heated under reflux in benzene for 2 h with an excess of triphenylphosphine, there is no replacement of the tris(*N*-pyrrolyl)phosphine ligand by triphenylphosphine, nor is any reductive elimination of toluene observed. However, CO is effective in replacing the tris(*N*-pyrrolyl)phosphine ligand and when **3** is treated with CO (4 atm for 30 min), OsH(*p*-tolyl)$(CO)_2(PPh_3)_2$ [5b] is formed in high yield.

### 2.3. Introduction of tris(N-pyrrolyl)phosphine to the osmium(0) complex, $Os(CO)_2(PPh_3)_3$

$Os(CO)_2(PPh_3)_3$ [6] has a labile triphenylphosphine ligand that can be replaced by many $\eta^1$- and $\eta^2$-ligands [7]. Accordingly, when a benzene solution containing tris(*N*-pyrrolyl)phosphine and $Os(CO)_2(PPh_3)_3$ is subjected to photolysis from a 1000 W tungsten–halogen lamp, $Os(CO)_2[P(NC_4H_4)_3](PPh_3)_2$ (**4**) is formed (see Scheme 3). While $Os(CO)_2(PPh_3)_3$ is a highly air-sensitive complex, **4** could be purified by column chromatography in the air. The IR spectrum of **4** shows η(CO) at 1922 and 1867 cm$^{-1}$ indicating that the two-carbonyl ligands are mutually *cis*. The $^1$H-NMR



Scheme 3. Synthesis of tris($N$-pyrrolyl)phosphine complexes of osmium(0).

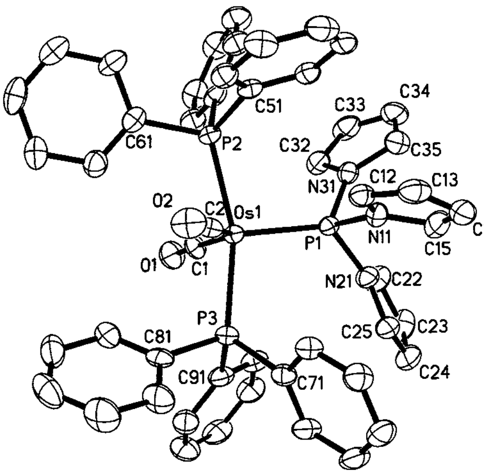


Fig. 1. Molecular geometry of $Os(CO)_2[P(NC_4H_4)_3](PPh_3)_2$ (**4**).

Table 1
Data collection and processing parameters for **4**

| | |
|---|---|
| Formula | $C_{50}H_{42}N_3O_2OsP_3$ |
| Molecular weight | 999.98 |
| Temperature (K) | 173 |
| Wavelength (Å) | 0.71069 |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| $a$ (Å) | 19.177(6) |
| $b$ (Å) | 12.429(8) |
| $c$ (Å) | 18.467(7) |
| $\beta$ (°) | 103.10(3) |
| $V$ (Å$^3$) | 4287(3) |
| Z | 4 |
| $D_{calc}$ (g cm$^{-3}$) | 1.549 |
| $F$(000) | 2000 |
| $\mu$ (mm$^{-1}$) | 3.13 |
| Crystal size (mm) | $0.47 \times 0.37 \times 0.35$ |
| $A$ (min–max) | 0.321 0.407 |
| $2\theta$ (min–max) (°) | 1–25 |
| Independent reflections | 7772 |
| Function minimised | $\Sigma w(F_o^2 - F_c^2)^2$ |
| Observed reflections | 5863 |
| Goodness of fit on $F^2$ | 1.007 |
| $R$, $wR_2$ (observed data) [a] | 0.0368, 0.0877 |
| $R$, $wR_2$ (all data) | 0.0639, 0.0970 |
| Difference map (min–max) (e Å$^{-3}$) | +0.90 −0.93 |

[a] $R = \Sigma|F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

spectrum of **4** shows broad multiplets at 6.00 and 6.22 ppm, which are assigned to the pyrrolyl protons. The $^{31}$P-NMR spectrum shows a doublet for the phosphorus resonance of the triphenylphosphine ligands at 9.43 ($^2J_{PP} = 30.0$ Hz) and a triplet for the $P(NC_4H_4)_3$ phosphorus at 83.64 ppm ($^2J_{PP} = 31.0$ Hz). This is consistent with the complex having a trigonal bipyramidal geometry with axial triphenylphosphine ligands and an equatorial tris($N$-pyrrolyl)phosphine ligand, as depicted in Scheme 3. This geometry was confirmed by an X-ray crystal structure determination.

### 2.4. *Crystal structure of $Os(CO)_2[P(NC_4H_4)_3](PPh_3)_2$ (4)*

The molecular geometry of **4** is shown in Fig. 1 and selected bond lengths and angles are presented in Tables 1 and 2. The geometry about osmium can be described as distorted trigonal bipyramidal with the triphenylphosphine ligands axial [P(2)–Os(1)–P(3), 160.66(6)°] and the two carbonyl ligands equatorial [C(1)–Os(1)–C(2), 133.2(3)°]. The osmium–triphenylphosphine distances and the osmium–carbonyl distances are normal. The tris($N$-pyrrolyl)phosphine ligand occupies an equatorial position of the trigonal bipyramidal structure, where maximum overlap with metal π-donor orbitals is possible. The osmium–tris($N$-pyrrolyl)phosphine distance [Os(1)–P(1), 2.2764(18) Å] is significantly shorter than that observed for the osmium–triphenylphosphine bonds [Os(1)–P(2), 2.392(2) Å; Os(1)–P(3), 2.370(2) Å]. A search of the Cambridge crystallographic database reveals that the osmium–tris($N$-pyrrolyl)phosphine distance in complex **4** is right at the short end of the range of observed Os–$PR_3$

Table 2
Selected bond lengths (Å) and angles (°) for **4**

| | |
|---|---|
| *Bond lengths* | |
| Os(1)–C(1) | 1.898(6) |
| Os(1)–C(2) | 1.911(7) |
| Os(1)–P(1) | 2.2764(18) |
| Os(1)–P(3) | 2.370(2) |
| Os(1)–P(2) | 2.392(2) |
| P(1)–N(31) | 1.719(5) |
| P(1)–N(11) | 1.727(5) |
| P(1)–N(21) | 1.744(5) |
| C(1)–O(1) | 1.156(7) |
| C(2)–O(2) | 1.135(8) |
| *Bond angles* | |
| C(1)–Os(1)–C(2) | 133.2(3) |
| C(1)–Os(1)–P(1) | 113.12(19) |
| C(2)–Os(1)–P(1) | 113.7(2) |
| C(1)–Os(1)–P(3) | 86.8(2) |
| C(2)–Os(1)–P(3) | 84.96(18) |
| P(1)–Os(1)–P(3) | 99.81(7) |
| C(1)–Os(1)–P(2) | 91.3(2) |
| C(2)–Os(1)–P(2) | 82.41(18) |
| P(1)–Os(1)–P(2) | 98.66(7) |
| P(3)–Os(1)–P(2) | 160.66(6) |
| O(1)–C(1)–Os(1) | 177.8(5) |
| O(2)–C(2)–Os(1) | 174.5(6) |

distances (the mean of 1450 observations is 2.363 Å with a standard deviation (S.D.) 0.051). The structure of a closely related complex, $Os(CO)_2[PH(OMe)Ph](PPh_3)_2$, has been determined [8] and found to have the same arrangement of ligands about osmium with the triphenylphosphine ligands axial and the two carbonyl ligands and PH(OMe)Ph occupying the equatorial positions. In this complex, the osmium–PH(OMe)Ph bond length is 2.299(4) Å, 0.023 Å longer than that of the corresponding osmium–tris(*N*-pyrrolyl)phosphine bond length in complex **4**.

The variation of phosphorus–nitrogen bond lengths in compounds with a M–P–N linkage has been used as a diagnostic tool to examine the extent of phosphorus back bonding [1]. In the general case $L_nM–PZ_3$, as the M–P bond distance decreases because of increased M–P back bonding, the P–Z distances are increased. This has been attributed to back bonding into P–Z $\sigma^*$ orbitals. Structural studies of the two rhodium complexes, $RhCl(CO)[P(NC_4H_4)_3]_2$ and $[PPN][Rh(CO)\{P(NC_4H_4)_3\}_3]$ [1], show that the P–N distances in the anionic complex, where greater back bonding is to be expected, were significantly longer (av. 1.735 Å) than those found in the neutral species (av. 1.690 Å). In complex **4** the P–N bond distances are long [1.744(5), 1.719(5) and 1.727(5) Å], consistent with the idea that the tris(*N*-pyrrolyl)phosphine ligand is behaving as a π-accepting ligand in this electron-rich osmium(0) complex. It can also be noted that the ν(CO) bands for **4** at 1922 and 1867 $cm^{-1}$ are some 20 $cm^{-1}$ higher than those observed for $Os(CO)_2[PH(OMe)Ph](PPh_3)_2$ (1904, 1847 $cm^{-1}$) [8] again pointing to the excellent π-accepting properties of the tris(*N*-pyrrolyl)phosphine ligand.

### *2.5. Introduction of tris(N-pyrrolyl)phosphine to the osmium(0) complex, $Os(CO)(CS)(PPh_3)_3$*

Reaction between $Os(CO)(CS)(PPh_3)_3$ and $P(NC_4H_4)_3$ again proceeds with displacement of one triphenylphosphine ligand to give $Os(CO)(CS)[P(NC_4H_4)_3](PPh_3)_2$ (**5**) (see Scheme 3). The IR spectrum of complex **5** reveals ν(CO) at 1904 $cm^{-1}$ and ν(CS) at 1247 $cm^{-1}$. The pyrrolyl ring carbon resonances appear as doublets at 110.86 ($^2J_{CP} = 6.0$ Hz) and 123.67 ($^3J_{CP} = 6.0$ Hz) in the $^{13}C$-NMR spectrum. The $^{31}P$-NMR spectrum shows a doublet at 8.96 ppm ($^2J_{PP} = 35.6$ Hz), which is assigned to the two phosphorus nuclei of the equivalent triphenylphosphine ligands, and a triplet at 83.38 ppm ($^2J_{PP} = 35.0$ Hz), which is assigned to the tris(*N*-pyrrolyl)phosphine ligand. This is consistent with a structure that is the same as that of complex **4** with CS replacing one CO.

## 3. Conclusions

Two new tris(*N*-pyrrolyl)phosphine complexes of osmium(II) have been prepared. Both showed IR carbonyl stretching absorptions at significantly higher frequencies than the analogous triphenylphosphine complexes, reflecting the π-acceptor nature of the tris(*N*-pyrrolyl)phosphine ligand. Two new osmium (0) complexes, $Os(CO)_2[P(NC_4H_4)_3](PPh_3)_2$ (**4**) and $Os(CO)(CS)[P(NC_4H_4)_3](PPh_3)_2$ (**5**) were also prepared and **4** was studied structurally. In **4**, the location of the tris(*N*-pyrrolyl)phosphine, the ν(CO) values and the Os–P and P–N distances all point to the tris(*N*-pyrrolyl)phosphine ligand acting as a very good π-acceptor in this complex.

## 4. Experimental

### *4.1. General procedures and instruments*

Standard laboratory procedures were followed as have been described previously [9]. The compound $Os(p\text{-tolyl})Cl(CO)(PPh_3)_2$ [10] was prepared according to the literature method.

IR spectra (4000–400 $cm^{-1}$) were recorded as Nujol mulls between KBr plates on a Perkin–Elmer Paragon 1000 spectrometer. NMR spectra were obtained on a Bruker DRX 400 at 25 °C. $^1H$-, $^{13}C$- and $^{31}P$-NMR spectra were obtained operating at 400.1 ($^1H$), 100.6 ($^{13}C$) and 162.0 ($^{31}P$) MHz, respectively. Resonances are quoted in ppm and $^1H$-NMR spectra referenced to either $Me_4Si$ (0.00 ppm) or the proteo-impurity in the solvent (7.25 ppm for $CHCl_3$). $^{13}C$-NMR spectra were referenced to $CDCl_3$ (77.00 ppm) and $^{31}P$-NMR spectra to 85% *ortho*-phosphoric acid (0.00 ppm) as an external standard. Mass spectra were recorded using the fast atom bombardment technique with a Varian VG 70-SE mass spectrometer. Elemental analyses were obtained from the Microanalytical Laboratory, University of Otago.

### *4.2. Preparation of $OsHCl(CO)[P(NC_4H_4)_3](PPh_3)_2$ (1)*

Freshly deoxygenated benzene (20.0 ml) was added to a Schlenk tube containing $OsHCl(CO)(PPh_3)_3$ (200 mg, 0.192 mmol) and $P(NC_4H_4)_3$ (44.0 mg, 0.19 mmol). The colourless solution was heated under reflux for 2 h and cooled. $C_6H_{12}$ (50 ml) was added and the resulting white flocculent powder was collected by filtration, washed with $C_6H_{12}$ (20 ml) and recrystallised from $CH_2Cl_2$–EtOH (25:10 ml) to yield white needles of pure **1** (176 mg, 91%). Anal. Calc. for $C_{49}H_{43}ClN_3OOsP_3$: C, 58.36; H, 4.30; N, 4.17. Found: C, 58.21; H, 4.47; N, 4.05%. IR ($cm^{-1}$): 1936 ν(CO); 2035 ν(OsH); 1178, 1088, 1061, 1040. $^1H$-NMR ($CDCl_3$; δ): −4.92 (dt, Os*H*, $^2J_{\mathrm{HP}trans} = 138.4$ Hz, $^2J_{\mathrm{HP}cis} = 25.2$ Hz); 6.04 (m, $\mathrm{P(NC_4\mathit{H}_4)_3}$); 6.13 (m, $\mathrm{P(NC_4\mathit{H}_4)_3}$); 7.00–7.31 (m, 30H, $\mathrm{PPh_3}$). $^{13}$C-NMR ($\mathrm{C_6D_6}$; $\delta$): 111.32 (d, $\mathrm{P(N\mathit{C}_4H_4)_3}$, $^2J_{\mathrm{CP}} = 5.0$ Hz); 123.98 (d, $\mathrm{P(N\mathit{C}_4H_4)_3}$, $^3J_{\mathrm{CP}} = 5.0$ Hz); 127.55 (t′ [9], $\mathrm{PPh_3}$ *ortho*, $^{2,4}J_{\mathrm{CP}} = 10.1$ Hz); 129.35 (s, $\mathrm{PPh_3}$ *para*); 134.37 (t′, $\mathrm{PPh_3}$ *meta* $^{3,5}J_{\mathrm{CP}} = 10.1$ Hz); 133.91 (t′, $\mathrm{PPh_3}$ *ipso*, $^{1,3}J_{\mathrm{CP}} = 42.3$ Hz). $^{31}$P-NMR ($\mathrm{CDCl_3}$; $\delta$): 3.71 (d, $\mathrm{PPh_3}$, $^2J_{\mathrm{PP}} = 13.4$ Hz); 68.74 (t, $\mathrm{P(NC_4H_4)_3}$, $^2J_{\mathrm{PP}} = 13.3$ Hz).

### 4.3. Preparation of Os(p-tolyl)($\eta^2$-$O_2CH$)(CO)($PPh_3$)$_2$ (**2**)

Os(*p*-tolyl)Cl(CO)($\mathrm{PPh_3}$)$_2$ (0.500 mg, 0.575 mmol) was added to $\mathrm{CH_2Cl_2}$ (80 ml). A solution of HCOONa (0.200 mg, 2.94 mmol) in EtOH (ca. 60 ml) and water (ca. 1 ml) was added slowly and the resulting suspension stirred at room temperature (r.t.) for ca. 1 h. During this time the red suspension turned into a yellow solution. The $\mathrm{CH_2Cl_2}$ was removed under reduced pressure without heating and the product collected and washed well with water, EtOH and $\mathrm{C_6H_{12}}$. Recrystallisation from $\mathrm{CH_2Cl_2}$–EtOH afforded yellow chunky crystals of pure **2** (0.490 mg, 97%). Anal. Calc. for $\mathrm{C_{45}H_{38}O_3OsP_2}$: C, 61.49; H, 4.36; P, 7.05. Found: C, 61.45; H, 4.57; P, 6.91%. IR (cm$^{-1}$): 1899 $\nu$(CO), 1543, 1359 $\nu$(CO) formate, 1308, 813, 801. $^1$H-NMR ($\mathrm{CD_2Cl_2}$–$d_6$-DMSO; $\delta$): 1.99 (s, C*H*$_3$); 6.21–6.19 (m, $\mathrm{C_6\mathit{H}_4CH_3}$); 6.69–6.68 (m, $\mathrm{C_6\mathit{H}_4CH_3}$); 7.38–7.29 (m, $\mathrm{PPh_3}$); 7.99 (t, $\mathrm{O_2C\mathit{H}}$, $^4J_{\mathrm{HP}} = 1.6$ Hz). Compound **2** is too insoluble for measurement of a satisfactory $^{13}$C-NMR spectrum.

### 4.4. Preparation of OsH(p-tolyl)(CO)[P($NC_4H_4$)$_3$]($PPh_3$)$_2$ (**3**)

Freshly distilled and deoxygenated $\mathrm{C_6H_6}$ (20 ml) was added to a Schlenk tube containing Os(*p*-tolyl)($\eta^2$-$\mathrm{O_2CH}$)(CO)($\mathrm{PPh_3}$)$_2$ (200 mg, 0.259 mmol) and $\mathrm{P(NC_4H_4)_3}$ (60 mg, 0.26 mmol). The colourless solution was heated to 60 °C for 5 min and then reduced in volume in vacuo. $\mathrm{C_6H_{12}}$ was added to effect crystallisation of colourless crystals of **3**, which were recrystallised from $\mathrm{CH_2Cl_2}$–EtOH (25:10 ml) to give pure **3** (194 mg, 80%). Anal. Calc. for $\mathrm{C_{56}H_{50}N_3OOsP_3 \cdot CH_2Cl_2}$: C, 59.58; H, 4.56; N, 3.65. Found: C, 60.20; H, 4.62; N, 4.17%. IR (cm$^{-1}$): 1935 $\nu$(CO), 2137 $\nu$(OsH), 1290, 1185, 1176, 1089, 1059, 1041, 796, 577, 555. $^1$H-NMR ($\mathrm{CDCl_3}$; $\delta$): $-6.44$ (dt, Os*H*, $^2J_{\mathrm{HP}trans} = 129.6$ Hz, $^2J_{\mathrm{HP}cis} = 28.8$ Hz); 2.43 (s, 3H, $\mathrm{C_6H_4C\mathit{H}_3}$); 6.05 (m, $\mathrm{P(NC_4\mathit{H}_4)_3}$); 6.06 (m, $\mathrm{P(NC_4\mathit{H}_4)_3}$); 6.92–7.32 (m, 30H $\mathrm{PPh_3}$). $^{13}$C-NMR ($\mathrm{C_6D_6}$; $\delta$): 23.0 (s, *C*H$_3$); 111.35 (d, $\mathrm{P(N\mathit{C}_4H_4)_3}$), $^3J_{\mathrm{CP}} = 5.0$ Hz); 123.50 (d, $\mathrm{P(N\mathit{C}_4H_4)_3}$), $^2J_{\mathrm{CP}} = 6.0$ Hz); 129.16 (s, $\mathrm{\mathit{C}_6H_4}$); 129.31 (s, $\mathrm{\mathit{C}_6H_4}$); 137.27 (s, $\mathrm{\mathit{C}_6H_4}$); 127.58 (t′, $\mathrm{PPh_3}$ *ortho*, $^{2,4}J_{\mathrm{CP}} = 10.1$ Hz), 129.31 (s, $\mathrm{PPh_3}$ *para*); 134.41 ($\mathrm{PPh_3}$ *ipso* $^{1,3}J_{\mathrm{CP}} = 52.3$ Hz); 134.41 (t′, $\mathrm{PPh_3}$ *meta*, $^{3,5}J_{\mathrm{CP}} = 10.1$ Hz). $^{31}$P-NMR ($\mathrm{CDCl_3}$; $\delta$): $-2.55$ (d, $\mathrm{PPh_3}$, $^2J_{\mathrm{PP}} = 13.2$ Hz); 78.08 (t, $\mathrm{P(NC_4H_4)_3}$, $^2J_{\mathrm{PP}} = 13.6$ Hz).

### 4.5. Preparation of Os(CO)$_2$[P($NC_4H_4$)$_3$]($PPh_3$)$_2$ (**4**)

Freshly distilled and deoxygenated $\mathrm{C_6H_6}$ (20 ml) was added to a Schlenk tube containing $\mathrm{Os(CO)_2(PPh_3)_3}$ (200 mg, 0.193 mmol) and $\mathrm{P(NC_4H_4)_3}$ (43.0 mg, 0.193 mmol). The bright yellow solution was then subjected to photolysis from a 1000 W tungsten–halogen lamp for a period of 25 min. Throughout the duration of this experiment the reaction mixture was kept between 30 and 40 °C and the bright yellow colour faded to a lighter shade of yellow. The volume of $\mathrm{C_6H_6}$ was then reduced and $\mathrm{C_6H_{12}}$ (50 ml) was added to yield a pale lemon-yellow solid. This solid was collected by filtration and either recrystallised from $\mathrm{CH_2Cl_2}$–EtOH (25:10 ml) or subjected to column chromatography on silica gel (5 × 1.5 cm) using $\mathrm{CH_2Cl_2}$ as eluant to give lemon-yellow crystals of pure **4** (172 mg, 89%). *m*/*z* 1001.2105; $\mathrm{C_{50}H_{42}N_3OsO_2P_3}$ requires 1001.2123. Anal. Calc. for $\mathrm{C_{50}H_{42}N_3OsO_2P_3}$: C, 60.05; H, 4.23; N, 4.20. Found: C, 59.55; H, 4.10; N, 4.35%. IR (cm$^{-1}$): 1922, 1867 $\nu$(CO), 1586, 1175, 1288, 1261, 1175, 1125, 1083, 1056, 1037, 803. $^1$H-NMR ($\mathrm{CDCl_3}$; $\delta$): 6.00 (m, $\mathrm{P(NC_4\mathit{H}_4)_3}$); 6.22 (m, $\mathrm{P(NC_4\mathit{H}_4)_3}$); 7.19–7.42 (m, 30H $\mathrm{PPh_3}$). $^{13}$C-NMR ($\mathrm{C_6D_6}$; $\delta$): 110.66 (d, $\mathrm{P(N\mathit{C}_4H_4)_3}$, $^2J_{\mathrm{CP}} = 6.0$ Hz); 123.32 (d, $\mathrm{P(N\mathit{C}_4H_4)_3}$, $^3J_{\mathrm{CP}} = 6.0$ Hz); 127.73 (t′, $\mathrm{PPh_3}$ *ortho*, $^{2,4}J_{\mathrm{CP}} = 10.1$); 129.21 (s, $\mathrm{PPh_3}$ *para*); 133.41 (t′, $\mathrm{PPh_3}$ *meta*, $^{3,5}J_{\mathrm{CP}} = 12.1$ Hz); 137.43 (t′, $\mathrm{PPh_3}$ *ipso*, $^{1,3}J_{\mathrm{CP}} = 49.3$ Hz); 204.78 (t, *C*O, $^2J_{\mathrm{CP}} = 11.1$ Hz); 204.81 (t, CO, $^2J_{\mathrm{CP}} = 11.06$ Hz). $^{31}$P-NMR ($\mathrm{CDCl_3}$; $\delta$): 9.43 (d, $\mathrm{PPh_3}$, $^2J_{\mathrm{PP}} = 30.0$ Hz); 83.64 (t, $\mathrm{P(NC_4H_4)_3}$, $^2J_{\mathrm{PP}} = 31.0$ Hz).

### 4.6. Preparation of Os(CO)(CS)[P($NC_4H_4$)$_3$]($PPh_3$)$_2$ (**5**)

$\mathrm{Os(CS)(CO)(PPh_3)_3}$ (200 mg, 0.193 mmol) was treated as in the preparation of complex **4** to yield light tan crystals of pure **5** (130 mg, 76%). Anal. Calc. for $\mathrm{C_{50}H_{42}N_3OOsP_3S \cdot 0.5CH_2Cl_2}$: C, 57.29; H, 4.10; N, 3.97. Found: C, 56.91; H, 4.50; N, 3.81%. IR (cm$^{-1}$): 1904 $\nu$(CO), 1247 $\nu$(CS), 1585, 1232, 1180, 1173, 1156, 1087, 1071, 1056, 1039, 999, 626, 615, 555. $^1$H-NMR ($\mathrm{CDCl_3}$; $\delta$): 6.00 (m, $\mathrm{P(NC_4\mathit{H}_4)_3}$); 6.23 (m, $\mathrm{P(NC_4\mathit{H}_4)_3}$), 7.21–7.42 (m, 30H $\mathrm{PPh_3}$). $^{13}$C-NMR ($\mathrm{C_6D_6}$; $\delta$): 110.86 (d, $\mathrm{P(N\mathit{C}_4H_4)_3}$, $^2J_{\mathrm{CP}} = 6.0$ Hz); 123.67 (d, $\mathrm{P(N\mathit{C}_4H_4)_3}$, $^3J_{\mathrm{CP}} = 6.0$ Hz); 128.24 (t′, $\mathrm{PPh_3}$ *ipso*, $^{1,3}J_{\mathrm{CP}} = 37.2$ Hz); 127.55 (t′, $\mathrm{PPh_3}$ *ortho*, $^{2,4}J_{\mathrm{CP}} = 10.1$ Hz); 129.50 (s, $\mathrm{PPh_3}$ *para*); 134.26 (t′, $\mathrm{PPh_3}$ *meta*, $^{3,5}J_{\mathrm{CP}} = 12.1$ Hz). $^{31}$P-NMR ($\mathrm{CDCl_3}$; $\delta$): 8.96 (d, $\mathrm{PPh_3}$, $^2J_{\mathrm{PP}} = 35.6$ Hz); 83.38 (t, $\mathrm{P(NC_4H_4)_3}$, $^2J_{\mathrm{PP}} = 35.0$ Hz).

### *4.7. X-ray crystal structure determination for complex **4***

X-ray data collection for **4** was on a Siemens SMART diffractometer with a CCD area detector, using graphite monochromated Mo–$K_\alpha$ radiation ($\lambda = 0.71073$ Å). Data were integrated and Lorentz and polarisation correction applied using SAINT [11] software. Semi-empirical absorption corrections were applied based on equivalent reflections using SADABS [12]. The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares on $F^2$ using programs SHELXS [13] and SHELXL [14]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in calculated positions and refined with a riding model with thermal parameter 20% greater than $U_{iso}$ of the carrier atom. Crystal data and refinement details are given in Table 1.

## 5. Supplementary material

Crystallographic data (excluding structure factors) for **4** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 164866. Copies of this information can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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