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Bromination and nitration reactions of metallated (Ru and Os) multiaromatic ligands and crystal structures of selected products

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Abstract

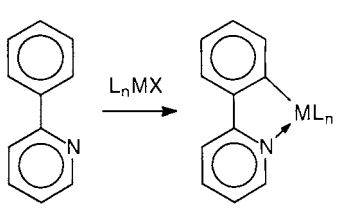
Three nitrogen-containing aromatic heterocycles, 2-(1′-naphthyl)pyridine, 2-phenylquinoline, and 2,3-diphenylquinoxaline, have been mercurated in the naphthyl or phenyl ring 2-position and then symmetrised to form the mercury compounds Ar_2Hg (Ar = Nppy (**3**), Phqn (**1**) or Dpqx (**5**), respectively). These reagents are suitable for *trans*-metallation and reaction with $MHCl(CO)(PPh_3)_3$ affords the complexes $M(\eta^2\text{-C,N–Ar})Cl(CO)(PPh_3)_2$, (**6**, M = Ru, Ar = Nppy; **7**, M = Os, Ar = Nppy; **8**, M = Ru, Ar = Phqn; **9**, M = Os, Ar = Phqn; **10**, M = Ru, Ar = Dpqx; **11**, M = Os, Ar = Dpqx) in which each product features an aryl ligand that forms a strongly chelated five-membered ring through coordination of the heterocyclic N atom. The chloride ligand in each of the complexes **6**–**11** can be replaced by dimethyl dithiocarbamate to give ultimately the mono-triphenylphosphine complexes, $M(\eta^2\text{-Ar})(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)$ (**12**, M = Ru, Ar = Nppy; **13**, M = Os, Ar = Nppy; **14**, M = Ru, Ar = Phqn; **15**, M = Os, Ar = Phqn; **16**, M = Ru, Ar = Dpqx; **17**, M = Os, Ar = Dpqx). Similarly, compound **10** when treated with Na(acac) gives $Ru(\eta^2\text{-Dpqx})(\eta^2\text{-acac})(CO)(PPh_3)$ (**18**), while treatment with trifluoroacetic acid gives $Ru(\eta^2\text{-Dpqx})(O_2CCF_3)(CO)(PPh_3)_2$ (**19**). Many of these complexes were found to be very robust, making them suitable for electrophilic aromatic substitution reactions under harsh conditions. In each case, the presence of the metal had both an activating and a directing effect on the aryl ring to which it was bonded. Bromination or nitration reactions, both of which are not normally possible with organometallic substrates, were carried out successfully, giving rise to monobrominated or dinitrated products, respectively. The following compounds were characterised, $M(\eta^2\text{-Ar-4-Br})Cl(CO)(PPh_3)_2$ (**20**, M = Ru, Ar = Phqn; **21**, M = Os, Ar = Phqn; **22**, M = Ru, Ar = Dpqx; **24**, M = Os, Ar = Dpqx), $M(\eta^2\text{-Dpqx-4-Br})(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)$ (**23**, M = Ru; **25**, M = Os), $Os(\eta^2\text{-Ar})Cl(CO)(PPh_3)_2$ (**26**, Ar = Nppy-6,8-$(NO_2)_2$; **27**, Ar = Phqn-4,6-$(NO_2)_2$). Crystal structures of compounds **7**, **12**, **15**, **18**, **19**, **21**, **23** and **25** have been determined.

Keywords: Ruthenium; Osmium; *ortho*-Metallation; *trans*-Metallation; Electrophilic aromatic substitution; X-ray structures

1. Introduction

Cyclometallated aryl ligands of platinum group metal complexes have long been known, and many examples exist in the literature. For example, the metallation of 2-phenylpyridine and derivatives thereof with a variety of electrophilic metal substrates occurs in the phenyl ring (see Scheme 1), *ortho* to the attached pyridyl substituent. This results in the formation of a five-membered chelate ring, structurally similar to complexes of the bipyridine ligand [1].

We have previously shown that by utilising the mercury reagent, $Phpy_2Hg$, which can be prepared by *ortho*-mercuration of the phenyl ring of 2-phenylpyridine followed by symmetrisation, the 2-phenylpyridyl ligand can be readily transferred to ruthenium and osmium complexes by reaction with the



Scheme 1.

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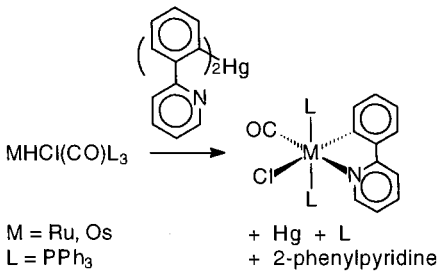


Scheme 2.

substrates $MHCl(CO)(PPh_3)_3$ (M = Ru, Os) [2] to form the corresponding cyclometallated products shown in Scheme 2. Similar *trans*-metallation reactions using mercury reagents of the form Ar_2Hg have been used to deliver a wide variety of σ-bound aryl fragments, chelating or non-chelating, to these ruthenium and osmium substrates. In each case the same stoichiometry is observed, with the deposition of elemental mercury, loss of one triphenylphosphine ligand and the formation of one equivalent of the unmetallated ligand, ArH [3].

It was found that complexes with chelating organometallic ligands, especially $M(\eta^2\text{-Phpy})Cl(CO)(PPh_3)_2$, were very robust, and seemingly resistant to a variety of reaction conditions that few organometallic compounds are able to withstand without suffering metal–carbon bond cleavage. This is thought to be due mainly to the favourable five-membered chelate ring. Because of this robustness, it was possible to take advantage of a specific activating and directing effect associated with these metal-ligand fragments. For both the ruthenium and osmium complexes, the σ-bound phenyl group of the Phpy ligand was found to be highly activated toward electrophilic aromatic substitution reactions, and both nitration and bromination reactions were able to be conducted under relatively mild conditions with excellent selectivity, and no discernible decomposition due to loss of the metal–carbon σ-bond.

Electrophilic substitution of organometallic ligands is currently a very uncommon method of introducing functional groups. Although there are numerous examples of substituted σ-aryl complexes of transition metals, the functionality is almost invariably introduced to the organic fragment prior to its attachment to a metal. We are interested in extending our studies on the electrophilic substitution reactions of organometallic ligands to include more complicated aromatic systems, as well as applying new techniques for introducing functional groups.

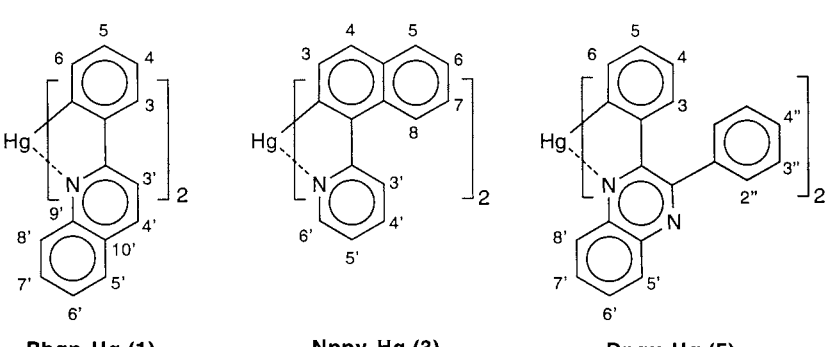
2. Results and discussion

2.1. Mercuration

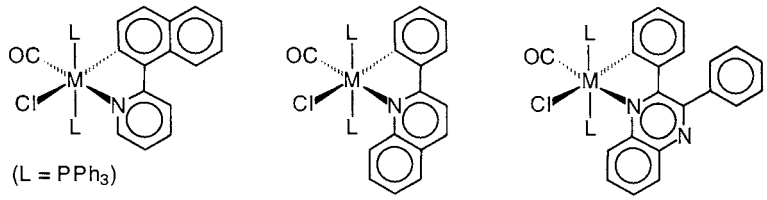
The aryl rings of the three organic compounds shown in Scheme 3, 2-(1′-naphthyl)pyridine, 2-phenylquinoline and 2,3-diphenylquinoxaline have each been directly mercurated in the position *ortho* to the nitrogen-containing attached side-arm. As shown in Scheme 3, the *ortho*-metallated forms of these ligands are denoted as Nppy, Phqn and Dpqx, respectively. The new compounds ArHgCl (**2**, Ar = Nppy; **4**, Ar = Dpqx), have been characterised. Upon symmetrisation, the organomercury chlorides, ArHgCl, yield Ar_2Hg (**1**, Ar = Phqn; **3**, Ar = Nppy; **5**, Ar = Dpqx). In the case of 2,3-diphenylquinoxaline, both phenyl rings could, in principle, undergo mercuration. Although in the related palladation reaction of this compound both rings are cyclopalladated [4], in this study mercuration was observed to occur in one position only, as indicated.

2.2. Trans-metallation

The reaction of $MHCl(CO)(PPh_3)_3$ (M = Ru, Os) with Ar_2Hg gives rise to $M(\eta^2\text{-Ar})Cl(CO)(PPh_3)_2$ (**6**, M = Ru, Ar = Nppy; **7**, M = Os, Ar = Nppy; **8**, M = Ru, Ar = Phqn; **9**, M = Os, Ar = Phqn; **10**, M = Ru, Ar = Dpqx; **11**, M = Os, Ar = Dpqx) as shown in Scheme 4 (IR data for all new complexes are given in



Scheme 3.



Scheme 4.

Table 1). The yields are good, although not as satisfactory as for some of the analogous *trans*-metallation reactions involving smaller, simpler aryl ligands. Complexes of the Phpy and Nppy ligands are yellow or pale orange, colours typical of related coordinatively saturated ruthenium(II) and osmium(II) compounds. Complexes of the Dpqx ligand are very intensely coloured, being deep red (ruthenium) or dark purple (osmium). The strong coloration is probably due to a charge-transfer transition, rather than coordinative unsaturation at the metal centre since the coordination face of this ligand is structurally very similar to Phqn.

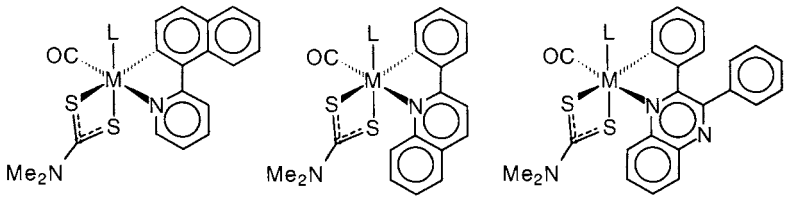
All of the resultant complexes were found to be very robust and easy to handle, being stable in air and not decomposed by conditions such as recrystallisation in the presence of mineral acids. The uncoordinated nitrogen atom in each of the complexes **10** and **11** was not very basic, and in fact was quite unreactive. Recrystallisation of either the ruthenium or osmium compound in the presence of dilute HCl gave rise to unchanged starting material, and heating under reflux in methyl iodide as solvent did not result in methylation at nitrogen. Recrystallisation of $Ru(\eta^2\text{-Dpqx})Cl(CO)(PPh_3)_2$ (**10**) in the presence of trifluoroacetic acid produced the compound $Ru(\eta^2\text{-Dpqx})(\eta^1\text{-}O_2CCF_3)(CO)(PPh_3)_2$ (**19**), in which the labile chloride ligand was replaced by monodentate trifluoroacetate. This product has been structurally characterised by X-ray crystallography (see below).

2.3. Metal-centred derivatisation

The reactivity of the complexes $M(\eta^2\text{-Ar})Cl(CO)(PPh_3)_2$ (**6**–**11**) largely parallels that of the previously reported complexes, $M(\eta^2\text{-Phpy})Cl(CO)(PPh_3)_2$ [2]. One method of derivatisation that was applied to all of the complexes **6**–**11** involved removal of the chloride ligand from each using $AgSbF_6$, followed by treatment of the resulting cation with sodium dimethyldithiocarbamate. The intermediate compound, in which the dithiocarbamate ligand was bound in a monodentate fashion, was in some cases observed by

Table 1
Infrared data for ruthenium and osmium complexes

Complex	ν(CO) (cm^{-1})	Other bands
$Ru(\eta^2\text{-Nppy})Cl(CO)(PPh_3)_2$ (**6**)	1915 s	
$Os(\eta^2\text{-Nppy})Cl(CO)(PPh_3)_2$ (**7**)	1898 s	
$Ru(\eta^2\text{-Phqn})Cl(CO)(PPh_3)_2$ (**8**)	1927 s	
$Os(\eta^2\text{-Phqn})Cl(CO)(PPh_3)_2$ (**9**)	1910 s	
$Ru(\eta^2\text{-Dpqx})Cl(CO)(PPh_3)_2$ (**10**)	1939 s	
$Os(\eta^2\text{-Dpqx})Cl(CO)(PPh_3)_2$ (**11**)	1920 s	
$Ru(\eta^2\text{-Nppy})(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)$ (**12**)	1923 s	1503 m (dithiocarbamate)
$Os(\eta^2\text{-Nppy})(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)$ (**13**)	1908 s	1531 m (dithiocarbamate)
$Ru(\eta^2\text{-Phqn})(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)$ (**14**)	1935 s	1513 m (dithiocarbamate)
$Os(\eta^2\text{-Phqn})(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)$ (**15**)	1917 s	1515 m (dithiocarbamate)
$Ru(\eta^2\text{-Dpqx})(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)$ (**16**)	1938 s	1519 m (dithiocarbamate)
$Os(\eta^2\text{-Dpqx})(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)$ (**17**)	1921 s	1515 m (dithiocarbamate)
$Ru(\eta^2\text{-Dpqx})(\eta^2\text{-acac})(CO)(PPh_3)$ (**18**)	1933 s	1515 m (acetylacetonate)
$Ru(\eta^2\text{-Dpqx})(O_2CCF_3)(CO)(PPh_3)_2$ (**19**)	1949 s	1682 m (trifluoroacetate)
$Ru(\eta^2\text{-Phqn-4-Br})Cl(CO)(PPh_3)_2$ (**20**)	1929 s	
$Os(\eta^2\text{-Phqn-4-Br})Cl(CO)(PPh_3)_2$ (**21**)	1907 s	
$Ru(\eta^2\text{-Dpqx-4-Br})Cl(CO)(PPh_3)_2$ (**22**)	1955 s	
$Ru(\eta^2\text{-Dpqx-4-Br})(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)$(**23**)	1949 s	1504 m (dithiocarbamate)
$Os(\eta^2\text{-Dpqx-4-Br})Cl(CO)(PPh_3)_2$ (**24**)	1922 s	
$Os(\eta^2\text{-Dpqx-4-Br})(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)$ (**25**)	1931 s	1505 m (dithiocarbamate)
$Os(\eta^2\text{-Nppy-6,8-}(NO_2)_2)Cl(CO)(PPh_3)_2$ (**26**)	1916 s	1538, 1531 m (nitro)
$Os(\eta^2\text{-Phqn-4,6-}(NO_2)_2)Cl(CO)(PPh_3)_2$ (**27**)	1943 s	1520, 1504 m (nitro)



(12) M = Ru
(13) M = Os
(L = PPh_3)

(14) M = Ru
(15) M = Os

(16) M = Ru
(17) M = Os

Scheme 5.

^{1}H-NMR spectroscopy. These intermediates rapidly lost one triphenylphosphine ligand in solution to give the complexes in which the dithiocarbamate ligand is bound to the metal in a bidentate manner. The compounds **12**–**17** were formed in this way (see Scheme 5). Qualitatively, it was observed that the loss of the triphenylphosphine ligand proceeded more rapidly when the metal was ruthenium than when it was osmium, and also more rapidly for the two ligands, Phqn and Dpqx, than for Nppy. These latter observations could possibly be a consequence of steric effects since Nppy must bring considerably less steric bulk to the metal coordination sphere than the other two ligands.

It was also found that Ru(η^2-Dpqx)Cl(CO)(PPh_3)$_2$ (**10**) reacted with sodium acetylacetonate in a manner similar to the reactions with dimethyldithiocarbamate, to form Ru(η^2-Dpqx)(η^2-acac)(CO)(PPh_3) (**18**).

2.4. Electrophilic aromatic substitution reactions

The cyclometallated ligands in the complexes **6**–**11** were found to be suitable substrates for electrophilic aromatic substitution reactions.

2.4.1. Bromination

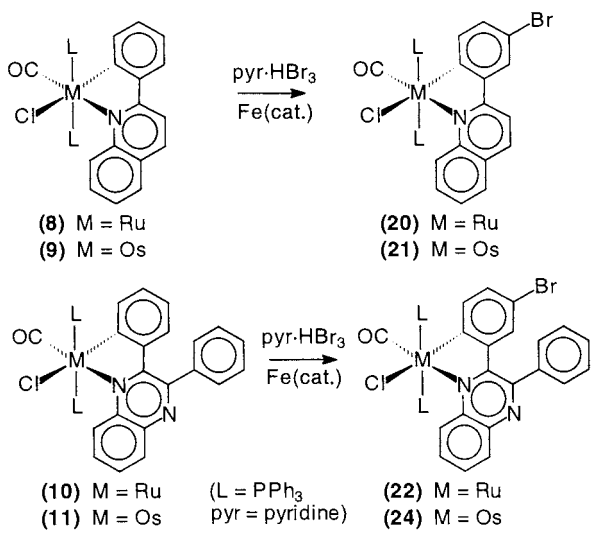
Reaction of organometallic compounds with molecular bromine usually results in cleavage of any metal–carbon σ-bonds that are present, although in some cases where suitable higher oxidation states of the metal are accessible (e.g. Pt^{II}), oxidative addition at the metal centre may be observed without metal–carbon bond cleavage. However, we have previously demonstrated that it is possible to brominate σ-bonded aryl ligands at specific positions on the aromatic ring without metal–carbon bond cleavage, provided the metal–aryl bonds are very robust [2,5].

It was found that bromination of the cyclometallated ligands in the complexes **8**, **9**, **10**, and **11**, did occur smoothly and cleanly as shown in Scheme 6. One equivalent of bromine was delivered in the form of [pyridineH]Br_3, a conveniently stable solid. A catalytic quantity of iron powder was also added, without which the reaction did not proceed at room temperature. In each case, a high yield of the product was obtained in which a bromo substituent had been introduced in the 4-position of the phenyl ring, directly *para* to the metal–carbon bond.

Although it would be expected that the 2-position, *ortho* to the metal–carbon bond, would also be electronically activated, in none of the bromination reactions was substitution observed in this position. Similar results have been observed for bromination of the analogous compounds containing the smaller Phpy [2] or 8-quinolyl [5] ligands. In these cases, the position *para* to the metal–aryl bond was substituted, and under no conditions was substitution on the heterocyclic ring observed.

It is interesting to note that for the ligands Phqn and Dpqx, no substitution occurs in the aromatic rings which are not activated by the coordinated metal. This supports the supposition that it is the activating and directing effect of the metal substituent which makes such electrophilic aromatic substitution reactions possible under conditions which would be considered mild for similar non-metallated substrates.

The complexes **22** and **24**, which contain the brominated η^2-Dpqx ligand, both react with dimethyldithio-



(8) M = Ru
(9) M = Os

pyr·HBr_3
Fe(cat.)

(20) M = Ru
(21) M = Os

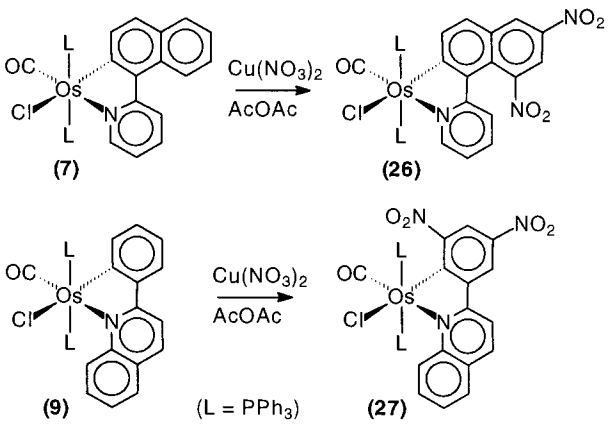
(10) M = Ru
(11) M = Os

pyr·HBr_3
Fe(cat.)

(L = PPh_3
pyr = pyridine)

(22) M = Ru
(24) M = Os

Scheme 6.



Scheme 7.

carbamate in the same way as the corresponding non-functionalised complexes and the resultant mono-triphenylphosphine products, M(η^2-Dpqx-4-Br)(η^2-S_2-$CNMe_2$)(CO)(PPh_3) (**23**, M = Ru; **25**, M = Os), are formed. Both **23** and **25** have been structurally characterised by X-ray crystallography (see below).

2.4.2. Nitration

Unlike bromination, we have in the past been successful at nitrating compounds with metal–aryl linkages that are more fragile than those in compounds **6**–**11**, albeit in low yields and often with numerous byproducts [6]. The reaction is much more straightforward, however, when robust substrates with chelated aryl ligands are used. Reasonably high yields and a single major product are typical in these cases [5].

Nitration of the substrates Os(η^2-Nppy)Cl(CO)-(PPh_3)$_2$ (**7**) and Os(η^2-Phqn)Cl(CO)(PPh_3)$_2$ (**9**) was undertaken, using an adaptation of the Menke conditions, which involve stirring the substrate in a slurry of $Cu(NO_3)_2$ in acetic anhydride [7] (see Scheme 7). For compound **9**, two nitro groups were introduced, in the 2- and 4-positions, that is *ortho* and *para* to the metal–carbon bond. We have previously observed similar substitution patterns for simple phenyl complexes [6,8].

Os(η^2-Nppy)Cl(CO)(PPh_3)$_2$ (**7**) differs significantly from **9** in that the most activated and available site for substitution, the position *para* to the metal, is at an aromatic ring junction, and is thus not available for functionalisation. However, it was ascertained by ^{1}H-NMR spectroscopy that two nitrations had occurred. Although crystals of sufficient quality for X-ray structural analysis were not able to be grown, the substitution pattern of the Nppy ligand was determined by COSY, HSQC and HMBC NMR techniques, and it was found that the two sites substituted were the 6- and 8-positions. The implications of this result are that the electronic activating effect of the electron-rich metal moiety is transmitted through the naphthyl ring, and the 6- and 8-positions are activated.

2.5. Crystal-structure determinations

Crystallographic details for the structure determinations of compounds **7**, **12**, **15**, **18**, **19**, **21**, **23**, and **25** are presented in Table 2, and molecular structures are presented in Figs. 1–8. The remaining crystallographic data has been deposited with the Cambridge Crystallographic Data Centre.

The principal value of the structural data lies in confirmation of the position of substitution of the aromatic ring. However, some useful conclusions can also be drawn, and for the purposes of comparison a summary of the M–C and M–N bond distances and C–M–N angles is given in Table 3. The metal–aryl bond distances vary only slightly depending on the organometallic ligand and the arrangement of the ancilliary ligands. The four ruthenium complexes structurally characterised have an average metal–aryl bond distance of 2.04 Å, the osmium complexes 2.05 Å. A search of the Cambridge Crystallographic Structural Database revealed 196 ruthenium–aryl complexes, with an average bond distance of 2.108(6) Å, and for osmium, 106 complexes, with an average bond distance of 2.13(10) Å. Therefore, the complexes of the ligands Nppy, Phqn and Dpqx possess shorter than average metal–aryl bonds, no doubt attributable to the presence of the five-membered chelate ring.

The structurally characterised complexes given in Table 3 exhibit averaged metal–nitrogen bond distances of 2.16 (Ru–N), and 2.19 Å (Os–N). A CCSD search for compounds with five-membered chelate rings featuring one or two pyridyl nitrogen donors (mostly complexes of 2,2′-bipyridine) revealed average bond distances of 2.05(6) (Ru–N, 644 compounds) and 2.06(8) Å (Os–N, 51 compounds). Therefore, the M–N distances observed in this work are longer than average.

It can be seen in Table 3 that the C–M–N bond angles are very closely similar for all eight structures.

2.6. Conclusions

The work described herein reinforces and extends our previous conclusions regarding the electrophilic substitution reactions undergone by metallated arenes. In particular we have found: (1) in more complicated chelated ring systems substitution still occurs preferentially *para* to the metal substituent, (2) the bromination of **10** and **11** shows that substitution occurs preferentially in the metallated phenyl ring rather than the non-metallated phenyl ring, (3) in one instance (nitration of **7**) the activating and directing effect of the metal substituent is transmitted through a fused naphthyl ring system so that substitution occurs in the non-metallated ring.

Table 2
Data collection and processing parameters

	7	12	15	18
Formula	$C_{52}H_{40}ClNOOsP_2$	$C_{37}H_{31}N_2O_2PruS_2$	$C_{37}H_{31}N_2OOsPS_2$	$C_{44}H_{35}N_2O_4PRu$
Molecular weight	982.44	731.80	804.93	787.78
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$Pna2_1$	$P2_1/c$
a (Å)	11.6650(1)	9.7032(1)	17.3375(2)	21.7287(2)
b (Å)	28.9526(1)	21.4602(1)	16.3242(2)	10.6347(1)
c (Å)	12.6381(2)	16.6156(2)	11.2616(1)	17.5246(1)
α (°)				
β (°)	102.73(1)	101.705(1)		107.49(1)
γ (°)				
V (Å^3)	4163.39(8)	3387.96(6)	3187.27(6)	3862.45
Z	4	4	4	4
D_{calc} (g cm^{-3})	1.576	1.435	1.677	1.355
$F(000)$	1960	1496	1592	1616
μ (mm^{-1})	3.24	0.67	4.22	0.49
θ (min–max) (°)	1.8–27.5	1.6–27.3	1.7–27.5	2.0–26.0
Reflections collected/unique	23681/9179	32629/7429	18065/5814	23234/7551
R_{int}	0.0451	0.0246	0.0456	0.0240
No. observed reflections $I>2\sigma(I)$	6911	6672	4430	6396
Crystal size (mm)	$0.20\times0.14\times0.14$	$0.65\times0.34\times0.22$	$0.34\times0.09\times0.07$	$0.38\times0.16\times0.07$
A (min-max)	0.563, 0.659	0.670, 0.887	0.328, 0.756	0.835, 0.966
Goodness of fit on F^2	1.084	1.107	1.056	1.076
R (observed data)	0.0436	0.0376	0.0425	0.416
WR_2 (all data)	0.0809	0.1129	0.0908	0.1320
Difference map (min–max) e Å^{-3}	+1.57, −0.73	+1.51, −0.76	+0.69, −1.01	+1.73, −0.71
	19	**21**	**23**	**25**
Formula	$C_{59}H_{34}F_3N_2O_3P_2Ru$	$C_{53}H_{41}BrCl_3NOOsP_2$	$C_{43}H_{35}BrCl_2N_3OPRuS_2$	$C_{42}H_{33}BrN_3O_4OsPS_2$
Molecular weight	1047.96	1146.27	956.71	1008.91
Crystal system	Monoclinic	Triclinic	Orthorhombic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$Pbca$	$P\bar{1}$
a (Å)	12.1376(1)	9.8350(1)	12.2938(2)	11.6579(2)
b (Å)	23.6920(4)	11.6149(1)	17.5246(2)	16.8450(3)
c (Å)	17.9721(3)	22.1280(1)	39.0487(7)	13.9706(3)
α (°)		86.829(1)		72.212(1)
β (°)	105.984(1)	84.068(1)		86.956(1)
γ (°)		65.132(1)		79.675(1)
V (Å^3)	4968.3(1)	2280.84(3)	8412.8(2)	2112.34(7)
Z	4	2	8	2
D_{calc} (g cm^{-3})	1.401	1.669	1.511	1.586
$F(000)$	2177	1132	3856	992
μ (mm^{-1})	0.44	3.96	1.63	4.14
2θ (min–max) (°)	1.5–27.5	1.8–27.5	1.0–25.0	1.5–27.5
Reflections collected/unique	29775/10870	22206/9827	45139/7414	20176/9138
R_{int}	0.0704	0.0242	0.0887	0.0248
No. observed reflections $I>2\sigma(I)$	7535	8942	5369	8417
Crystal size (mm)	$0.38\times0.18\times0.14$	$0.38\times0.07\times0.07$	$0.30\times0.25\times0.13$	$0.45\times0.20\times0.15$
A (min–max)	0.851, 0.941	0.314, 0.769	0.641, 0.816	0.257, 0.575
Goodness of fit on F^2	1.034	1.099	1.132	1.041
R (observed data)	0.0641	0.0375	0.0732	0.342
wR_2 (all data)	0.2117	0.0957	0.1556	0.1074
Difference map (min–max) (e Å^{-3})	+1.29, −0.75	+2.13, −2.55	+2.06, −0.91	+2.86, −1.27
$R=\Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$	$wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$			

3. Experimental

3.1. General

Most reactions were undertaken under atmospheric conditions using standard reagents and solvents. Where specified, solvents were degassed using three freeze–thaw–degas cycles, in Schlenk tubes, and the reactions carried out under oxygen-free nitrogen. Infrared spectra were recorded as Nujol mulls between KBr plates on a Perkin–Elmer Paragon 1000 spectrometer. NMR

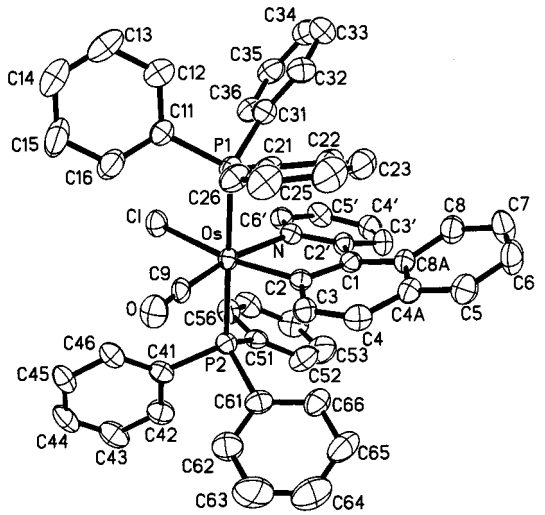


Fig. 1. Molecular structure of **7**. Hydrogen atoms have been omitted for clarity.

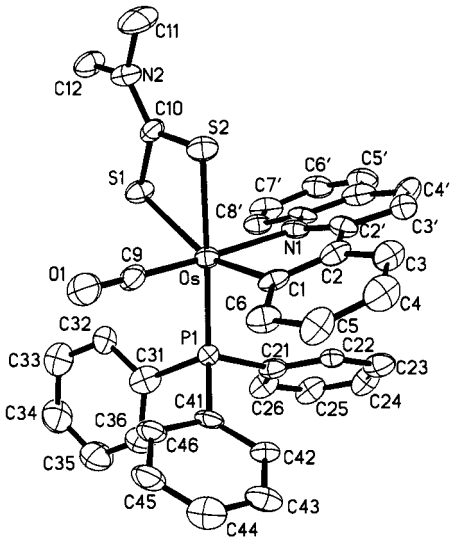


Fig. 3. Molecular structure of **15**. Hydrogen atoms have been omitted for clarity.

spectra were obtained on a Bruker DRX 400 at 25°C in $CDCl_3$ solution, and referenced with tetramethylsilane. Multiplicity and coupling data is given as experimentally observed, and apparent triplets (atoms coupling to two similar but non-identical vicinal atoms) are written as triplets, with coupling data listed for both vicinal nuclei as an average. Where necessary, assignment of the ^1H spectra was made by possible by running a COSY spectrum. Where ^{13}C-NMR data are given, assignments were made by also performing HSQC and HMBC experiments to correlate carbon chemical shifts with the corresponding protons. The numbering scheme used in all the NMR assignments is given in Scheme 3. Mass spectra were recorded using the fast atom bombardment technique with a Varian VG 70-SE mass spectrometer. The following starting materials were prepared according to literature procedures: $RuHCl(CO)(PPh_3)_3$ [9], $OsHCl(CO)(PPh_3)_3$ [10], 2-phenylquinoline [11], 2-(1′-naphthyl)pyridine [12], and 2,3-diphenylquinoxaline [13]. Infrared data are shown in Table 1, and other characterisation data are given following the preparative details for each new compound.

3.2. Preparation of $Phqn_2Hg$ (1)

Mercuration of 2-phenylquinoline was carried out using a method very similar to that described in the literature [11]. PhqnHgCl (1.5 g) was added to a solution of sodium thiosulfate (5 g) in water (100 ml) and

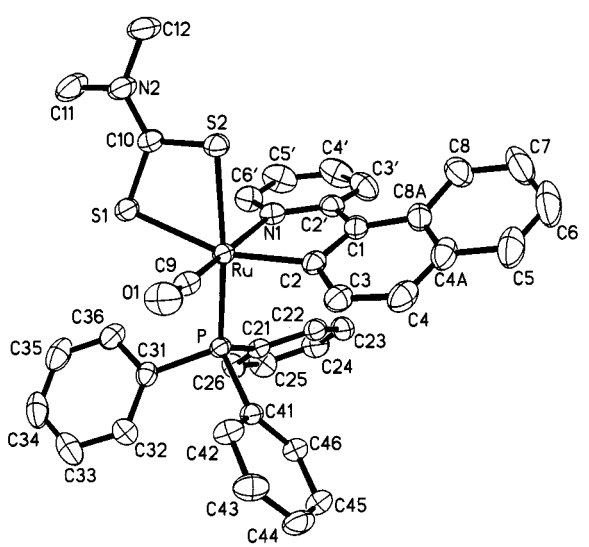


Fig. 2. Molecular structure of **12**. Hydrogen atoms have been omitted for clarity.

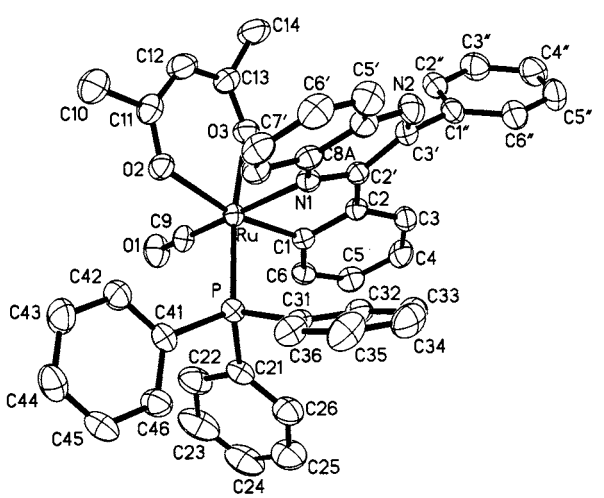


Fig. 4. Molecular structure of **18**. Hydrogen atoms have been omitted for clarity.

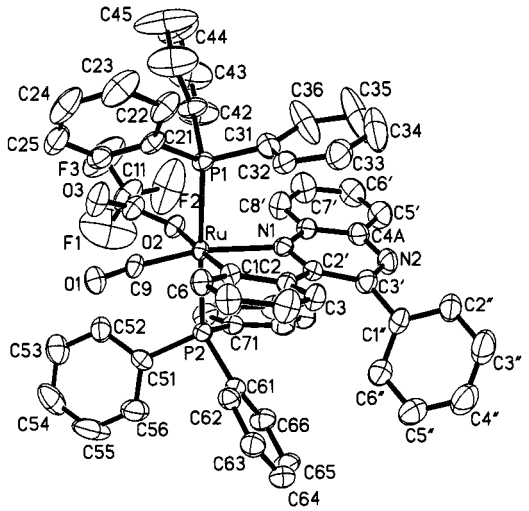


Fig. 5. Molecular structure of **19**. Hydrogen atoms have been omitted for clarity.

the mixture thoroughly stirred. After 1 h, the substrate had largely dissolved and a milky precipitate had begun to form. The flask was left to stand overnight at 0°C, and then the white solid was removed by filtration. The filtrate was extracted with dichloromethane, and the organic phase then used to dissolve the solid product. The resulting solution was filtered through filter paper, heptane added, and the volume reduced in vacuo until precipitation was complete. The pure, cream-coloured **1** was obtained by filtration (680 mg, 66%). ^{1}H-NMR: δ 7.99 (d, $J_{H4} = 7.68$ Hz, 2H, H3), 7.40 (dt, $J_{H6} = 1.26$, $J_{H3+H5} = 7.56$ Hz, 2H, H4), 7.55 (dt, $J_{H3} = 1.08$, $J_{H4+H6} = 7.12$ Hz, 2H, H5), 7.85 (dd, $J_{H4} = 1.02$, $J_{H5} = 7.10$ Hz, 2H, H6), 7.58 (d, $J_{H4} = 8.68$ Hz, 2H, H3′), 7.70 (d, $J_{H3'} = 8.64$ Hz, 2H, H4′), 7.46 (dd, $J_{H7'} = 1.36$, $J_{H6} = 8.16$ Hz, 2H, H5′), 7.24 (dt, $J_{H8'} = 1.36$, $J_{H5'+H7'} = 7.36$ Hz, 2H, H6′), 7.19 (dt,

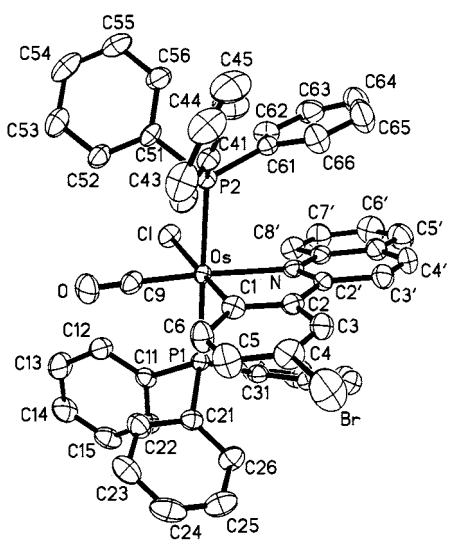


Fig. 6. Molecular structure of **21**. Hydrogen atoms have been omitted for clarity.

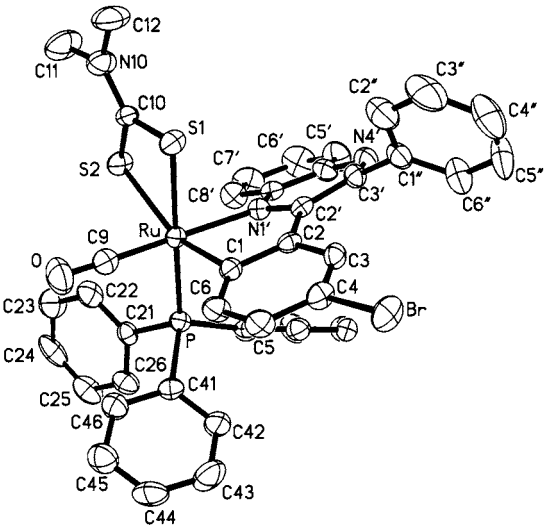


Fig. 7. Molecular structure of **23**. Hydrogen atoms have been omitted for clarity.

$J_{H5'} = 1.42$, $J_{H6'+H8'} = 6.86$ Hz, 2H, H7′), 7.42 (d, $J_{H7'} = 8.20$ Hz, 2H, H8′) ppm. ^{13}C{^{1}H}-NMR: δ 168.53 (s, C1), 146.88 (s, C2), 128.22 (s, C3), 126.92 (s, C4), 128.97 (s, C5), 139.64 (s, C6), 160.21 (s, C2′), 119.77 (s, C3′), 135.97 (s, C4′), 126.39 (s, C10′), 126.85 (s, C5′), 125.60 (s, C6′), 129.18 (s, C7′), 128.97 (s, C8′), 146.58 (s, C9′) ppm. MS, m/z: 407 [MI − Hg − H], 610 [MI]. Anal. Calc. for $C_{30}H_{20}HgN_2 \cdot (1/3)CH_2Cl_2$: C, 57.16; H, 3.27; N, 4.40. Found: C, 56.87; H, 3.02; N, 4.38%.

3.3. Preparation of NppyHgCl (2)

2-(1′-Naphthyl)pyridine [12] (7 g) was added to a solution of mercuric acetate (11 g) in ethanol (60 ml), and the mixture heated under reflux for 2 h. A solution of lithium chloride (3 g) in methanol (100 ml) was

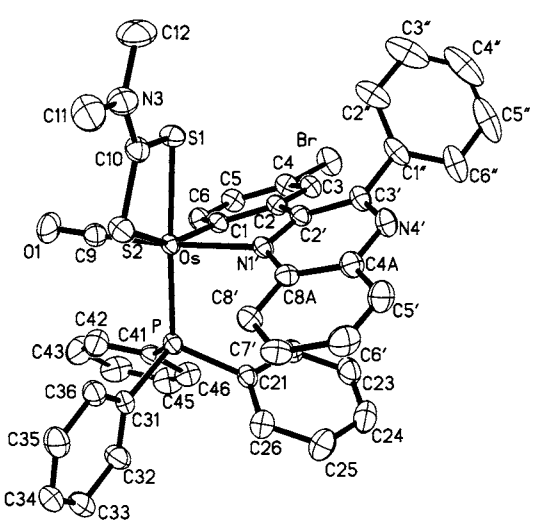


Fig. 8. Molecular structure of **25**. Hydrogen atoms have been omitted for clarity.

Table 3
Summary of M–C and M–N bond lengths (Å) and C–M–N angles (°) for **7**, **12**, **15**, **18**, **19**, **21**, **23**, **25**

	d(M–C)	*d*(M–N)	∠(C–M–N)
Os(η^2-Nppy)Cl(CO)(PPh_3)$_2$ (**7**)	2.057(5)	2.151(4)	77.47(17)
Ru(η^2-Nppy)(η^2-S_2CNMe_2)(CO)(PPh_3) (**12**)	2.068(3)	2.145(2)	77.53(11)
Os(η^2-Phqn)(η^2-S_2CNMe_2)(CO)(PPh_3) (**15**)	2.030(9)	2.217(6)	77.3(4)
Ru(η^2-Dpqx)(η^2-acac)(CO)(PPh_3) (**18**)	2.017(3)	2.159(3)	78.87(11)
Ru(η^2-Dpqx)(η^1-O_2CCF_3)(CO)(PPh_3)$_2$ (**19**)	2.036(4)	2.205(4)	77.71(17)
Os(η^2-Phqn-4-Br)Cl(CO)(PPh_3)$_2$ (**21**)	2.050(5)	2.268(4)	76.59(18)
Ru(η^2-Dpqx-4-Br)(η^2-S_2CNMe_2)(CO)(PPh_3) (**23**)	2.042(7)	2.146(6)	78.6(3)
Os(η^2-Dpqx-4-Br)(η^2-S_2CNMe_2)(CO)(PPh_3) (**25**)	2.047(4)	2.166(4)	77.60(17)

added to the hot solution, and the mixture permitted to cool to room temperature. The solution was filtered and the solid extracted with several portions of dichloromethane (total ca. 50 ml). Crystallisation was induced by adding heptane and reducing the solvent volume in vacuo. The pure, cream **2** that formed was obtained by filtration (3.6 g, 24%). ^{1}H-NMR: δ 7.46–8.81 (m, 10H, ArH) ppm. MS, *m*/*z*: 204 [MI–Hg–Cl], 440 [MI–H].

3.4. Preparation of $Nppy_2Hg$ (3)

2 (2.5 g) was added to a solution of sodium thiosulfate (5 g) in water (100 ml) as described in Section 3.1. The solid was filtered from the aqueous solution, dissolved in dichloromethane, placed on a short column (5 × 3 cm) of silica gel and eluted using dichloromethane. The pale yellow, motile band was collected and crystallisation induced by adding heptane and reducing the volume in vacuo. Pure **3** was collected as a pale yellow solid by filtration (400 mg, 23%). ^{1}H-NMR: δ 7.28–8.81 (m, 20H, ArH) ppm. MS, *m*/*z*: 611 [MI + H], 204 [MI–Hg–Nppy]. Anal. Calc. for $C_{30}H_{20}HgN_2.CH_2Cl_2$: C, 53.65; H, 3.19; N, 4.04. Found: C, 53.55; H, 2.79; N, 4.08%.

3.5. Preparation of DpqxHgCl (4)

2,3-Diphenylquinoxaline [13] (5 g) was added to a solution of mercuric acetate (7.6 g) in ethanol (50 ml) and heated under reflux for 30 h. A solution of lithium chloride (2.5 g) in methanol (40 ml) was added to the hot solution, and the voluminous precipitate that formed was filtered whilst the solution was still warm. The solid product was added to a flask of ethanol, which was heated to boiling for several minutes to dissolve any soluble impurities, and the hot solution was filtered to obtain a white solid (4.6 g, 50%). The analytical sample of **4** was obtained by recrystallisation from dichloromethane–heptane. ^{1}H-NMR: δ 7.00–8.31 (m, 13H, ArH) ppm. MS, *m*/*z*: 518 [MI]. Anal. Calc. for $C_{20}H_{13}ClHgN_2 \cdot 1/3CH_2Cl_2$: C, 57.16; H, 3.27; N, 4.40. Found: C, 56.87; H, 3.02; N, 4.38%.

3.6. Preparation of $Dpqx_2Hg$ (5)

4 (6.5 g) was added to a solution of sodium thiosulfate (5 g) in water (100 ml) as described in Section 3.1. The solid was filtered from aqueous solution and extracted with several portions of dichloromethane (total ca. 50 ml). Heptane was added and the solvent volume reduced in vacuo to induce crystallisation. The cream-coloured, pure **4** was then collected by filtration (2.75 g, 29%). ^{1}H-NMR: δ 7.33 (d, $J_{H4} = 8.24$ Hz, 2H, *H3*), 7.41 (t, $J_{H3+H5} = 7.28$ Hz, 2H, *H4*), 7.00 (t, $J_{H4+H6} = 7.62$ Hz, 2H, *H5*), 7.20 (d, $J_{H5} = 7.52$ Hz, 2H, *H6*), 7.75 (d, $J_{H6'} = 8.24$ Hz, 2H, *H5′*), 7.60 (s, 2H, *H6′*), 7.54 (s, 2H, *H7′*), 7.93 (d, $J_{H7'} = 8.12$ Hz, 2H, *H8′*), 7.67 (s, 4H, *H2″*), 7.35 (s, 4H, *H3″*), 7.33 (s, 2H, *H4″*) ppm. MS, *m*/*z*: 765 [MI + H]. Anal. Calc. for $C_{40}H_{26}HgN_4 \cdot (2/3)CH_2Cl_2$: C, 59.58; H, 3.36; N, 6.83. Found: C, 59.20; H, 3.71; N, 6.71%.

3.7. Preparation of Ru(η^2-Nppy)Cl(CO)(PPh_3)$_2$ (6)

$RuHCl(CO)(PPh_3)_3$ (100 mg) and $Nppy_2Hg$ (90 mg) were added to deoxygenated toluene (10 ml) and the mixture heated under reflux under a nitrogen atmosphere for 2 h. After this time the solution was distinctly yellow and deposition of elemental mercury was observed. The toluene solution was placed on a short column (10 × 3 cm) of silica gel. The column was eluted with hexane to expel the soluble byproducts. The eluant was changed to dichloromethane and the yellow band that eluted from the column was collected. Ethanol was added, the solvent volume reduced in vacuo and the pure crystals of **6** that formed were collected by filtration (87 mg, 85%). ^{1}H-NMR: δ 6.98–7.31 (m, 31H, ArH), 8.75 (d, $J_{H5'} = 5.60$ Hz, 1H, *H6′*), 8.08 (d, $J_{H7} = 8.52$ Hz, 1H, *H8*), 7.92 (d, $J_{H4'} = 8.00$ Hz, 1H, *H3′*), 7.52 (d, $J_{H6} = 7.92$ Hz, 1H, *H5*), 7.35 (t, $J_{H6+H8} = 7.70$ Hz, 1H, *H7*), 7.20 (t, $J_{H3'+H5'} = 7.40$ Hz, 1H, *H4′*), 6.86 (d, $J_{H4} = 8.36$ Hz, 1H, *H3*), 6.54 (d, $J_{H3} = 8.40$ Hz, 1H, *H4*), 6.21 (t, $J_{H4'+H6'} = 6.52$ Hz, 1H, *H5′*) ppm. MS, *m*/*z*: 893 [MI], 858 [MI–Cl]. Anal. Calc. for $C_{52}H_{40}ClNOP_2Ru$: C, 69.91; H, 4.51; N, 1.57. Found: C, 69.94; H, 4.61; N, 1.70%.

3.8. Preparation of $Os(\eta^2\text{-}Nppy)Cl(CO)(PPh_3)_2$ (7)

$OsHCl(CO)(PPh_3)_3$ (100 mg) and $Nppy_2Hg$ (90 mg) were added to deoxygenated toluene (10 ml) and the mixture heated under reflux under nitrogen for 4 h, after which time the solution was distinctly yellow and deposition of elemental mercury was observed. The product was purified and isolated as described above in 3.6 to give deep yellow microcrystals of pure **7**, (72 mg, 76%). ^{1}H-NMR: δ 7.03–7.28 (m, 30H, *ArH*), 6.58 (d, $J_{H3} = 8.36$ Hz, 1H, *H4*), 7.00 (d, $J_{H4} = 8.44$ Hz, 1H, *H3*), 7.56 (d, $J_{H6} = 7.88$ Hz, 1H, *H5*), 7.20 (s, 1H, *H6*), 7.38 (t, $J_{H6+H8} = 7.62$ Hz, 1H, *H7*), 8.10 (d, $J_{H7} = 8.64$ Hz, 1H, *H8*), 7.98 (d, $J_{H4'} = 8.56$ Hz, 1H, *H3′*), ~7.25 (s, 1H, *H4′*), 6.17 (t, $J_{H4'+H6'} = 6.42$ Hz, 1H, *H5′*), 8.60 (d, $J_{H5'} = 5.56$ Hz, 1H, *H6′*) ppm. MS, *m*/*z*: 983 [MI], 948 [MI]. Anal. Calc. for $C_{52}H_{40}ClNOOsP_2$: C, 63.57; H, 4.10; N, 1.43. Found: C, 63.43; H, 3.80; N, 1.32%.

3.9. Preparation of $Ru(\eta^2\text{-}Phqn)Cl(CO)(PPh_3)_2$ (8)

$RuHCl(CO)(PPh_3)_3$ (300 mg) and $Phqn_2Hg$ (250 mg) were added to deoxygenated toluene (30 ml). The solution was heated under reflux under nitrogen for 16 h, after which time a deep brown–red solution was observed, as well as deposition of elemental mercury. The solution was placed on a short column (10 × 3 cm) of silica gel and eluted with dichloromethane. The strongly coloured band that eluted first was discarded. The eluant was then changed to dichloromethane containing acetone (ca. 10%) and the intense red band that then eluted was collected. Heptane was added and on reducing the solvent volume in vacuo yellow crystals of pure **8** formed and these were collected by filtration (140 mg, 50%). ^{1}H-NMR: δ 6.87–7.24 (m, 33H, *ArH*), 7.36 (d, $J_{H4} \approx 6$ Hz, 1H, *H3*), 6.63 (t, $J_{H3+H5} = 7.38$ Hz, 1H, *H4*), 6.29 (t, $J_{H4+H6} = 7.22$ Hz, 1H, *H5*), 7.65 (d, $J_{H4'} = 9.56$ Hz, 1H, *H3′*), 7.75 (d, $J_{H3'} = 8.64$ Hz, 1H, *H4′*), 7.31 (d, $J_{H6'} = 7.88$ Hz, 1H, *H5′*), 9.68 (d, $J_{H7'} \approx 8$ Hz, 1H, *H8′*) ppm. MS, *m*/*z*: 858 [MI–Cl]. Anal. Calc. for $C_{52}H_{40}ClNOP_2Ru \cdot (1/3)CH_2Cl_2$: C, 68.20; H, 4.45; N, 1.52. Found: C, 68.13; H, 4.40; N, 1.65%.

3.10. Preparation of $Os(\eta^2\text{-}Phqn)Cl(CO)(PPh_3)_2$ (9)

$OsHCl(CO)(PPh_3)_3$ (250 mg) and $Phqn_2Hg$ (180 mg) were added to deoxygenated toluene (30 ml). The solution was heated under reflux under nitrogen for 16 h, after which time the solution had turned deep orange in colour and elemental mercury had deposited. The solution was placed on a short column (10 × 3 cm) of silica gel and eluted with dichloromethane. The fastest moving band was deep red, and was discarded. The deep orange band that subsequently eluted was collected, heptane added and the solvent volume reduced in vacuo. The orange crystals of pure **9** were collected by filtration (160 mg, 68%). ^{1}H-NMR: δ 6.87–7.25 (m, 30H, *ArH*), 7.35 (d, $J_{H4} = 7.72$ Hz, 1H, *H3*), 6.58 (t, $J_{H3+H5} = 7.40$ Hz, 1H, *H4*), 6.21 (t, $J_{H4+H6} = 6.80$ Hz, 1H, *H5*), ~6.85 (s, 1H, *H6*), 7.54 (d, $J_{H4'} = 8.84$ Hz, 1H, *H3′*), 7.69 (d, $J_{H3'} = 8.72$ Hz, 1H, *H4′*), 7.30 (d, $J_{H6'} = 7.30$ Hz, 1H, *H5′*), ~7.15 (s, 1H, *H6′*), ~7.15 (s, 1H, *H7′*), 9.51 (d, $J_{H7'} = 8.60$ Hz, 1H, *H8′*) ppm. ^{13}C{^{1}H}-NMR: δ 185.94 (t, $J_P = 10.0$ Hz, CO), 133.84 (t, $J_P = 5.0$ Hz, PPh_3 ortho), 132.23 (t, $J_P = 24.5$ Hz, PPh_3 *ipso*), 128.76 (s, PPh_3 *para*), 127.07 (t, $J_P = 4.5$ Hz, PPh_3 *meta*), 141.10 (s, C6), 137.57 (s, C4′), 130.74 (s, C8′), 129.86 (s, C5), 126.34 (s, C5′), 125.38 (s, C3), 119.34 (s, C4), 116.28 (s, C3′) ppm. Anal. Calc. for $C_{52}H_{40}ClNOOsP_2 \cdot (2/3)CH_2Cl_2$: C, 60.88; H, 4.01; N, 1.35. Found: C, 60.80; H, 3.73; N, 1.48%.

3.11. Preparation of $Ru(\eta^2\text{-}Dpqx)Cl(CO)(PPh_3)_2$ (10)

$RuHCl(CO)(PPh_3)_3$ (200 mg) and $Dpqx_2Hg$ (200 mg) were added to deoxygenated toluene (20 ml). The solution was heated under reflux under nitrogen for 24 h, after which time solution had become deep red in colour and elemental mercury had deposited. The solution was placed on a short column (10 × 3 cm) of silica gel. The rapidly moving orange band was eluted with dichloromethane and discarded. The eluant was then changed to dichloromethane containing acetone (ca. 10%). The bright red band that eluted was collected, heptane was added and the solvent volume reduced in vacuo. The red crystals of pure **10** were collected by filtration (140 mg, 69%). ^{1}H-NMR: δ 6.95–7.97 (m, 35H, *ArH*), 9.64 (d, $J_{H7'} = 8.60$ Hz, 1H, *H8′*), 7.78 (d, $J_{H6'} = 8.16$ Hz, 1H, *H5′*), ~7.3 (s, 1H, *H6′*), ~7.2 (s, 1H, *H3*), ~7.1 (s, 1H, *H7′*), 6.79 (d, $J_{H5} = 7.96$ Hz, 1H, *H6*), 6.30 (t, 1H, *H5*), 6.26 (t, 1H, *H4*) ppm. MS, *m*/*z*: 935 [MI–Cl]. Anal. Calc. for $C_{57}H_{43}ClN_2OP_2Ru \cdot (1/2)CH_2Cl_2$: C, 68.18; H, 4.38; N, 2.77. Found: C, 68.15; H, 4.67; N, 3.01%.

3.12. Preparation of $Os(\eta^2\text{-}Dpqx)Cl(CO)(PPh_3)_2$ (11)

$OsHCl(CO)(PPh_3)_3$ (500 mg) and $Dpqx_2Hg$ (400 mg) were added to deoxygenated toluene (30 ml). The solution was heated under reflux under nitrogen for 24 h, after which time the solution had become deep purple and elemental mercury had deposited. Hydrochloric acid (30%, 1 ml) was added to the solution to decompose any residual $Dpqx_2Hg$, and after several minutes of stirring the resulting mixture, the organic phase was separated and washed with water. The toluene solution was placed on a column (15 × 3 cm) of silica gel, and eluted with toluene. The eluant was then changed to dichloromethane, and the fast-moving green band discarded. The purple band that eluted next was collected,

heptane added and the solvent volume reduced in vacuo to give pure, purple crystals of **11** which were collected by filtration (320 mg, 63%). ^{1}H-NMR: δ 6.89–7.33 (m, 35H, *ArH*), ~7.10 (s, 1H, *H3*), 6.13 (t, $J_{H3+H5}=7.28$ Hz, 1H, *H4*), 6.21 (t, $J_{H4+H6}=7.64$ Hz, 1H, *H5*), 6.77 (t, $J_{H5}=7.96$ Hz, 1H, *H6*), 7.66 (d, $J_{H6'}=8.12$ Hz, 1H, *H5′*), ~7.30 (s, 1H, *H6′*), ~7.05 (s, 1H, *H7′*), 9.47 (d, $J_{H7'}=8.84$ Hz, 1H, *H8′*) ppm. MS, *m*/*z*: 1060 [MI], 1025 [MI–Cl]. Anal. Calc. for $C_{57}H_{43}ClN_2OOsP_2\cdot C_6H_5CH_3$: C, 66.74; H, 4.46; N, 2.43. Found: C, 66.40; H, 4.43; N, 3.07%.

3.13. Preparation of Ru(η^2-Nppy)(η^2-S_2CNMe_2)(CO)(PPh_3) (**12**)

Ru(η^2-Nppy)Cl(CO)(PPh_3)$_2$ (30 mg) was dissolved in dichloromethane (10 ml), to which was added $AgSbF_6$ (20 mg) in water (2 ml) and ethanol (5 ml). The resulting solution was stirred for 10 minutes, after which time excess water was added and the organic layer collected. NaS_2CNMe_2 (15 mg) in water (2 ml) and ethanol (5 ml) was added, and the solution stirred for 10 min. Excess water was then added and once again the organic layer was separated, then filtered. The resulting solution was heated under reflux for 10 min, then heptane was added and the solvent volume reduced in vacuo to give pure, deep yellow crystals of **12**which were collected by filtration (20 mg, 82%). ^{1}H-NMR: δ 7.06–7.40 (m, 15H, *ArH*), 7.71 (d, $J_{H4}=7.92$ Hz, 1H, *H3*), ~7.3 (s, 1H, *H4*), 8.06 (d, $J_{H6}=8.12$ Hz, 1H, *H5*), ~7.3 (s, 1H, *H6*), ~7.4 (s, 1H, *H7*), 8.16 (d, $J_{H7}=8.56$ Hz, 1H, *H8*), 8.07 (d, $J_{H4'}=8.08$ Hz, 1H, *H3′*), 7.50 (t, $J_{H3'+H5'}=7.27$ Hz, 1H, *H4′*), 6.67 (t, $J_{H4'+H5'}=5.96$ Hz, 1H, *H5′*), 8.80 (d, $J_{H5'}=8.80$ Hz, 1H, *H6′*), 3.34 (s, 3H, N–Me), 3.13 (s, 3H, N–Me) ppm. Anal. Calc. for $C_{37}H_{31}N_2OPRuS_2\cdot(1/6)CH_2Cl_2$: C, 61.15; H, 4.33; N, 3.84. Found: C, 61.29; H, 4.67; N, 3.53%.

3.14. Preparation of Os(η^2-Nppy)(η^2-S_2CNMe_2)(CO)(PPh_3) (**13**)

Os(η^2-Nppy)Cl(CO)(PPh_3)$_2$ (30 mg) was treated in the same manner as described in Section 3.13, giving rise to deep yellow crystals of pure **13** (20 mg, 80%). ^{1}H-NMR: δ 6.99–7.29 (m, 17H, *ArH*), 8.67 (d, $J_{H5'}=5.32$ Hz, 1H, *H6′*), 8.19 (d, $J_{H7}=8.44$ Hz, 1H, *H8*), 8.14 (d, $J_{H4'}=8.24$ Hz, 1H, *H3′*), 8.10 (d, $J_{H6}=8.20$ Hz, 1H, *H5*), 7.70 (d, $J_{H4}=8.24$ Hz, 1H, *H3*), 7.47 (t, $J_{H3'+H5'}=7.68$ Hz, 1H, *H4′*), 7.36 (t, $J_{H6+H8}=7.50$ Hz, 1H, *H7*), 6.60 (t, $J_{H4'+H6'}=6.60$ Hz, 1H, *H5′*), 3.26 (s, 3H, N–Me), 3.02 (s, 3H, N–Me) ppm. Anal. Calc. for $C_{37}H_{31}N_2OOsPS_2\cdot(1/4)C_7H_{16}$: C, 56.07; H, 4.25; N, 3.38. Found: C, 56.34; H, 3.99; N, 3.29%.

3.15. Preparation of Ru(η^2-Phqn)(η^2-S_2CNMe_2)(CO)(PPh_3) (**14**)

Ru(η^2-Phqn)Cl(CO)(PPh_3)$_2$ (40 mg) was treated in the same manner as in Section 3.12, giving rise to yellow crystals of pure **14** (30 mg, 94%). ^{1}H-NMR: δ 7.00–7.50 (m, 18H, *ArH*), 8.69 (d, $J_{H7'}=$ ~8 Hz, 1H, *H8′*), 7.96 (d, $J_{H3'}=8.96$ Hz, 1H, *H4′*), 7.93 (d, $J_{H4'}=8.88$ Hz, 1H, *H3′*), 7.80 (d, $J_{H5}=7.28$ Hz, 1H, *H6*), 7.57 (d, $J_{H4}=7.56$ Hz, 1H, *H3*), 6.88 (t, $J_{H4+H6}=6.96$ Hz, 1H, *H5*), 6.77 (t, $J_{H3+H5}=7.28$ Hz, 1H, *H4*), 3.21 (s, 3H, *N–Me*), 2.99 (s, 3H, *N–Me*) ppm. Anal. Calc. for $C_{37}H_{31}N_2OPRuS_2\cdot(1/3)CH_2Cl_2$: C, 60.26; H, 4.29; N, 3.76. Found: C, 60.50; H, 4.58; N, 3.55%.

3.16. Preparation of Os(η^2-Phqn)(η^2-S_2CNMe_2)(CO)(PPh_3) (**15**)

Os(η^2-Phqn)Cl(CO)(PPh_3)$_2$ (25 mg) was treated in the same manner as described in Section 3.13, to give light orange crystals of pure **15** (38 mg, 93%). ^{1}H-NMR: δ 7.01–7.40 (m, 15H, *ArH*), 8.52 (d, $J_{H7'}=8.48$ Hz, 1H, *H8′*), 7.98 (d, $J_{H3'}=8.84$ Hz, 1H, *H4′*), 7.94 (d, $J_{H4'}=8.92$ Hz, 1H, *H3′*), 7.80 (d, $J_{H5}=7.76$ Hz, 1H, *H6*), 7.51 (d, $J_{H4}=7.44$ Hz, 1H, *H3*), 7.45 (d, $J_{H6'}=7.84$ Hz, 1H, *H5′*), ~7.15 (s, 1H, *H6′*), ~7.10 (s, 1H, *H7′*), 6.85 (t, $J_{H4+H6}=7.44$ Hz, 1H, *H5*), 6.74 (t, $J_{H3+H5}=7.32$ Hz, 1H, *H4*), 3.12 (s, 3H, *N–Me*), 2.88 (s, 3H, *N–Me*) ppm. MS, *m*/*z*: 806 [MI], 778 [MI–CO]. Anal. Calc. for $C_{37}H_{31}N_2OOsPS_2$: C, 55.21; H, 3.88; N, 3.48. Found: C, 55.38; H, 3.62; N, 3.37%.

3.17. Preparation of Ru(η^2-Dpqx)(η^2-S_2CNMe_2)(CO)(PPh_3) (**16**)

Ru(η^2-Dpqx)Cl(CO)(PPh_3)$_2$ (30 mg) was treated in the same manner as described in Section 3.13, to give dark pink crystals of pure **16** (20 mg, 82%). ^{1}H-NMR: δ 6.98–7.78 (m, 24H, *ArH*), 8.46 (d, $J_{H7'}=8.68$ Hz, 1H, *H8′*), 7.92 (d, $J_{H6'}=7.80$ Hz, 1H, *H5′*), 6.52 (t, $J_{H4+H6}=6.78$ Hz, 1H, *H5*), 6.46 (t, $J_{H3+H5}=7.28$ Hz, 1H, *H4*), 3.22 (s, 3H, *N–Me*), 3.04 (s, 3H, *N–Me*) ppm. Anal. Calc. for $C_{42}H_{34}N_3OPRuS_2\cdot(3/4)CH_2Cl_2$: C, 59.94; H, 4.18; N, 4.91. Found: C, 59.61; H, 3.56; N, 5.36%.

3.18. Preparation of Os(η^2-Dpqx)(η^2-S_2CNMe_2)(CO)(PPh_3) (**17**)

Os(η^2-Dpqx)Cl(CO)(PPh_3)$_2$ (30 mg) was treated in the same manner as described in Section 3.13, to give purple crystals of pure **17** (15 mg, 60%). ^{1}H-NMR: δ 7.02–7.45 (m, 24H, *ArH*), 8.29 (d, $J_{H7'}=8.44$ Hz, 1H, *H8′*), 7.75 (d, $J_{H6'}=8.24$ Hz, 1H, *H5′*), 6.47 (t, $J_{H4+H6}=7.12$ Hz, 1H, *H5*), 6.43 (t, $J_{H3+H5}=7.20$ Hz, 1H, *H4*), 3.13 (s, 3H, *N–Me*), 2.94 (s, 3H, *N–Me*) ppm.

MS, m/z: 883 [MI], 855 [MI–CO]. Anal. Calc. for $C_{42}H_{34}N_3OOsPS_2 \cdot (1/4)CH_2Cl_2$: C, 56.18; H, 3.85; N, 4.65. Found: C, 56.13; H, 3.74; N, 4.28%.

3.19. Preparation of Ru(η²-Dpqx)(η²-acac)(CO)(PPh₃) (18)

Ru(η²-Dpqx)Cl(CO)$(PPh_3)_2$ (100 mg) was added to a solution of methanol (20 ml), acetylacetone (1 ml) and sodium metal (ca. 50 mg). The suspension was stirred overnight (16 h), after which time dichloromethane (5 ml) was added, and stirring continued for 1 h. Excess water was added, the organic layer separated, and the solvent volume reduced in vacuo. The remaining solution was then placed on a short column (10 × 3 cm) of silica gel, and eluted with excess hexane to remove impurities such as acetylacetone. The eluant was then changed to dichloromethane and the bright red band that eluted from the column was collected. Ethanol and a little water were added to this red solution and the solvent volume reduced in vacuo to induce the crystallisation of pure **18**, which was collected by filtration (35 mg, 44%). ^{1}H-NMR: δ 6.42 (t, $J_{H3+H5} = 7.14$ Hz, 1H, *H4*), 7.03–7.86 (m, 25H, *ArH*), 6.88 (d, $J_{H5} = 7.44$ Hz, 1H, *H6*), 6.50 (t, $J_{H4+H6} = 7.44$ Hz, 1H, *H5*), 4.86 (s, 1H, *CH[acac]*), 1.93 (s, 3H, *CH₃[acac]*), 1.57 (s, 3H, *CH₃[acac]*) ppm. Anal. Calc. for $C_{44}H_{35}N_2O_3PRu \cdot (1/3)CH_2Cl_2$: C, 66.55; H, 4.49; N, 3.50. Found: C, 66.45; H, 4.81; N, 3.48%.

3.20. Preparation of Ru(η²-Dpqx)(O₂CCF₃)(CO)(PPh₃)₂ (19)

Ru(η²-Dpqx)Cl(CO)$(PPh_3)_2$ was recrystallised from dichloromethane, ethanol and a little water containing a single drop of trifluoroacetic acid. The pure **19** thus formed was collected by filtration. ^{1}H-NMR: δ 6.94–7.56 (m, 36H, *ArH*), 9.48 (d, $J_{H7'} = 8.76$ Hz, 1H, *H8′*), 7.92 (d, $J_{H6'} = 7.72$ Hz, 1H, *H5′*), 7.76 (t, $J_{H5'+H7'} = 8.12$ Hz, 1H, *H6′*), 7.20 (d, $J_{H4'} = 7.92$ Hz, 1H, *H3*), 7.71 (d, $J_{H5} = 8.08$ Hz, 1H, *H6*), 6.51 (t, $J_{H4+H6} = 7.28$ Hz, 1H, *H5*), 6.45 (t, $J_{H3+H5} = 7.58$ Hz, 1H, *H4*) ppm. Anal. Calc. for $C_{59}H_{43}F_3N_2O_3P_2Ru \cdot CH_2Cl_2$: C, 63.61; H, 4.00; N, 2.47. Found: C, 63.26; H, 3.85; N, 3.48%.

3.21. Preparation of Ru(η²-Phqn-4-Br)Cl(CO)(PPh₃)₂ (20)

Ru(η²-Phqn)Cl(CO)$(PPh_3)_2$ (200 mg) was dissolved in dichloromethane (20 ml), to which was added pyridine·HBr_3 (100 mg) in methanol (5 ml). A small amount of iron powder (ca. 1 mg) was added, and the solution stirred for 1 h. The solution was washed with water, and then $AgSbF_6$ (120 mg) in water (5 ml) and ethanol (5 ml) was added to the organic phase. The resulting solution was stirred for 10 min, and then a large excess of sodium chloride (0.5 g) in water (20 ml) was added. The resulting solution was stirred for a further 10 min. The organic layer was separated, filtered through filter paper, concentrated in volume under reduced pressure, and then placed on a 10 × 3 cm column of silica gel. The column was eluted with dichloromethane, and the slow-moving orange band was collected, heptane added, and the solvent volume reduced in vacuo to induce crystallisation of pure, orange crystals of **20.** These were collected by filtration (107 mg, 49%). ^{1}H-NMR: δ 6.89–7.24 (m, 33H, *ArH*), 9.71 (m, 1H, *H8′*), 7.82 (d, $J_{H3'} = 8.72$ Hz, 1H, *H4′*), 7.50 (d, $J_{H4'} = 8.80$ Hz, 1H, *H3′*), 7.39 (d, $J_{H4} = 2.00$ Hz, 1H, *H3*), 6.75 (d, $J_{H5} = 8.28$ Hz, 1H, *H6*), 6.34 (dd, $J_{H3} = 2.02$ Hz, $J_{H4} = 8.26$ Hz, 1H, *H5*) ppm. Anal. Calc. for $C_{52}H_{39}BrClNOP_2Ru \cdot (1/4)CH_2Cl_2$: C, 63.17; H, 4.01; N, 1.41. Found: C, 63.40; H, 3.82; N, 1.60%.

3.22. Preparation of Os(η²-Phqn-4-Br)Cl(CO)(PPh₃)₂ (21)

Os(η²-Phqn)Cl(CO)$(PPh_3)_2$ (140 mg) was dissolved in dichloromethane (10 ml) to which was added pyridine·HBr_3 (50 mg) in methanol (5 ml). The mixture was treated as in Section 3.21. The bright orange band was eluted from the column, heptane added and the solvent volume reduced in vacuo to give orange microcrystals of pure **21** (140 mg, 92%). ^{1}H-NMR: δ 6.88–7.24 (m, 32H, *ArH*), 9.55 (d, $J_{H7'} = 8.60$ Hz, 1H, *H8′*), 7.76 (d, $J_{H3'} = 8.64$ Hz, 1H, *H4′*), 7.50 (d, $J_{H4'} = 8.76$ Hz, 1H, *H3′*), 7.44 (d, $J_{H5} = 1.60$ Hz, 1H, *H3*), 7.35 (d, $J_{H6'} = 7.08$ Hz, 1H, *H5′*), 6.67 (d, $J_{H5} = 8.28$ Hz, 1H, *H6*), 6.26 (dd, $J_{H3} = 1.72$ Hz, $J_{H6} = 8.24$ Hz, 1H, *H5*) ppm. MS, m/z: 1026 [MI–Cl]. Anal. Calc. for $C_{52}H_{39}BrClNOOsP_2$: C, 58.84; H, 3.70; N, 1.32. Found: C, 58.64; H, 3.54; N, 1.51%.

3.23. Preparation of Ru(η²-Dpqx-4-Br)Cl(CO)(PPh₃)₂ (22)

Ru(η²-Dpqx)Cl(CO)$(PPh_3)_2$ (85 mg) was dissolved in dichloromethane (10 ml), to which was added pyridine·HBr_3 (80 mg) in methanol (5 ml). The mixture was treated as in Section 3.21. Heptane was added to the eluted red band and the solvent volume reduced to afford dark peach microcrystals of pure **22** (25 mg, 27%). ^{1}H-NMR: δ 6.07–9.60 (m, 42H, *ArH*) ppm. Anal. Calc. for $C_{57}H_{42}BrClN_2OP_2Ru \cdot (1/2)CH_2Cl_2$: C, 63.26; H, 3.97; N, 2.57. Found: C, 63.03; H, 4.34; N, 2.99%.

3.24. Preparation of Ru(η²-Dpqx-4-Br)(η²-S₂CNMe₂)(CO)(PPh₃) (23)

Ru(η²-Dpqx-4-Br)Cl(CO)$(PPh_3)_2$ (25 mg) was treated as described above in Section 3.13, to give dark pink

microcrystals of pure **23** (15 mg, 72%). ^{1}H-NMR: δ 7.05–7.50 (m, 23H, *ArH*), 8.46 (d, $J_{H7'} = 8.68$ Hz, 1H, *H8′*), 7.79 (d, $J_{H6'} = 8.24$ Hz, 1H, *H5′*), 7.38 (t, $J_{H5'+H7'} = 7.58$ Hz, 1H, *H6′*), 6.62 (dd, $J_{H3} = 2.10$ Hz, $J_{H6} = 8.10$ Hz, 1H, *H5*), 3.23 (s, 3H, *N–Me*), 3.03 (s, 3H, *N–Me*) ppm. Anal. Calc. for $C_{43}H_{33}BrN_3OPRuS_2 \cdot CH_2Cl_2$: C, 53.98; H, 3.69; N, 4.39. Found: C, 54.21; H, 5.01; N, 5.60%.

3.25. Preparation of Os(η²-Dpqx-4-Br)Cl(CO)(PPh₃)₂ (24)

Os(η²-Dpqx)Cl(CO)$(PPh_3)_2$ (90 mg) was dissolved in dichloromethane (10 ml), to which was added pyridine·HBr_3 (50 mg) in methanol (5 ml). The mixture was treated as described in Section 3.21. Heptane was added to the eluted band and the solvent volume reduced in vacuo, to afford blue–purple microcrystals of pure **24** (50 mg, 52%). ^{1}H-NMR: δ 6.95–7.50 (m, 37H, *ArH*), 9.45 (d, $J_{H7'} = 8.88$ Hz, 1H, *H8′*), 7.70 (d, $J_{H6'} = 8.16$ Hz, 1H, *H5′*), 6.86 (d, $J_{H5} = 8.40$ Hz, 1H, *H6*), 6.77 (d, $J_{H5} = 2.08$ Hz, 1H, *H3*), 6.18 (dd, $J_{H3} = 2.04$ Hz, $J_{H6} = 8.32$ Hz, 1H, *H5*) ppm. MS, *m/z*: 1138 [MI], 1103 [MI–Cl]. Anal. Calc. for $C_{57}H_{42}BrClN_2OOsP_2$: C, 60.14; H, 3.72; N, 2.46. Found: C, 60.11; H, 3.97; N, 2.42%.

3.26. Preparation of Os(η²-Dpqx-4-Br)(η²-S₂CNMe₂)(CO)(PPh₃) (25)

Os(η²-Dpqx-4-Br)Cl(CO)$(PPh_3)_2$ (30 mg) was treated as described in Section 3.13, to give purple microcrystals of pure **25** (20 mg, 79%). ^{1}H-NMR: δ 7.04–7.52 (m, 23H, *ArH*), 8.30 (d, $J_{H7'} = 8.24$ Hz, 1H, *H8′*), 7.78 (dd, $J_{H7'} = 1.20$ Hz, $J_{H6'} = 8.28$ Hz, 1H, *H5′*), 7.36 (t, $J_{H5'+H7'} = 7.68$ Hz, 1H, *H6′*), 6.57 (dd, $J_{H3} = 2.08$ Hz, $J_{H8} = 8.24$ Hz, 1H, *H5*), 3.13 (s, 3H, *N–Me*), 2.93 (s, 3H, *N–Me*) ppm. MS, *m/z*: 961 [MI], 933 [MI–CO]. Anal. Calc. for $C_{42}H_{33}BrN_3OOsPS_2 \cdot (1/3)C_6H_{14}$: C, 53.40; H, 3.84; N, 4.25. Found: C, 53.39; H, 4.05; N, 4.01%.

3.27. Preparation of Os(η²-Nppy-6,8-(NO₂)₂)Cl(CO)(PPh₃)₂ (26)

Os(η²-Nppy)Cl(CO)$(PPh_3)_2$ (100 mg) and $Cu(NO_3)_2$ (100 mg) were added to acetic anhydride (2.5 ml) and the mixture stirred for 20 minutes. A solution of sodium acetate (200 mg) in water (10 ml) was added and the stirring continued until the product had coagulated sufficiently for filtration. After filtration, the solid was dissolved in dichloromethane and the solution placed on a short column (10 × 3 cm) of silica gel. The column was eluted with dichloromethane and the dark red band collected. Ethanol was added to the red eluate, and red microcrystals of pure **26** were obtained on reducing solvent volume in vacuo (95 mg, 87%). ^{1}H-NMR: δ 6.98–7.40 (m, 33H, *ArH*), 8.78 (d, $J_{H5} = 2.32$ Hz, 1H, *H7*), 8.63 (d, $J_{H7} = 2.36$ Hz, 1H, *H5*), 8.46 (d, $J_{H3'} = 5.64$ Hz, 1H, *H2′*), 6.58 (d, $J_{H3} = 8.40$ Hz, 1H, *H4*), 6.32 (t, $J_{H2'+H4'} = 6.48$ Hz, 1H, *H3′*) ppm. Anal. Calc. for $C_{52}H_{38}ClN_3O_5OsP_2$: C, 58.24; H, 3.57; N, 3.92. Found: C, 57.95; H, 3.50; N, 4.04%.

3.28. Preparation of Os(η²-Phqn-4,6-(NO₂)₂)Cl(CO)(PPh₃)₂ (27)

Os(η²-Phqn)Cl(CO)$(PPh_3)_2$ (50 mg) and $Cu(NO_3)_2$ (140 mg) were added to acetic anhydride (3 ml) at room temperature, and the slurry stirred for 1 h. To the resulting greenish solution was added sodium acetate (100 mg) in water (20 ml), and the mixture was stirred until the product coagulated sufficiently for filtration. After filtration, the resulting paste was redissolved in dichloromethane and placed on a short column (10 × 3 cm) of silica gel. The product was eluted with dichloromethane containing acetone (20%). Pure microcrystals of **27** were obtained by adding heptane to the eluate and reducing the solvent volume in vacuo (20 mg, 37%). ^{1}H-NMR: δ 6.92–7.24 (m, 30H, *ArH*), 9.72 (d, $J_{H7'} = 8.92$ Hz, 1H, *H8′*), 8.06 (d, $J_{H3'} = 8.68$ Hz, 1H, *H4′*), 7.97 (s, 1H, *H5*), 7.64 (d, $J_{H4'} = 8.80$ Hz, 1H, *H3′*), 7.58 (s, 1H, *H3*), 7.56 (d, $J_{H6'} = 8.24$ Hz, 1H, *H5′*), 7.36 (t, $J_{H6'+H8'} = 7.32$ Hz, 1H, *H7′*), 7.14 (t, $J_{H5'+H7'} = 7.96$ Hz, 1H, *H6′*) ppm. MS, *m/z*: 1038 [MI–Cl]. Anal. Calc. for $C_{52}H_{38}ClN_3O_5OsP_2 \cdot (3/4)CH_2Cl_2$: C, 55.76; H, 3.50; N, 3.70. Found: C, 55.65; H, 3.57; N, 3.97%.

3.29. X-ray crystal structures for 7, 12, 15, 18, 19, 21, 23, 25

Data were collected on a Siemens SMART diffractometer with a CCD area detector and graphite monochromated Mo–K_α radiation, $\lambda = 0.71073$ Å. Unit cell parameters were obtained from a least-squares fit to all data with $I > 10\sigma(I)$. The data were corrected for Lorentz and polarisation effects and empirical absorption corrections applied [14]. Equivalent reflections were averaged to give the unique data set. Details of crystal data and data collection parameters are given in Table 1.

3.30. Structure solution and refinement

The structures were solved by Patterson and Fourier techniques using SHELXS [15] and refined by full-matrix least squares on F^2 using SHELXL [16]. All non-hydrogen atoms were allowed to refine anisotropically. Hydrogen atoms were placed geometrically and refined with a riding model (including free rotation of methyl groups) with U_{iso} fixed at 20% greater than the carrier atom. Refinement details are given in Table 1.

4. Supplementary material

Tables of thermal and H atom parameters and complete lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Database Centre. The deposition numbers CCDC 134378–134385 have been allocated to the compounds **7**, **12**, **15**, **18**, **19**, **21**, **23**, **25**, respectively. Copies of this information can 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 www: http://www.ccdc.cam.ac.uk).

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References

[1] (a) I. Omae, Coord. Chem. Rev. 83 (1988) 137. (b) F.O. Garces, K.A. King, R.J. Watts, Inorg. Chem. 27 (1988) 3464. (c) A. Zilian, U. Maeder, A. von Zelewski, H.U. Güdel, J. Am. Chem. Soc. 111 (1989) 3855. (d) C.A. Craig, R.J. Watts, Inorg. Chem. 28 (1989) 309. (e) C.A. Craig, F.O. Garces, R.J. Watts, R. Palmans, A.J. Frank, Coord. Chem. Rev. 97 (1990) 193. (f) E.C Constable, A.M.W.C. Thompson, T.A. Leese, D.G.F. Leese, D.A. Tocher, Inorg. Chim. Acta 182 (1991) 93. (g) A. Ford, E. Sinn, S. Woodward, J. Organomet. Chem. 493 (1995) 215. (h) J.-P. Djukic, K.H. Dötz, M. Pfeffer, A. De Cian, J. Fischer, Organometallics, 16 (1997) 5171. (i) Y. Guari, S. Sabo-Etienne, B. Chaudret, J. Am. Chem. Soc. 120 (1998) 4228. (j) D.J. de Geest, P.J. Steel, Inorg. Chem. Commun. 1 (1998) 358.

[2] A.M. Clark, C.E.F. Rickard, W.R. Roper, L.J. Wright, Organometallics 18 (1999) 2813.

[3] (a) W.R. Roper, L.J. Wright, J. Organomet. Chem. 142 (1977) C1. (b) C.E.F. Rickard, W.R. Roper, G.E. Taylor, J.M. Waters, L.J. Wright, J. Organomet. Chem. 389 (1990) 375. (c) M.M.P. Ng, W.R. Roper, L.J. Wright, Organometallics 13 (1994) 2563. (d) G.R. Clark, M.M.P. Ng, W.R. Roper, L.J. Wright, J. Organomet. Chem. 491 (1995) 219. (e) K. Hübler, U. Hübler, W.R. Roper, L.J. Wright, J. Organomet. Chem. 526 (1996) 199. (f) A.M. Clark, C.E.F. Rickard, W.R. Roper, L.J. Wright, J. Organomet. Chem. 545 (1997) 619.

[4] P.J. Steel, G.B. Caygill, J. Organomet. Chem. 395 (1990) 359.

[5] A.M. Clark, C.E.F. Rickard, W.R. Roper, L.J. Wright, Organometallics 17 (1998) 4535.

[6] G.R. Clark, C.E.L. Headford, W.R. Roper, L.J. Wright, V.P.D. Yap, Inorg. Chim. Acta 220 (1994) 261.

[7] J.B. Menke, Recl. Trav. Chim. Pays-Bas 44 (1925) 141.

[8] G.R. Clark, C.E.F. Rickard, W.R. Roper, L.J. Wright, V.P.D. Yap, Inorg. Chim. Acta 251 (1996) 65.

[9] P.S. Hallman, B.R. McGarvey, G. Wilkinson, J. Chem. Soc. (A) (1968) 3143.

[10] L. Vaska, J. Am. Chem. Soc. 86 (1964) 1943.

[11] N. Al Salim, A.A. West, W.R. McWhinnie, T.A. Hamor, J. Chem. Soc. Dalton Trans. (1988) 2363.

[12] C.K. Bradsher, L.E. Beavers, J. Am. Chem. Soc. 78 (1956) 2459.

[13] Y. Cohen, A.Y. Meyer, M. Rabinovitz, J. Am. Chem. Soc. 108 (1986) 7039.

[14] R.H. Blessing, Acta Crystallogr. Sect. A 51 (1995) 33.

[15] G.M. Sheldrick, Acta Crystallogr. Sect. A 46 (1990) 467.

[16] G.M. Sheldrick, Program for crystal structure refinement. University of Göttingen, Germany, 1997.