Electrophilic Substitution Reactions at the Phenyl Ring of the Chelated 2-(2′-Pyridyl)phenyl Ligand Bound to Ruthenium(II) or Osmium(II)

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Reaction between $(PyPh)_2Hg$ (PyPh = 2-(2′-pyridyl)phenyl) and $MHCl(CO)(PPh_3)_3$ proceeds smoothly to form $M(\eta^2\text{-PyPh})Cl(CO)(PPh_3)_2$ (M = Ru (**1a**); M = Os (**1b**)). In both complexes the PyPh ligand is bound as a stable five-membered chelate ring. The chloride ligand in these complexes can be removed through reaction with a silver salt and other ligands then introduced. In this way the compounds $M(\eta^2\text{-PyPh})I(CO)(PPh_3)_2$ (M = Ru (**2a**); M = Os (**2b**)), $[M(\eta^2\text{-PyPh})(CO)_2(PPh_3)_2]SbF_6$ (M = Ru (**3a**); M = Os (**3b**)), and $M(\eta^2\text{-PyPh})(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)$ (M = Ru (**4a**); M = Os (**4b**)) have been prepared. The coordinated PyPh ligand in **1a** and **1b** is activated by the metal toward electrophilic substitution at the phenyl ring. Nitration occurs in both the phenyl 4- and 6-positions of **1a** or **1b,** i.e., ortho and para to the metal, to give $M(\eta^2\text{-PyPh-4,6-}(NO_2)_2)Cl(CO)(PPh_3)_2$ (M = Ru (**5a**); M = Os (**5b**)). Under appropriate conditions the mono-nitrated derivative, $Os(\eta^2\text{-PyPh-4-}NO_2)Cl(CO)(PPh_3)_2$ (**5c**), can also be isolated. Bromination of **1a** or **1b** occurs in the phenyl 4-position, i.e., para to the metal, to give $M(\eta^2\text{-PyPh-4-Br})Cl(CO)(PPh_3)_2$ (M = Ru (**6a**); M = Os (**6b**)). With excess brominating agent ([PyrH][Br_3]) and a longer reaction time the unusual mixed triphenylphosphine/pyridine complex, $Os(\eta^2\text{-PyPh-4-Br})Cl(CO)(Pyr)(PPh_3)$ (**6c**) (Pyr = pyridine), is formed. The brominated osmium substrate (**6b**) can be lithiated through reaction with BuLi. Although this intermediate has not been isolated, further treatment with the electrophiles CO_2/H^+ or Bu_3SnCl forms $Os(\eta^2\text{-PyPh-4-}CO_2H)Cl(CO)(PPh_3)_2$ (**7a**) or $Os(\eta^2\text{-PyPh-4-}SnBu_3)Cl(CO)(PPh_3)_2$ (**7b**), respectively. The functionalized pyridylphenyl ligand in **6a** can be removed by heating with acid, to give 2′-(3-bromophenyl)pyridine, in modest isolated yield. The structures of $[Os(\eta^2\text{-PyPh})(CO)_2(PPh_3)_2]SbF_6$ (**3b**), $Os(\eta^2\text{-PyPh})(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)$ (**4b**), $Os(\eta^2\text{-PyPh-4-}NO_2)Cl(CO)(PPh_3)_2$ (**5c**), $Os(\eta^2\text{-PyPh-4-Br})Cl(CO)(PPh_3)_2$ (**6b**), and $Os(\eta^2\text{-PyPh-4-Br})Cl(CO)(Pyr)(PPh_3)$ (**6c**) have all been determined by X-ray crystal structure analyses.

Introduction

Many metal complexes containing the PyPh (2-(2′-pyridyl)phenyl) ligand have been prepared previously by direct metalation of 2-phenylpyridine. Metalation of the phenyl ring invariably occurs in the ortho position, and the resulting five-membered chelate ring is usually very stable.[1] We have shown that a convenient high-yield route to the coordinatively unsaturated aryl complexes $M(Ar)Cl(CO)(PPh_3)_2$ (M = Ru or Os) involves the reaction of $MHCl(CO)(PPh_3)_3$ with Ar_2Hg. This reaction is general and works well for a wide range of different aryl groups including the 2-(2′-pyridyl)phenyl ligand, which is the subject of this paper.[2]

In recent studies we have shown that simple aryl ligands in $M(Ar)Cl(CO)(PPh_3)_2$ or the corresponding saturated complexes, $M(Ar)Cl(CO)L(PPh_3)_2$ (L = CO, CNR), are strongly activated by the metal toward electrophilic aromatic substitution reactions.[3] While the metal−carbon bond remains intact during many of these reactions involving mild reagents, the use of more vigorous reagents can cause bond cleavage. When the aryl ligand contains a functional group which coordinates to the metal and forms a chelate ring, the metal−carbon bond is considerably more resistant to attack by external reagents. We have previously reported the preparation of $Os(\eta^2\text{-Qn})Cl(CO)(PPh_3)_2$ (Qn = 8-quinolyl).[4]

(1) (a) Kasahara, A. *Bull. Chem. Soc. Jpn* **1968**, *41*, 1272. (b) Chassot, L.; von Zewelsky, A. *Inorg. Chem.* **1987**, *26*, 2814. (c) Steel, P. J.; Caygill, G. B. *J. Organomet. Chem.* **1987**, *327*, 101. (d) Garces, F. O.; King, K. A.; Watts, R. J. *Inorg. Chem.* **1988**, *27*, 3464. (e) Craig, C. A.; Watts, R. J. *Inorg. Chem.* **1989**, *28*, 309. (f) Zilian, A.; Marder, U.; von Zelewski, A.; Güdel, H. U. *J. Am. Chem. Soc.* **1989**, *111*, 3855. (g) Craig, C. A.; Garces, F. O.; Watts, R. J.; Palmans, R.; Frank, A. J. *Coord. Chem. Rev.* **1990**, *97*, 193. (h) Steel, P. J.; Caygill, G. B. *J. Organomet. Chem.* **1990**, *395*, 359. (i) Constable, E. C.; Cargil Thompson, A. M. W.; Leese, T. A.; Reese, D. G. F.; Tocher, D. A. *Inorg. Chim. Acta* **1991**, *182*, 93. (j) Djukic, J.-P.; Dötz, K. H.; Pfeffer, M.; Cian, A. D.; Fischer, J. *Organometallics* **1997**, *16*, 5171. (k) Guari, Y.; Sabo-Etienne, S.; Chaudret, B. *J. Am. Chem. Soc.* **1998**, *120*, 4228.

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

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

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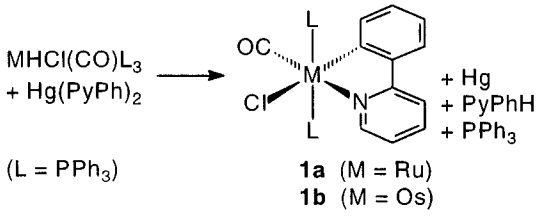
Scheme 1



The Qn ligand contains a nitrogen placed suitably for coordination to the metal, forming a four-membered chelate ring. The 8-quinolyl ring system was found to be very activated toward electrophilic aromatic substitution and readily underwent bromination or nitration in the position para to the osmium−carbon bond.[5] In addition, it was found that the bromoquinolyl complex Os(η^2-Qn-5-Br)Cl(CO)(PPh_3)$_2$ could be lithiated with BuLi without cleaving the osmium−carbon bond, thus making possible introduction of a variety of functional groups.[5] Up to this point the usual method for preparing functionalized aryl ligands has been to include the functionality prior to metalation.[6]

Our main interest in using a metal−ligand fragment as an activating/directing substituent in electrophilic aromatic substitution reactions is to access complexes with specially substituted organometallic ligands, which in turn offer a wide scope for further ligand elaboration.[6g] It should not be overlooked, however, that removal of the substituted ligands from the metal could, in principle, constitute a route to unusually substituted organics that are difficult to prepare by other means. Accordingly, one example of the cleavage of a substituted ligand is briefly explored in this work.

In this paper we report (i) the preparation of 2-(2′-pyridyl)phenyl complexes of ruthenium(II) and osmium(II), (ii) a study of the electrophilic substitution reactions occurring at the 2-(2′-pyridyl)phenyl ligands, (iii) lithiation followed by further derivatization of the bromo-substituted derivatives, (iv) an observation of the replacement with pyridine of one triphenylphosphine, in a bis(triphenylphosphine) complex, through use of the brominating reagent [PyrH][Br_3], and (v) an example of the removal from the metal of a functionalized ligand fragment as an unusually substituted 2-(phenyl)pyridine.

Results and Discussion

Transmetalation. Treatment of MHCl(CO)(PPh_3)$_3$ with $PyPh_2Hg$ forms M(η^2-PyPh)Cl(CO)(PPh_3)$_2$ (M = Ru (**1a**), Os (**1b**)) (see Scheme 1; IR data for these and all other new compounds are collected in Table 1, NMR data is presented in the Experimental Section, and the numbering system used for NMR assignments and the naming of compounds is as depicted in the molecular structure diagrams, Figures1−5). The 2-(2′-pyridyl)-phenyl ligand binds to the metal in a bidentate fashion, forming a five-membered chelate ring which is robust, and attempts to displace the nitrogen from the metal center through addition of other potential ligands such as CO or CNR failed, even under forcing conditions. Likewise, introduction of the powerfully chelating ligand dimethyldithiocarbamate did not displace the nitrogen atom (see below).

Table 1. Infrared Data (cm^{-1})[a] for New 2-(2′-Pyridyl)phenyl Complexes

complex	ν(C=O)	other bands
Ru(η^2-PyPh)Cl(CO)(PPh_3)$_2$ (**1a**)	1919 s	
Os(η^2-PyPh)Cl(CO)(PPh_3)$_2$ (**1b**)	1898 s	
Ru(η^2-PyPh)I(CO)(PPh_3)$_2$ (**2a**)	1915 s	
Os(η^2-PyPh)I(CO)(PPh_3)$_2$ (**2b**)	1902 s	
[Ru(η^2-PyPh)(CO)$_2$(PPh_3)$_2$]SbF_6 (**3a**)	1994, 2049 s	999, 656 s (SbF_6)
[Os(η^2-PyPh)(CO)$_2$(PPh_3)$_2$]SbF_6 (**3b**)	1953, 2023 s	999, 660 s (SbF_6)
Ru(η^2-PyPh)(η^2-S_2CNMe_2)(CO)(PPh_3) (**4a**)	1921 s	1504 m (dithiocarbamate)
Os(η^2-PyPh)(η^2-S_2CNMe_2)(CO)(PPh_3) (**4b**)	1903 s	1518 m (dithiocarbamate)
Ru(η^2-PyPh-(4,6-$(NO_2)_2$)Cl(CO)(PPh_3)$_2$ (**5a**)	1948 s	1530, 1506 m (NO_2)
Os(η^2-PyPh-(4,6-$(NO_2)_2$)Cl(CO)(PPh_3)$_2$ (**5b**)	1929 s	1531, 1504 m (NO_2)
Os(η^2-PyPh-4-NO_2)Cl(CO)(PPh_3)$_2$ (**5c**)	1915 s	1496 m (NO_2)
Ru(η^2-PyPh-4-Br)Cl(CO)(PPh_3)$_2$ (**6a**)	1927 s	
Os(η^2-PyPh-4-Br)Cl(CO)(PPh_3)$_2$ (**6b**)	1911 s	
Os(η^2-PyPh-4-Br)Cl(CO)(Pyr)(PPh_3) (**6c**)	1907 s	
Os(η^2-PyPh-4-CO_2H)Cl(CO)(PPh_3)$_2$ (**7a**)	1906 s	1673 s (CO_2H)
Os(η^2-PyPh-4-$SnBu_3$)Cl(CO)(PPh_3)$_2$ (**7b**)	1904 s	

[a] Spectra were recorded as Nujol mulls between KBr plates.

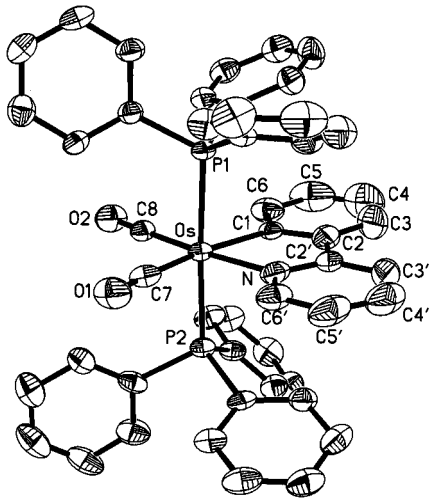


Figure 1. Molecular structure of [Os(η^2-PyPh)(CO)$_2$(PPh_3)$_2$]SbF_6 **(3b)** (cation only) with thermal ellipsoids at the 50% probability level.

Derivatives of 1a and 1b through Chloride Replacement. The chloride ligand in either **1a** or **1b** is relatively labile and can be easily removed by treatment in solution with $AgSbF_6$. Subsequent treatment of the cationic intermediate (which was not isolated) with anionic or neutral donors provides a simple route to new

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(5) Clark, A. M.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *Organometallics* **1998**, *17*, 4535.
(6) (a) Kawata, N.; Mizoroki, T.; Ozaki, A. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1807. (b) Reveco, P.; Schmehl, R. H.; Cherry, W. R.; Fronczek, F. R.; Selbin, J. *Inorg. Chem.* **1985**, *24*, 4078. (c) Debaerdemaeker, T.; Stapp, B.; Brune, H. A. *Acta Crystallogr.* **1987**, *C43*, 473. (d) Tam, W.; Calabrese, J. C. *Chem. Phys. Lett.* **1988**, *144*, 79. (e) Vicente, J.; Arcas, A.; Borrachero, M. V.; Molíns, E.; Miravitlles, C. *J. Organomet. Chem.* **1992**, *441*, 487. (f) Kim, Y.-J.; Sato, R.; Maruyama, T.; Osakada, K.; Yamamoto, T. *J. Chem. Soc., Dalton Trans.* **1994**, 943. (g) Clark, G. R.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J.; Yap, V. P. D. *Inorg. Chim. Acta* **1996**, *251*, 65. (h) Forsyth, R.; Pyman, F. L. *J. Chem. Soc.* **1926**, 2912.

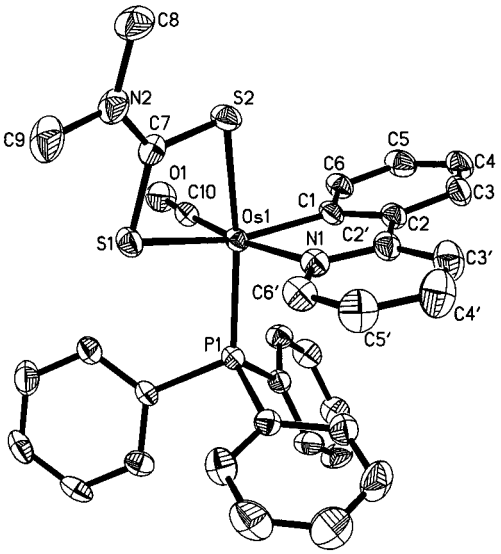


Figure 2. Molecular structure of Os(η^2-PyPh)(η^2-S_2CNMe_2)-(CO)(PPh_3) (**4b**) (one enantiomer only) with thermal ellipsoids at the 50% probability level.

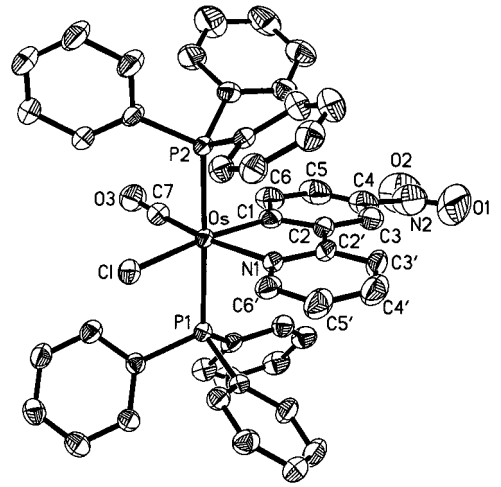


Figure 3. Molecular structure of Os(η^2-PyPh-4-NO_2)Cl-(CO)(PPh_3)$_2$ (**5c**) with thermal ellipsoids at the 50% probability level.

derivatives (see Scheme 2). Reaction with sodium iodide gives the products of simple halide exchange, M(η^2-PyPh)I(CO)(PPh_3)$_2$ (M = Ru (**2a**); M = Os (**2b**)), while reaction with carbon monoxide gives the dicarbonyl salts [M(η^2-PyPh)(CO)$_2$(PPh_3)$_2$]SbF_6 (M = Ru (**3a**); M = Os (**3b**)). Sodium dimethyldithiocarbamate adds to the metal center rapidly at room temperature, and then in a slower step which is accelerated by heating triphenylphosphine is displaced and the dimethyldithiocarbamate ligand coordinates in a bidentate fashion to give M(η^2-PyPh)(η^2-S_2CNMe_2)(CO)(PPh_3) (M = Ru (**4a**); M = Os (**4b**)).

Electrophilic Aromatic Substitution. Nitration of free 2-phenylpyridine has been reported to occur in the phenyl ring to give two mono-nitrated isomers, the major isomer being that with the nitro group para to the ring junction. The conditions for this nitration involve heating 2-phenylpyridine nitrate in concentrated H_2SO_4 at 100 °C for 30 min.[6h] In contrast, the metal-bound 2-phenylpyridine ligand in complexes **1a** and **1b** is highly activated toward electrophilic aromatic nitration. The activated positions are on the phenyl ring,

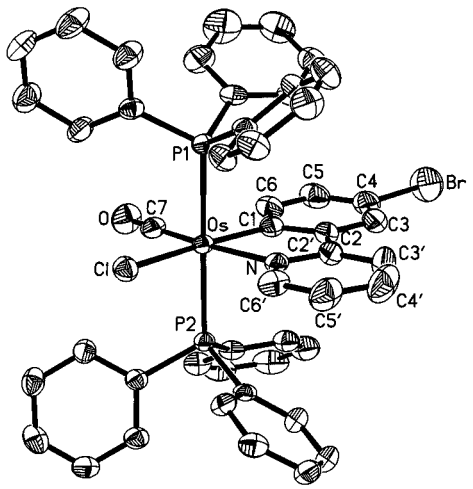


Figure 4. Molecular structure of Os(η^2-PyPh-4-Br)Cl(CO)-(PPh_3)$_2$ (**6b**) with thermal ellipsoids at the 50% probability level.

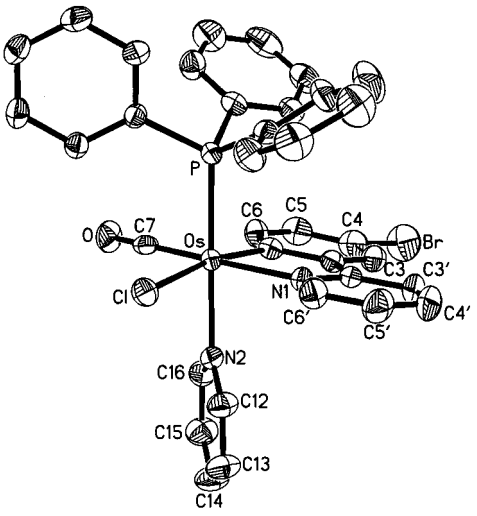
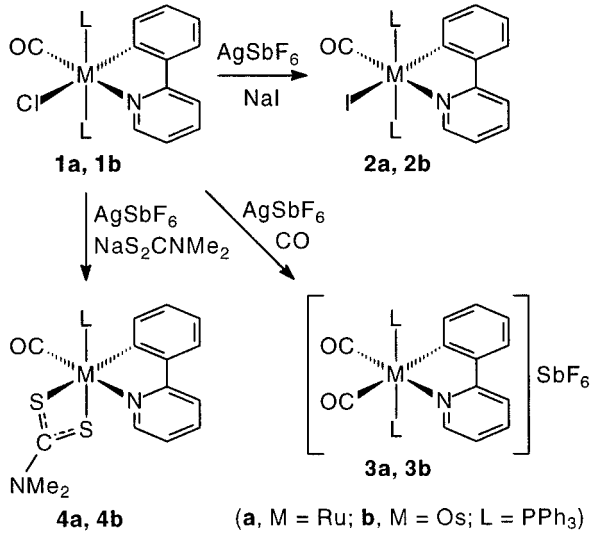


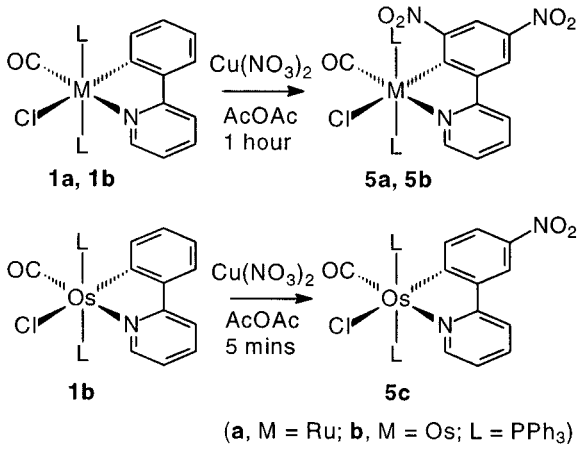
Figure 5. Molecular structure of Os(η^2-PyPh-4-Br)Cl(CO)-(Pyr)(PPh_3) (**6c**) (one enantiomer only) with thermal ellipsoids at the 50% probability level.

Scheme 2

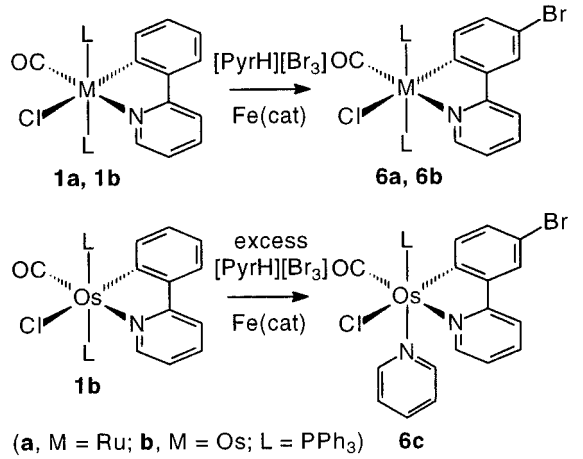


ortho and para to the metal substituent. Nitration of **1a** or **1b** with excess $Cu(NO_3)_2$ in acetic anhydride for 1 h at room temperature gives exclusively the dinitrated

Scheme 3



Scheme 4

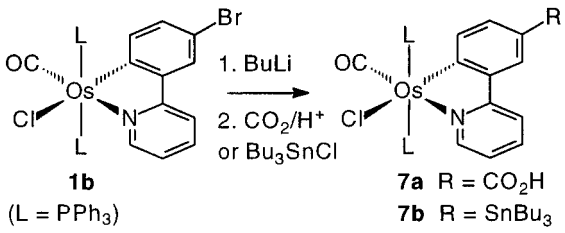


products M(η^2-PyPh-4,6-$(NO_2)_2$)Cl(CO)$(PPh_3)_2$ (M = Ru (**5a**); M = Os (**5b**)) (see Scheme 3). While the osmium complex **5b** can be prepared in reasonable yield (36%), the ruthenium complex **5a** is produced in lower yield (18%), even when the reaction is performed at 0 °C.

Under similar nitrating conditions, but utilizing a very short reaction time, it was possible to prepare the para-substituted, mono-nitrated osmium complex, Os(η^2-PyPh-4-NO_2)Cl(CO)$(PPh_3)_2$ (**5c**), albeit in low yield. None of the 6-substituted product, Os(η^2-PyPh-6-NO_2)Cl(CO)$(PPh_3)_2$, was observed, presumably because the 4-position is more accessible to attack than the 6-position. Clearly, introduction of the first nitro group does not significantly deactivate the phenyl ring toward further nitration.

Bromination of the metal-bound 2-phenylpyridine ligand in complexes **1a** and **1b** also occurs more readily than does bromination of simple phenyl derivatives. Moreover, the reaction is highly selective, and only one isomer is formed, that in which the bromine is introduced para to the metal. Room-temperature bromination of **1a** or **1b** by addition of 1 equiv of bromine (in the form of [PyrH][Br_3]), in the presence of a catalytic quantity of iron powder, gives rise to the mono-brominated products, M(η^2-PyPh-4-Br)Cl(CO)$(PPh_3)_2$ (M = Ru (**6a**); M = Os (**6b**)) (see Scheme 4). Good yields are obtained in both cases. However, unlike the nitration reaction, no dibrominated products were observed even when an excess of [PyrH][Br_3] was used and with longer

Scheme 5



reaction times. Under these conditions, **6b** gave the unusual product Os(η^2-PyPh-4-Br)Cl(CO)(Pyr)(PPh_3) (**6c**), in which not only is the PyPh ligand brominated but in addition pyridine replaces one triphenylphosphine ligand (see Scheme 4). It appears that one of the triphenylphosphine ligands dissociates and is oxidized by the excess bromine, leaving only a pyridine molecule to occupy the vacant site. This approach could offer an interesting general route to mixed triphenylphosphine/pyridine complexes of osmium(II), but we have not yet explored this further.

Lithiation. It was found that lithiation of the phenyl ring of complex **6b** could be achieved by reaction with excess BuLi at 0 °C. Although the intermediate product, Os(η^2-PyPh-4-Li)Cl(CO)$(PPh_3)_2$, was not isolated, two derivatives have been fully characterized (see Scheme 5). Reaction of this intermediate with CO_2/H^+ gives the carboxylic acid derivative, Os(η^2-PyPh-4-CO_2H)Cl(CO)-$(PPh_3)_2$ (**7a**). Similarly, treatment of the intermediate with an excess of Bu_3SnCl gives Os(η^2-PyPh-4-$SnBu_3$)-Cl(CO)$(PPh_3)_2$ (**7b**).

Structures. Bond distances and angles for **3b**, **4b**, **5c**, **6b,** and **6c** are given in Tables3−7, respectively. The compounds **3b**, **4b**, **5c**, **6b,** and **6c** all exhibit essentially octahedral coordination geometries, and **3b**, **5c,** and **6b** all have mutually trans triphenylphosphine ligands, with angles P(1)−Os−P(2) close to 180° (176.78(6)°, 174.97(3)°, and 177.13(7)°, respectively). The structure of **6c** is very similar to that of **6b**, except that a pyridine ligand replaces one of the triphenylphosphine ligands. As a consequence of the introduction of the pyridine, the remaining Os−P distance in **6c** is shortened by more than 0.06 Å compared to the Os−P distances in **6b**. On the other hand, the individual bond lengths and angles within the 2-(2′-pyridyl)phenyl ligands in **3b**, **4b**, **5c**, **6b,** and **6c** show little variation. The Os−C bond lengths in **4b**, **5c**, **6b,** and **6c** are remarkably similar (2.077(6), 2.041(4), 2.050(9) and 2.044(5) Å, respectively), even though the substitution patterns on the phenyl rings differ considerably and the ancillary ligands are not the same. The corresponding Os−C distance in **3b** is longer (2.125(6) Å), presumably because this compound is cationic and also the trans ligand is CO. The Os−N bond in **3b** is also shorter (2.127(6) Å) than the corresponding distances in **4b**, **5c**, **6b,** and **6c** (2.167(6), 2.153(3), 2.157-(7), and 2.173(4) Å, respectively). Presumably this is a result of the cationic nature of the metal center in **3b**.

Demetalation. Cleavage of the brominated 2-phenylpyridine ligand from **6a** or **6b** with HCl was investigated. For the osmium complex, **6b**, only trace amounts of 2′-(3-bromophenyl)pyridine (**8**) were released from the metal. However, when the ruthenium substrate, **6a**, was dissolved in toluene and heated under reflux overnight with a large excess of concentrated HCl, the complex was decomposed entirely, and a modest yield of 2′-(3-

Table 2. Crystal and Refinement Data for 3b, 4b, 5c, 6b, and 6c

	3b·$^1/_2CH_2Cl_2$	**4b**	**5c**	**6b**	**6c**·$CHCl_3$
formula	$C_{49}H_{38}NO_2P_2Os{\cdot}SbF_6{\cdot}1/2CH_2Cl_2$	$C_{33}H_{29}N_2OOsPS_2$	$C_{48}H_{37}ClN_2O_3OsP_2$	$C_{48}H_{37}BrClNOOsP_2$	$C_{35}H_{26}BrClN_2OOsP_2{\cdot}CHCl_3$
molecular wt	1203.16	754.87	977.39	1011.29	946.48
cryst syst	triclinic	monoclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a, Å	11.8966(2)	11.3840(1)	11.2393(2)	11.3911(1)	10.679(1)
b, Å	13.9035(2)	15.3789(1)	12.2801(2)	12.0481(1)	22.350(3)
c, Å	15.1958(2)	34.5340(1)	16.0510(3)	17.3575(1)	14.803(2)
α, deg	90.949(1)		73.292(1)	76.656(1)	
β, deg	98.017(1)	93.128(1)	76.092(1)	78.776(1)	90.896(1)
γ, deg	101.46(1)		73.717(1)	11.193(1)	
V , Å^3	24636.70(6)	6036.98(7)	2005.73(6)	2234.19(4)	3532.71(7)
Z	2	8	2	2	4
d(calc), g cm^{-3}	1.640	1.661	1.618	1.503	1.780
F(000)	1174	2976	972	996	1836
μ, mm^{-1}	3.34	4.44	3.371	3.91	5.12
θ (min−max), deg	1.3−28.3	2.2−27.4	1.78−27.47	1.8−28.2	1.6−27.4
unique reflns	10740	13053	8732	9847	7702
no. of obsd reflns $I > 2\sigma(I)$	9288	12701	7958	8134	6466
cryst size, mm	0.50 × 0.22 × 0.09	0.20 × 0.20 × 0.19	0.48 × 0.23 × 0.06	0.32 × 0.08 × 0.05	0.40 × 0.10 × 0.08
A, (min, max)	0.286, 0.753	0.470, 0.485	0.2945, 0.8233	0.367, 0.828	0.234, 0.685
no. of variables in LS	571	725	514	496	414
goodness of fit on F^2	0.950	1.005	1.034	0.698	1.040
R (obsd data)	0.0512	0.0338	0.0285	0.0511	0.0387
wR2 (all data)	0.1469	0.0812	0.0736	0.1788	0.0922
diff map (min, max), e Å^{-3}	−1.99, +1.64	−1.15, +0.58	1.129, 1.840	−1.71, +2.07	−1.88, +2.01

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex 3b

Interatomic Distances			
Os−C(7)	1.904(7)	Os−N	2.127(6)
Os−C(8)	1.912(6)	Os−P(2)	2.4038(15)
Os−C(1)	2.125(6)	Os−P(1)	2.4087(15)
Interatomic Angles			
C(7)−Os−C(8)	95.2(3)	C(1)−Os−P(2)	89.73(16)
C(7)−Os−C(1)	168.4(3)	N−Os−P(2)	89.56(16)
C(8)−Os−C(1)	96.5(3)	C(7)−Os−P(1)	92.7(2)
C(7)−Os−N	90.2(3)	C(8)−Os−P(1)	89.70(19)
C(8)−Os−N	174.6(3)	C(1)−Os−P(1)	87.09(16)
C(1)−Os−N	78.2(3)	N−Os−P(1)	89.33(16)
C(7)−Os−P(2)	90.3(2)	P(2)−Os−P(1)	176.79(6)
C(8)−Os−P(2)	91.12(19)		

Table 4. Selected Bond Distances (Å) and Angles (deg) for Complex 4b

Interatomic Distances			
Os(1)−C(10)	1.844(7)	Os(1)−P(1)	2.3263(16)
Os(1)−C(1)	2.077(6)	Os(1)−S(2)	2.4556(17)
Os(1)−N(1)	2.167(6)	Os(1)−S(1)	2.4874(17)
Interatomic Angles			
C(10)−Os(1)−C(1)	94.1(3)	N(1)−Os(1)−S(2)	84.49(16)
C(10)−Os(1)−N(1)	171.2(3)	P(1)−Os(1)−S(2)	167.83(6)
C(1)−Os(1)−N(1)	77.5(3)	C(10)−Os(1)−S(1)	96.3(2)
C(10)−Os(1)−P(1)	92.3(2)	C(1)−Os(1)−S(1)	160.25(18)
C(1)−Os(1)−P(1)	99.08(18)	N(1)−Os(1)−S(1)	91.13(15)
N(1)−Os(1)−P(1)	91.43(15)	P(1)−Os(1)−S(1)	97.27(6)
C(10)−Os(1)−S(2)	93.4(2)	S(2)−Os(1)−S(1)	71.41(6)
C(1)−Os(1)−S(2)	91.25(18)		

bromophenyl)pyridine (25%) was obtained. The ruthenium-containing product formed during this reaction was not fully characterized, but IR absorption bands were consistent with the formation of the triply chloro-bridged dimer $[(Ph_3P)Cl(OC)Ru(\mu\text{-}Cl)_3Ru(CO)(PPh_3)_2]$.[7]

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Table 5. Selected Bond Distances (Å) and Angles (deg) for Complex 5c

Interatomic Distances			
Os−C(7)	1.848(4)	Os−Cl	2.5204(9)
Os−C(1)	2.041(4)	Os−P(2)	2.3894(8)
Os−N(1)	2.153(3)	Os−P(1)	2.4172(8)
Interatomic Angles			
C(7)−Os−C(1)	91.54(16)	N(1)−Os−P(1)	88.91(7)
C(7)−Os−N(1)	169.85(14)	C(7)−Os−Cl	98.76(12)
C(1)−Os−N(1)	78.42(14)	C(1)−Os−Cl	169.69(11)
C(7)−Os−P(2)	89.68(12)	N(1)−Os−Cl	91.29(8)
C(1)−Os−P(2)	91.25(9)	P(2)−Os−Cl	89.29(3)
N(1)−Os−P(2)	88.98(7)	P(1)−Os−Cl	86.19(3)
C(7)−Os−P(1)	93.19(11)	P(2)−Os−P(1)	174.97(3)
C(1)−Os−P(1)	92.80(9)		

Table 6. Selected Bond Distances (Å) and Angles (deg) for Complex 6b

Interatomic Distances			
Os−C(7)	1.865(10)	Os−P(2)	2.3801(19)
Os−C(1)	2.050(9)	Os−P(1)	2.3958(19)
Os−N	2.157(7)	Br−C(4)	1.903(9)
Os−Cl	2.527(2)		
Interatomic Angles			
C(7)−Os−C(1)	92.3(4)	N−Os−P(1)	88.54(17)
C(7)−Os−N	170.5(3)	P(2)−Os−P(1)	177.13(7)
C(1)−Os−N	78.3(3)	C(7)−Os−Cl	97.6(3)
C(7)−Os−P(2)	90.4(3)	C(1)−Os−Cl	170.0(2)
C(1)−Os−P(2)	91.4(2)	N−Os−Cl	91.9(2)
N−Os−P(2)	89.02(17)	P(2)−Os−Cl	90.24(7)
C(7)−Os−P(1)	92.2(3)	P(1)−Os−Cl	88.34(7)
C(1)−Os−P(1)	89.6(2)		

Although 2′-(3-bromophenyl)pyridine cannot be prepared by direct bromination of 2-(phenyl)pyridine,[8] it can be prepared by the action of a diazonium salt of *m*-bromoaniline on pyridine.[9] This reaction forms a mixture of three isomers, substituted in the 2′, 3′, and

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Table 7. Selected Bond Distances (Å) and Angles (deg) for Complex 6c

Interatomic Distances			
Os−C(7)	1.845(5)	Os−P	2.3241(13)
Os−C(1)	2.044(5)	Os−Cl	2.5169(13)
Os−N(1)	2.173(4)	Br−C(4)	1.910(6)
Os−N(2)	2.174(4)		
Interatomic Angles			
C(7)−Os−C(1)	92.4(2)	N(1)−Os−P	93.10(11)
C(7)−Os−N(1)	170.3(2)	N(2)−Os−P	177.21(12)
C(1)−Os−N(1)	78.12(19)	C(7)−Os−Cl	96.48(17)
C(7)−Os−N(2)	92.62(19)	C(1)−Os−Cl	168.97(15)
C(1)−Os−N(2)	86.73(19)	N(1)−Os−Cl	92.75(12)
N(1)−Os−N(2)	84.95(16)	N(2)−Os−Cl	86.32(12)
C(7)−Os−P	89.63(15)	P−Os−Cl	91.80(5)
C(1)−Os−P	94.82(14)		

4′ positions of pyridine, which have to be separated by chromatography. The transition metal-mediated bromination described above, in which only one isomer is produced, suggests a potentially useful new methodology for the preparation of selectively substituted aromatic molecules.

Conclusion. The 2-(2′-pyridyl)phenyl ligand coordinates strongly to ruthenium or osmium in the complexes M(η^2-PyPh)Cl(CO)(PPh_3)$_2$ (**1a**, **1b**) by forming a five-membered chelate ring. The transition metal−carbon(phenyl) bonds in these complexes are relatively resistant to attack by electrophiles, and this enables electrophilic aromatic substitution reactions to be carried out effectively on the coordinated phenyl ring. The special activating/directing effects of the metal center enable derivatives with very unusual substitution patterns on the phenyl ring to be prepared. Finally, it is demonstrated that [PyrH][Br_3] has potential as a reagent for effecting the replacement of ligated triphenylphosphine by ligated pyridine.

Experimental Section

General Considerations. The general experimental and spectroscopic techniques employed in this work were the same as those described previously.[10] Mass spectra were recorded on a Varian VG 70-SE. IR spectra were recorded on a Perkin-Elmer 1000 FTIR spectrometer. NMR spectra were recorded on a Bruker DRX 400 spectrometer at 25 °C in $CDCl_3$ using 2D COSY, where appropriate to clarify proton assignments. Chemical shifts were referenced to Me_4Si (δ 0.00). Splitting patterns and line shapes are indicated as follows: s = singlet, d = doublet, t = triplet. RuHCl(CO)(PPh_3)$_3$,[11] OsHCl(CO)(PPh_3)$_3$,[12] and ($PyPh$)$_2$Hg[13] were prepared by literature methods.

Ru(η^2-PyPh)Cl(CO)(PPh_3)$_2$ (1a). RuHCl(CO)(PPh_3)$_3$ (500 mg) and ($PyPh$)$_2$Hg (450 mg) were combined in freeze−thaw−degassed toluene (20 mL) under a nitrogen atmosphere and heated under reflux for 6 h. The toluene was removed in vacuo, and the resulting paste dissolved in a small amount of dichloromethane. A few drops of dilute HCl were added, to decompose any residual mercury reagent. The HCl was removed by washing with water, and the dichloromethane solution was purified by chromatography on a short silica column (3 cm × 10 cm), using dichloromethane as eluant. The yellow band was collected. Ethanol was added to the solution and the volume reduced until crystallization occurred. Bright yellow microcrystals of pure **1a** were collected by filtration (380 mg, 86%). Anal. Calcd for $C_{48}H_{38}ClNOP_2Ru\cdot{}^1/_4CH_2Cl_2$: C, 67.03; H, 4.49; N, 1.62. Found: C, 67.21; H, 4.78; N, 1.97. ^{1}H NMR ($CDCl_3$): δ 7.05−7.30 (m, 31H, Ar*H*), 7.33 (d, $^3J_{HH}$ = 7.56 Hz, 1H, *H*3), 6.23 (t apparent, 2H, *H*4 and *H*5), 6.77 (d, $^3J_{HH}$ = 7.60 Hz, 1H, *H*6), 7.42 (d, $^3J_{HH}$ = 8.00 Hz, 1H, *H*3′), 6.61 (t apparent, 1H, *H*5′), 8.54 (d, $^3J_{HH}$ = 5.56 Hz, 1H, *H*6′) (H denotes phenyl ring, H′ denotes pyridyl ring).

Os(η^2-PyPh)Cl(CO)(PPh_3)$_2$ (1b). OsHCl(CO)(PPh_3)$_3$ (500 mg) and ($PyPh$)$_2$Hg (400 mg) were treated as in the preparation of **1a** above. Bright yellow microcrystals of pure **1b** were obtained (390 mg, 87%). Anal. Calcd for $C_{48}H_{38}ClNOOsP_2$: C, 61.83; H, 4.11; N, 1.50. Found: C, 61.28; H, 4.05; N, 1.57. ^{1}H NMR ($CDCl_3$): δ 7.05−7.36 (m, 30H, Ar*H*), 7.31 (d, $^3J_{HH}$ = 7.76 Hz, 1H, *H*3), 6.25 (t apparent, 1H, *H*4), 6.57 (t apparent, 1H, *H*5), 6.84 (d, $^3J_{HH}$ = 7.64 Hz, 1H, *H*6), 7.20 (m, 1H, *H*3′), 7.41 (t apparent, 1H, *H*4′), 6.17 (t apparent, 1H, *H*5′), 8.37 (d, $^3J_{HH}$ = 8.37 Hz, 1H, *H*6′).

Ru(η^2-PyPh)I(CO)(PPh_3)$_2$ (2a). To a solution of **1a** (100 mg) in dichloromethane (10 mL) was added $AgSbF_6$ (50 mg) dissolved in water (5 mL). Ethanol (5 mL) was added, and the solution was stirred for 10 min, after which time a large excess of NaI (0.5 g) in water (20 mL) was added. After a further 10 min of stirring, the organic phase was separated and filtered through paper. Ethanol was added to the filtrate, and the volume was reduced in vacuo until crystallization occurred. Bright yellow microcrystals of pure **2a** were collected by filtration (95 mg, 86%). Anal. Calcd for $C_{48}H_{38}INOP_2Ru\cdot{}^2/_3CH_2Cl_2$: C, 58.96; H, 4.00; N, 1.41. Found: C, 58.69; H, 3.87; N, 1.81.^{1}H NMR ($CDCl_3$): δ 7.00−7.35 (m, 32H, Ar*H*), 7.44 (d, $^3J_{HH}$ = 8.09 Hz, 1H, *H*3), 6.26 (t apparent, 1H, *H*4), 6.64 (t apparent, 1H, *H*5), 6.85 (d, $^3J_{HH}$ = 7.56 Hz, 1H, *H*6), 6.16 (t apparent, 1H, *H*5′), 8.77 (d, $^3J_{HH}$ = 5.78 Hz, 1H, *H*6′).

Os(η^2-PyPh)I(CO)(PPh_3)$_2$ (2b). 1b (100 mg) was treated as in the preparation of **2a** above. Bright yellow microcrystals of pure **2b** were obtained (80 mg, 73%). Anal. Calcd for $C_{48}H_{38}INOOsP_2$: C, 56.31; H, 3.74; N, 1.37. Found: C, 56.54; H, 3.69; N, 1.51. ^{1}H NMR ($CDCl_3$): δ 6.99−7.31 (m, 32H, Ar*H*), 7.43 (d, $^3J_{HH}$ = 8.08 Hz, 1H, *H*3), 6.25 (t apparent, 1H, *H*4), 6.59 (t apparent, 1H, *H*5), 6.90 (d, $^3J_{HH}$ = 7.64 Hz, 1H, *H*6), 6.07 (t apparent, 1H, *H*5′), 8.65 (d, $^3J_{HH}$ = 5.60 Hz, 1H, *H*6′).

[Ru(η^2-PyPh)(CO)$_2$(PPh_3)$_2$][SbF_6] (3a). To a solution of **1a** (100 mg) in dichloromethane (10 mL) was added $AgSbF_6$ (50 mg) dissolved in water (5 mL). Ethanol (5 mL) was added, and CO gas was slowly passed through the solution until it became colorless. The solution was washed with water, the organic phase separated and filtered through paper. Ethanol was added to the filtrate, and the volume was reduced in vacuo. The colorless crystals of **3a** that formed were collected by filtration (105 mg, 83%). MS, *m*/*z*: 836 (MI − SbF_6), 808 (MI − SbF_6 − CO). Anal. Calcd for $C_{49}H_{38}F_6NO_2P_2RuSb\cdot{}^1/_2CH_2Cl_2$: C, 53.37; H, 3.53; N, 1.26. Found: C, 53.59; H, 3.74; N, 1.50. ^{1}H NMR ($CDCl_3$): δ 6.98−7.37 (m, 31H, Ar*H*), 7.44 (d, $^3J_{HH}$ = 7.28 Hz, 1H, *H*3), 6.73 (t apparent, 1H, *H*5), 6.91 (d, $^3J_{HH}$ = 7.48 Hz, 1H, *H*6), 7.06 (d, $^3J_{HH}$ = 7.16 Hz, 1H, *H*3′), 7.51 (t apparent, 1H, *H*4′), 6.71 (t apparent, 1H, *H*5′), 7.87 (d, $^3J_{HH}$ = 5.56 Hz, 1H, *H*6′).

[Os(η^2-PyPh)(CO)$_2$(PPh_3)$_2$][SbF_6] (3b). 1b (100 mg) was treated as in the preparation of **3a** above. Colorless crystals of pure **3b** were obtained (110 mg, 88%). MS, *m*/*z*: 926 (MI − SbF_6), 898 (MI − SbF_6 − CO). Anal. Calcd for $C_{49}H_{38}F_6NO_2OsP_2Sb$: C, 50.70; H, 3.30; N, 1.21. Found: C, 50.81; H, 3.29; N, 130.^{1}H NMR ($CDCl_3$): δ 6.99−7.36 (m, 31H, Ar*H*), 7.48 (d, $^3J_{HH}$ = 7.68 Hz, 1H, *H*3), 6.69 (t apparent, 1H, *H*5), 6.89 (d, $^3J_{HH}$ = 6.94 Hz, 1H, *H*6), 7.41 (d, $^3J_{HH}$ = 8.20 Hz, 1H, *H*3′), 7.57 (t apparent, 1H, *H*4′), 6.62 (t apparent, 1H, *H*5′), 7.80 (d, $^3J_{HH}$ = 5.60 Hz, 1H, *H*6′).

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Ru(η^2-PyPh)(η^2-S_2CNMe_2)(CO)(PPh_3) (4a). To a solution of **1a** (100 mg) in dichloromethane (10 mL) was added $AgSbF_6$ (50 mg) dissolved in water (5 mL). Ethanol (5 mL) was added, and the solution was stirred for 10 min. After this time water (50 mL) was added and the organic phase separated and filtered through paper. To the filtrate was added a solution of NaS_2CNMe_2 (50 mg) dissolved in a mixture of water (5 mL) and ethanol (5 mL). The solution was stirred for a further 10 min, the organic phase washed with water, separated, and filtered through paper. The resulting yellow filtrate was heated gently for several minutes, then ethanol was added. Reduction of the solvent volume in vacuo gave yellow microcrystals of pure **4a** (60 mg, 76%). Anal. Calcd for $C_{33}H_{29}N_2OPRuS_2$: C, 59.53; H, 4.39; N, 4.21. Found: C, 59.25; H, 4.22; N, 4.25. ^{1}H NMR ($CDCl_3$): δ 7.10−7.23 (m, 15H, Ar*H*), 7.84 (m, 1H, *H*3), 6.82 (t apparent, 2H, *H*4 and *H*5), 7.53 (m, 1H, *H*6), 7.60 (d, $^3J_{HH}$ = 8.12 Hz, 1H, *H*3′), 7.48 (t apparent, 1H, *H*4′), 6.64 (t apparent, 1H, *H*5′), 8.57 (d, $^3J_{HH}$ = 5.32 Hz, 1H, *H*6′), 3.33 (s, 3H, N*Me*), 3.12 (s, 3H, N*Me*).

Os(η^2-PyPh)(η^2-S_2CNMe_2)(CO)(PPh_3) (4b). 1b (100 mg) was treated as in the preparation of **4a** above. Since loss of the phosphine ligand was less facile, the final yellow dichloromethane solution was heated under reflux for 10 min, then ethanol was added. Reduction of volume in vacuo gave yellow microcrystals of pure **4b** (65 mg, 80%). Anal. Calcd for $C_{33}H_{29}N_2OOsPS_2$: C, 52.50; H, 3.87; N, 3.71. Found: C, 52.78; H, 4.06; N, 3.47.^{1}H NMR ($CDCl_3$): δ 7.10−7.23 (m, 15H, Ar*H*), 7.88 (d, $^3J_{HH}$ = 7.32 Hz 1H, *H*3), 6.79 (t apparent, 2H, *H*4 and *H*5), 7.53 (d, $^3J_{HH}$ = 7.32 Hz, 1H, *H*6), 7.63 (d, $^3J_{HH}$ = 8.04 Hz, 1H, *H*3′), 7.46 (t apparent, 1H, *H*4′), 6.59 (t apparent, 1H, *H*5′), 8.45 (d, $^3J_{HH}$ = 5.40 Hz, 1H, *H*6′), 3.25 (s, 3H, N*Me*), 3.02 (s, 3H, N*Me*).

Ru(η^2-PyPh-(4,6-$(NO_2)_2$)Cl(CO)(PPh_3)$_2$ (5a). To **1a** (100 mg) was added acetic anhydride (2.5 mL) and $Cu(NO_3)_2{\cdot}xH_2O$ (100 mg) in an ice bath. The mixture was stirred for 1 h, during which time it was slowly allowed to warm to room temperature and a deep green color developed. A solution of NaOAc (500 mg) in water (20 mL) was added, and the solution was stirred until the product coagulated. The solution was filtered, and the resulting sticky oil that was collected was dissolved in dichloromethane and purified by chromatography on a short (10 cm × 3 cm) column of silica gel using dichloromethane as eluant. The first bright yellow band was collected, and crystals of pure **5a** were obtained by adding ethanol and reducing the volume in vacuo (20 mg, 18%). Anal. Calcd for $C_{48}H_{36}ClN_3O_5P_2Ru{\cdot}2CH_2Cl_2$: C, 54.44; H, 3.65; N, 3.81. Found: C, 54.69; H, 3.74; N, 3.88. ^{1}H NMR ($CDCl_3$): δ 7.07−7.25 (m, 30H, Ar*H*), 7.63 (d, $^3J_{HH}$ = 2.12 Hz, 1H, *H*3), 8.22 (d, $^3J_{HH}$ = 2.24 Hz, 1H, *H*5), 7.72 (d, $^3J_{HH}$ = 7.68 Hz, 1H, *H*3′), 7.57 (t apparent, 1H, *H*4′), 6.49 (t apparent, 1H, *H*5′), 8.50 (d, $^3J_{HH}$ = 5.08 Hz, 1H, *H*6′).

Os(η^2-PyPh-(4,6-$(NO_2)_2$)Cl(CO)(PPh_3)$_2$ (5b). To **1a** (100 mg) was added acetic anhydride (5 mL) and $Cu(NO_3)_2{\cdot}xH_2O$ (150 mg). The mixture was stirred for 1 h, during which time a deep green color developed. A solution of NaOAc (500 mg) in water (20 mL) was added, and the solution was stirred until the product coagulated. The solution was filtered, and the resulting sticky oil that was collected was dissolved in dichloromethane and purified by chromatography on a short (10 cm × 3 cm) column of silica gel using dichloromethane as eluant. The light orange band eluting first was collected. Light orange microcrystals of pure **5b** were obtained by adding hexane and reducing the volume in vacuo (40 mg, 36%). Anal. Calcd for $C_{30}H_{21}ClN_3O_5OsP{\cdot}CH_2Cl_2$: C, 53.15; H, 3.46; N, 3.79. Found: C, 52.88; H, 3.43; N, 3.67. ^{1}H NMR ($CDCl_3$): δ 7.08−7.32 (m, 30H, Ar*H*), 7.60 (d, $^3J_{HH}$ = 2.32 Hz, 1H, *H*3), 8.29 (d, $^3J_{HH}$ = 2.28 Hz, 1H, *H*5), 7.72 (d, $^3J_{HH}$ = 8.04 Hz, 1H, *H*3′), 7.51 (t apparent, 1H, *H*4′), 6.42 (t apparent, 1H, *H*5′), 8.35 (d, $^3J_{HH}$ = 5.44 Hz, 1H, *H*6′).

Os(η^2-PyPh-4-NO_2)Cl(CO)(PPh_3)$_2$ (5c). Acetic anhydride (2.5 mL) was added to $Cu(NO_3)_2{\cdot}xH_2O$ (50 mg), and the solution was allowed to stir for 10 min at room temperature. **1a** (50 mg) was added, followed after 5 min by sodium acetate (200 mg) in water (10 mL). The resulting mixture was stirred until the solid product had coagulated. This was then removed by filtration and then dissolved in dichloromethane. The resulting solution was then purified by chromatography on a 20 cm × 3 cm column of silica gel using dichloromethane as eluant. The light orange band was collected, heptane added, and the volume reduced in vacuo to obtain pure **5a** as a yellow powder (5 mg, 10%). Anal. Calcd for $C_{48}H_{37}ClN_2O_3OsP_2{\cdot}{}^1/_3CH_2Cl_2$: C, 57.72; H, 3.77; N, 2.79. Found: C, 57.62; H, 3.86; N, 2.75. ^{1}H NMR ($CDCl_3$): δ 7.00−7.32 (m, 30H, Ar*H*), 8.16 (s, 1H, *H*3), 7.63 (d, $^3J_{HH}$ = 7.81 Hz, 1H, *H*5), 7.00 (m, 1H, *H*6), 7.42 (d, $^3J_{HH}$ = 7.71 Hz, 1H, *H*3′), 7.20 (m, 1H, *H*4′), 6.35 (t apparent, 1H, *H*5′), 8.40 (d, $^3J_{HH}$ = 4.90 Hz, 1H, *H*6′).

Ru(η^2-PyPh-4-Br)Cl(CO)(PPh_3)$_2$ (6a). 1a (200 mg) was dissolved in dichloromethane (50 mL), to which was added 1 equiv of [PyrH][Br_3] (76 mg) in methanol (5 mL). A catalytic quantity of iron powder (1 mg) was added, and the mixture stirred for 1 h. The solution was washed with water, and a solution of $AgSbF_6$ (100 mg) in water (10 mL) was added, followed by ethanol (10 mL). After stirring for 10 min, NaCl (1.0 g) in water (50 mL) was added, and the mixture stirred for a further 10 min. The organic layer was separated and filtered through paper, then concentrated by reduction of the solvent volume in vacuo. The resulting solution was then purified by chromatography on a short silica column (10 cm × 3 cm) using dichloromethane as the eluant. The first yellow band was collected. Heptane was added and the volume reduced in vacuo. The resulting yellow crystals of **6a** were collected by filtration (150 mg, 69%). Anal. Calcd for $C_{48}H_{37}BrClNOP_2Ru{\cdot}{}^1/_4CH_2Cl_2$: C, 61.43; H, 4.01; N, 1.48. Found: C, 61.78; H, 3.81; N, 1.57. ^{1}H NMR ($CDCl_3$): δ 7.07−7.32 (m, 31H, Ar*H*), 7.45 (d, $^3J_{HH}$ = 2.12 Hz, 1H, *H*3), 6.28 (dd, J_{HH} = 8.28, 2.12 Hz, 1H, *H*5), 6.52 (d, $^3J_{HH}$ = 8.28 Hz, 1H, *H*6), 7.39 (d, $^3J_{HH}$ = 7.96 Hz, 1H, *H*3′), 6.32 (t apparent, 1H, *H*5′), 8.62 (d, $^3J_{HH}$ = 5.24 Hz, 1H, *H*6′).

Os(η^2-PyPh-4-Br)Cl(CO)(PPh_3)$_2$ (6b). 1b (200 mg) was treated as in the preparation of **6a** above, using 1 equiv of [PyrH][Br_3] (69 mg). The first yellow band from the column was collected. Heptane was added and the volume reduced in vacuo until pure **6b** crystallized as a yellow solid (170 mg, 78%). Anal. Calcd for $C_{48}H_{37}BrClNOOsP_2{\cdot}{}^1/_4CH_2Cl_2$: C, 56.13; H, 3.66; N, 1.36. Found: C, 56.29; H, 3.67; N, 1.56. ^{1}H NMR ($CDCl_3$): δ 7.07−7.30 (m, 31H, Ar*H*), 7.43 (d, $^3J_{HH}$ = 2.08 Hz, 1H, *H*3), 6.30 (dd, J_{HH} = 8.28, 2.08 Hz, 1H, *H*5), 6.61 (d, $^3J_{HH}$ = 8.28 Hz, 1H, *H*6), 7.38 (d, $^3J_{HH}$ = 7.96 Hz, 1H, *H*3′), 6.25 (t apparent, 1H, *H*5′), 8.44 (d, $^3J_{HH}$ = 5.72 Hz, 1H, *H*6′).

Os(η^2-PyPh-4-Br)Cl(CO)(Pyr)(PPh_3) (6c). 1b was treated as in the preparation of **6b** above except that 2 equiv of [PyrH][Br_3] (138 mg) was used and the mixture was stirred for 16 h. The product was worked up as described above. Upon purification by column chromatography, a small amount of **6b** eluted first, followed by a darker band. This darker band was collected, heptane added, and the solvent volume reduced in vacuo to give pure **6c** as a yellow solid (55 mg, 31%). Anal. Calcd for $C_{35}H_{27}BrClN_2OOsP{\cdot}{}^1/_2C_7H_{16}$: C, 52.71; H, 3.91; N, 3.19. Found: C, 52.68; H, 3.87; N, 2.91. ^{1}H NMR ($CDCl_3$): δ 7.11−7.39 (m, 16H, Ar*H*), 6.77 (m, 1H, *H*5), 7.30 (m, 1H, *H*6), 7.20 (m, 1H, *H*3′), 7.57 (t apparent, 1H, *H*4′), 6.79 (t apparent, 1H, *H*5′), 9.05 (d, $^3J_{HH}$ = 5.68 Hz, 1H, *H*6′), 7.53 (d, $^3J_{HH}$ = 6.08 Hz, 2H, *H*2″), 7.00 (t apparent, 2H, *H*3″), 8.56 (m, 1H, *H*4″).

Os(η^2-PyPh-4-CO_2H)Cl(CO)(PPh_3)$_2$ (7a). 6b (100 mg) was dissolved in dry, deoxygenated tetrahydrofuran (20 mL) under an atmosphere of nitrogen and cooled to 0 °C. BuLi in hexanes (2 equiv, 0.116 mL 1.7 mol L^{-1}) was added dropwise, and the mixture stirred for 10 min. A stream of CO_2 was passed through the solution for several minutes, after which time the solvent was removed entirely in vacuo. The resulting paste was dissolved in ethanol (10 mL) and water (2 mL) and a small

pellet of NaOH added. The resulting solution was filtered, and several drops of diluted HCl added to the filtrate until it was slightly acidic. The solvent volume was reduced in vacuo, to give a yellow solid, which was isolated by filtration. The solid was recrystallized from dichloromethane, ethanol, and water to give pure **7a** (25 mg, 26%). MS, *m*/*z*: 977 (MI), 942 (MI − Cl). Anal. Calcd for $C_{49}H_{38}ClNO_3OsP_2.^2/_3CH_2Cl_2$: C, 57.75; H, 3.84; N, 1.36. Found: C, 57.71; H, 4.36; N, 1.35. ^{1}H NMR ($CDCl_3$): δ 7.09−7.27 (m, 31H, Ar*H*), 8.04 (s, 1H, *H*3), 6.88 (d, $^3J_{HH}$ = 8.00 Hz, 1H, *H*5), 7.02 (d, $^3J_{HH}$ = 8.12 Hz, 1H, *H*6) 7.60 (d, $^3J_{HH}$ = 7.96 Hz, 1H, *H*3′), 6.27 (t apparent, 1H, *H*5′), 8.40 (d, $^3J_{HH}$ = 4.28 Hz, 1H, *H*6′), CO_2H not located.

Os(η^2-PyPh-4-SnBu$_3$)Cl(CO)(PPh$_3$)$_2$ (7b). 6b (200 mg) was dissolved in dry, deoxygenated tetrahydrofuran (30 mL) under an atmosphere of nitrogen and cooled to 0 °C. BuLi in hexanes (2 equiv, 0.232 mL, 1.7 mol L^{-1}) was added dropwise, and the mixture stirred for 10 min. An excess of Bu_3SnCl (0.4 mL) was added, and the mixture stirred for 10 min, after which time the solvent was removed in vacuo. The resulting paste was dissolved in dichloromethane and filtered through paper. Ethanol was added to the filtrate and the solvent volume reduced in vacuo, to give pure **7b** as a waxy yellow solid (110 mg, 46%). Anal. Calcd for $C_{60}H_{64}ClNOOsP_2Sn\cdot^1/_3CH_2Cl_2$: C, 57.98; H, 5.22; N, 1.12. Found: C, 58.04; H, 5.29; N, 1.57. ^{1}H NMR ($CDCl_3$): δ 7.04−7.30 (m, 31H, Ar*H*), 7.34 (m, 1H, *H*3), 6.24 (m, 1H, *H*5), 6.70 (d, $^3J_{HH}$ = 7.44 Hz, 1H, *H*6) 7.42 (d, $^3J_{HH}$ = 8.04 Hz, 1H, *H*3′), 6.19 (t apparent, 1H, *H*5′), 8.41 (d, $^3J_{HH}$ = 5.28 Hz, 1H, *H*6′), 0.99 (m, 6H, CH_2), 1.36 (m, 6H, CH_2), 1.55 (m, 6H, CH_2), 0.93 (t apparent, 9H, CH_3).

2′-(3-Bromophenyl)pyridine (8). 6a (100 mg) was dissolved in toluene (20 mL), and concentrated HCl (1 mL) was added. The solution was heated under reflux while exposed to air, for 16 h, after which time water (50 mL) was added and the aqueous layer separated. To this solution was then added NaOH (5.0 g) dissolved in water (100 mL). The cloudy solution was then stirred with dichloromethane (50 mL) and ethanol (1 mL) for 1 h, after which time the cloudiness had disappeared. The organic layer was separated and filtered through paper, and the volume reduced in vacuo until only **8**, as a viscous oil, remained (7 mg, 25%). MS, *m*/*z*: 233, 235 (MI), 154 (MI − Br); high resolution, 232.98484, 234.98104 (requires 232.98401, 234.98196). ^{1}H NMR: δ 8.16 (s, 1H, *H*2), 7.90 (d, $^3J_{HH}$ = 7.72 Hz, 1H, *H*4), 7.33 (t apparent, 1H, *H*5), 7.53 (d, $^3J_{HH}$ = 7.76 Hz, 1H, *H*6), 7.69 (d, $^3J_{HH}$ = 7.92 Hz, 1H, *H*3′), 7.76 (t apparent, 1H, *H*4′), 7.26 (dd, $^3J_{HH}$ = 8.69, 4.72 Hz, 1H, *H*5′), 8.69 (d, $^3J_{HH}$ = 4.72 Hz, 1H, *H*6′) ppm. ^{13}C NMR: δ, 155.78, 141.25, 123.04 (C1, C3, C2′); 149.68, 137.01, 131.89, 130.25, 130.02, 125.41, 122.69, 120.65 ppm (C2, C4−6, C3′-6′) (C denotes phenyl ring, C′ denotes pyridyl ring).

X-ray Crystallography. The crystal data, data collection, and refinement parameters for the five structures are listed in Table 2.

All measurements were made on a Siemens SMART diffractometer using graphite-monochromated Mo Kα radiation, λ = 0.71073 Å. Data collection covered a nominal sphere (hemisphere for monoclinic) of reciprocal space by a series of four (three) sets of exposures each covering 0.3° in ω. Crystal decay was monitored by repeating the initial frames at the end of the data collection and analyzing duplicate reflections. Unit cell parameters were obtained by least-squares fit to all data with $I > 10\sigma(I)$. Lorentz and polarization corrections were applied and absorption corrections by analyzing equivalent reflections.[14]

The structures were solved by Patterson and difference Fourier methods using SHELXS-97[15] and refined on F^2 using all data by full-matrix least squares with the program SHELXL-97.[16] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions with thermal parameter 20% greater than the carrier atom. In **3b** there is a half molecule of dichloromethane solvent, and in **6c** there is a molecule of chloroform.

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Supporting Information Available: Tables of crystal data, collection and refinement parameters, positional and anisotropic displacement parameters, and bond distances and angles for **3b**, **4b**, **5c**, **6b**, and **6c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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