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Ligand-assisted *O*-dealkylation of bis(bipyridyl) ruthenium(II) phosphine-ether complexes †

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The preparation and characterization of three $[Ru(bpy)_2(POR\text{-}P,O)](PF_6)_2$ complexes are reported where POR = 2-methoxyphenyldiphenylphosphine in **1**, 2-ethoxyphenyldiphenylphosphine in **2** and 2-methoxyethyldiphenylphosphine in **3**. Complexes **1** and **2** undergo ligand-assisted *O*-dealkylation by the same weakly basic phosphines, a reaction typically observed for complexes containing highly basic phosphines with multiple ether substituents. The electron deficiency of the Ru(II) centre in these complexes is likely responsible for how readily they are dealkylated to yield the aryloxide complexes. Complex **3** is not susceptible to ligand-assisted dealkylation, primarily because the lower steric demand of its phosphine-ether ligand permits the thermodynamically favoured direct attack of phosphines at the Ru centre.

Introduction

Ruthenium bis(bipyridyl) complexes that contain hemilabile phosphine-ether ligands are of interest for the purpose of developing new types of molecule-based chemical sensors.[1] In the course of our investigations into this class of complexes, we observed that the ruthenium-bound ether in $[Ru(bpy)_2(POMe\text{-}P,O)]^{2+}$ **1** (POMe = 2-methoxyphenyldiphenylphosphine) is susceptible to *O*-demethylation in the presence of free POMe. In general, *O*-dealkylation of both free and metal-coordinated ethers can be accomplished by a variety of reagents, commonly through the action of alkali metals, organometallic reagents, and strong Lewis or Brönsted acids.[2] C–O bond activation by transition metal complexes has recently been reviewed;[3] a recent example from the literature describes metal-specific regioselectivity in aryl–alkyl ether cleavage.[4] Metal-mediated ether cleavage is an important class of reactions that is relevant to diverse fields of study, ranging from understanding metabolic processes in biological systems (*e.g.*, P450 enzymes),[5] to designing catalysts for the hydrocracking of coal and oil,[6] to interfering with the photoyellowing of paper.[7,8]

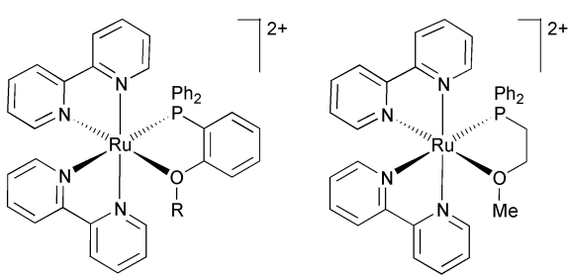
A considerable number of transition metal complexes have been reported using the family of triphenylphosphine derivatives with *ortho*-methoxy substituents.[9–12] Those containing multiple methoxy groups are highly basic and nucleophilic, with the basicity increasing with the degree of ether substitution: triphenylphosphine ($pK_a = 2.73$) < (2,6-dimethoxyphenyl)diphenylphosphine (MDMPP) ($pK_a = 5.39$) < bis(2,6-dimethoxyphenyl)phenylphosphine (BDMPP) ($pK_a = 7.28$) < tris(2,4,6-trimethoxyphenyl)phosphine (TMPP) ($pK_a = 11.02$).[13,14] These phosphine-ether ligands typically dealkylate when reacted with metal halides to form σ-bonded aryloxide complexes.[9,14–16] However, a variety of ether complexes has also been prepared with these ligands, and in some cases, ligand-assisted *O*-dealkylation has been observed.[11,17–21] Such *ligand-assisted* dealkylations proceed *via* nucleophilic attack by the free ligand's phosphorus to produce the stable alkylphosphonium salt, which drives the reaction. For example, (Cp*)RhCl(MDMPP),[16] Pt and Pd BDMPP methylallyl complexes,[17] and Pt and Pd TMPP complexes[11] are all known to demethylate in the presence of excess phosphine-ether; however, we have not encountered reports of similar dealkylations on Ru(II).

Although Pt and Pd halide complexes bearing phosphine-ether ligands such as POMe have been observed to dealkylate *via* loss of MeX,[22] to the best of our knowledge there are no other examples of ligand-assisted *O*-dealkylation of complexes containing phosphine-ether ligands with only one ether substituent. This type of dealkylation reaction provides an alternate route to linked phosphine-aryloxide complexes from readily prepared phosphine-ether complexes, which may be convenient for syntheses where use of a phosphine-phenol or -phenolate directly is undesirable. In this context, we set out to investigate the occurrence of ligand-assisted dealkylation in a set of $[Ru(bpy)_2(POR\text{-}P,O)]^{2+}$ complexes that contain phosphines with only one ether substituent.

Results and discussion

Synthesis and structural characterization of 1–3

The ruthenium complexes **1**–**3** were prepared by reacting



1 R = Me
2 R = Et

3

$[Ru(bpy)_2(Me_2CO)_2]^{2+}$ with one equivalent of the desired phosphine-ether ligand in acetone solution heated to 56 °C. Crystals of **1**–**3** suitable for X-ray crystallographic analysis were

† Electronic supplementary information (ESI) available: NMR data for reactions of **1**–**3** with POR, and descriptions of the syntheses of the Me and Et phosphonium salts of POMe, POEt and PC2OMe. See http://www.rsc.org/suppdata/dt/b0/b0089311/

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Table 1 Crystallographic data, collection and refinement details for complexes **1**, **2** and **3**

	1	**2**	**3**
Formula	$C_{39}H_{33}F_{12}N_4OP_3Ru$	$C_{40}H_{35}F_{12}N_4OP_3Ru$	$C_{35}H_{33}F_{12}N_4OP_3Ru$
M	995.69	1009.71	947.64
μ/cm^{-1}	6.00	5.77	6.41
T/K	173(1)	173(1)	173(1)
Colour, habit	Red, block	Orange, needle	Red, prism
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/n$ (no. 14)	$Pna2_1$ (no. 33)	$P2_12_12_1$ (no. 19)
a/Å	12.0656(4)	29.844(1)	13.2591(4)
b/Å	20.2301(5)	10.7577(6)	14.2123(5)
c/Å	16.9836(6)	26.255(1)	19.930(1)
β/°	102.651(2)	90	90
V/Å^3	4044.9(2)	8429(1)	3755.7(2)
Z	4	8	4
Refl. collected/unique/R_{int}	33540/8759/0.038	35277/12548/0.115	32001/8135/0.059
R_1 [c]	0.031 [a]	0.055 [b]	0.048 [a]
wR_2 [c]	0.086	0.118	0.119

[a] $I > 3\sigma(I)$. [b] $I > 2\sigma(I)$. [c] $R_1 = \Sigma||F_o| - ||F_c||/\Sigma|F_o|$ (observed data); $wR_2 = (\Sigma(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2)^{\frac{1}{2}}$ (all data).

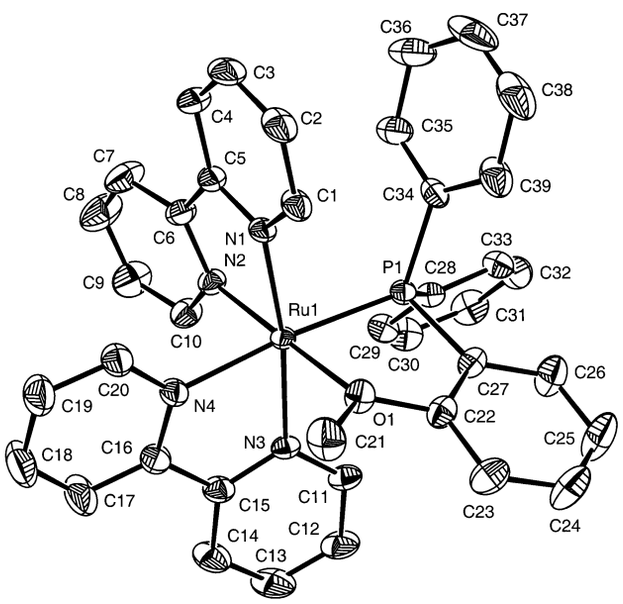


Fig. 1 ORTEP representation of the solid state molecular structure of $[Ru(bpy)_2(POMe\text{-}P,O)](PF_6)_2$ **1**. Hydrogen atoms and hexafluorophosphate ions are omitted for clarity.

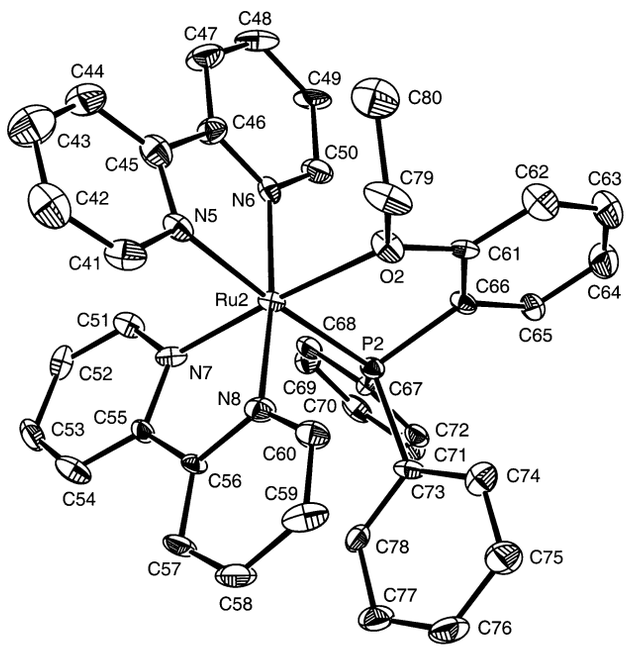
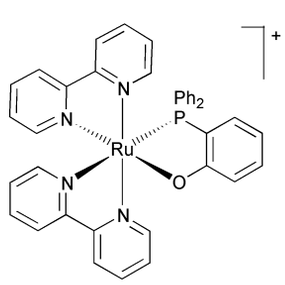


Fig. 2 ORTEP representations of the solid state molecular structure of $[Ru(bpy)_2(POEt\text{-}P,O)](PF_6)_2$ **2**. Note that there are two inequivalent salt moieties in the asymmetric unit but only one cationic unit, containing Ru(2) as listed in Table 3, is depicted here. Hydrogen atoms and hexafluorophosphate ions are omitted for clarity.

grown from methanol; crystallographic data are provided in Table 1. In the solid state, the POMe ligand in **1** is bound in a bidentate fashion (Fig. 1), which matches the solution structure determined from NMR spectroscopic studies.[1] The solid state molecular structures of **2** and **3** are similar and are shown in Figs. 2 and 3, respectively. The geometry of these complexes is distorted octahedral. Relevant bond lengths and angles in these complexes are listed in Tables 2, 3 and 4. The Ru–O bond lengths of 2.172(2) Å for **1**, 2.199(6) Å and 2.200(6) Å for **2**, and 2.174(3) Å for **3** are shorter than those in $RuCl_2(POR)_2$ complexes containing the same phosphine-ether ligands (2.299 and 2.257 Å in the POMe complex, 2.262 and 2.265 Å in the 2-methoxyethyldiphenylphosphine (PC2OMe) complex);[9,23,24] in fact, they are closer to the Ru–O distance (2.143 Å) observed in an Ru(III) ester complex.[25] These relatively short Ru–O distances are consistent with the observation that complexes **1**–**3** show diminished reactivity with respect to ether substitution by nucleophilic small molecules (*e.g.*, acetonitrile, DMSO, CO)[1] compared to other Ru(II) phosphine-ether complexes.[9,10,26] The Ru–P bond lengths of 2.2908(6) Å in **1**, 2.289(2) Å and 2.277(2) Å in **2**, and 2.286(2) Å in **3** are somewhat longer than those in the corresponding $RuCl_2(POR)_2$ complexes (≈2.218 Å).[23,24]

Studies of dealkylation of 1–3

In the synthesis of complex **1**, it was observed that when an excess of the phosphine-ether ligand is used, dealkylation of the ether group occurs as a side reaction to yield the monocationic Ru(II) aryloxide complex **4**. A second phosphorus-containing product forms concurrently, and is identified as $[Me(POMe)]^+$ by comparison to the ^1H and ^{31}P NMR spectra of an authentic sample of [Me(POMe)]I. The presence of the phosphonium



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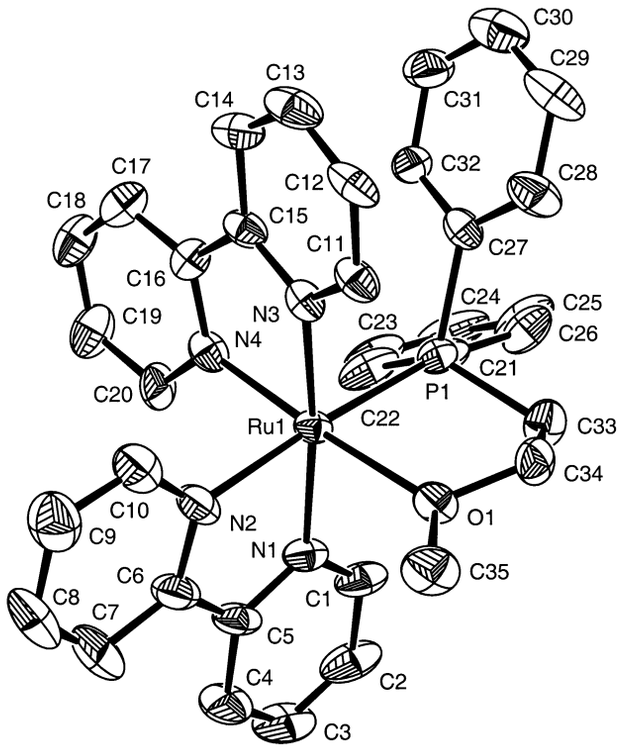
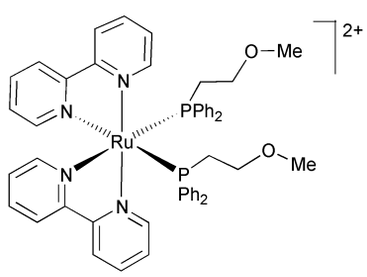


Fig. 3 ORTEP representation of the solid state molecular structure of $[Ru(bpy)_2(PC2OMe\text{-}P,O)](PF_6)_2$ **3**. Hydrogen atoms and hexafluorophosphate ions are omitted for clarity.

salt suggests that the side reaction proceeds *via* nucleophilic attack of the free ligand's phosphorus on the carbon of the Ru-bound methoxy group.

We became interested in discovering which factors are important in determining whether such a ligand-assisted dealkylation reaction occurs. To this end, we prepared complexes **2** and **3**, which contain modified phosphine-ether ligands. Increasing the electron-donating ability of the ether R group should lead to decreased electrophilicity of the carbon α to the Ru-bound oxygen, and therefore, decreased dealkylation by free ligand. Indeed, changing the ether R group to Et sufficiently alters the electronic environment of the α-carbon that performing the synthesis of the complex $Ru(POEt\text{-}P,O)^{2+}$ **2**, with 2 equivalents of 2-ethoxyphenyldiphenylphosphine (POEt), does not result in dealkylation. Modification of the ligand framework to include an alkyl linker between the phosphorus and oxygen in place of the phenylene bridge also reduces the occurrence of ligand-assisted *O*-dealkylation. Specifically, reacting $[Ru(bpy)_2(Me_2CO)_2]^{2+}$ with 2 equivalents of the less sterically demanding phosphine PC2OMe in acetone at 56 °C leads to formation of the bisphosphine complex $Ru(PC2OMe\text{-}P)_2^{2+}$ **5**, rather than the alkoxide complex that would arise from *O*-dealkylation of **3**.



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In order to compare α-carbon electrophilicity in the complexes, **1**–**3** were each treated with free POMe in acetone at 56 °C for 18 h. For **1**, an orange-to-dark brown colour change occurs within 2 h, and the ^{31}P NMR spectrum of the crude reaction mixture shows the presence of the aryloxide complex **4**, $[Me(POMe)]^+$ and small amounts of unreacted **1** and POMe. The reaction mixtures containing **2** and **3** change colour more slowly, requiring several hours, and exhibit more complicated ^{31}P NMR spectra. Analysis of the ^{31}P NMR spectrum shows that free POEt, **1** and $[Me(POMe)]^+$ are present in the **2** + POMe reaction mixture, along with aryloxide **4**, $[Et(POMe)]^+$, and a small amount of unreacted **2**. No unreacted POMe remains. From this it can be concluded that **2** undergoes two reactions with POMe: primarily *O*-dealkylation by POMe, but also ligand exchange with POMe to form **1**, which is then dealkylated by free POMe.

The ^{31}P NMR spectrum of the **3** + POMe reaction mixture shows mainly unreacted **3**, as well as some bisphosphine complex **5** and small amounts of the products of dealkylation of **1** by POMe. Two other small peaks are likely due to the bisphosphine complex $[Ru(PC2OMe\text{-}P)(POMe\text{-}P)]^{2+}$, based on the similarity of the ^{31}P chemical shifts (δ 24.4, 24.2) to that of $[Ru(PC2OMe\text{-}P)_2]^{2+}$ (δ 22.3); however, this complex has not been isolated. In summary, the dominant reaction of **3** with POMe is ligand exchange to release free PC2OMe, which reacts by ether displacement with **3** to form the bisphosphine complex. Based on the increase in phosphine size involved

Table 2 Selected bond distances (Å) and angles (°) for **1**

Ru(1)–O(1)	2.171(2)	Ru(1)–P(1)	2.2908(6)
Ru(1)–N(1)	2.050(2)	Ru(1)–N(2)	2.030(2)
Ru(1)–N(3)	2.095(2)	Ru(1)–N(4)	2.112(2)
O(1)–C(21)	1.441(3)	O(1)–C(22)	1.395(3)
P(1)–Ru(1)–O(1)	80.14(4)	P(1)–Ru(1)–N(1)	89.85(5)
P(1)–Ru(1)–N(2)	101.89(6)	P(1)–Ru(1)–N(3)	98.76(5)
O(1)–Ru(1)–N(1)	96.68(7)	O(1)–Ru(1)–N(3)	85.70(6)
O(1)–Ru(1)–N(4)	95.23(7)	N(1)–Ru(1)–N(2)	79.04(7)
N(1)–Ru(1)–N(4)	93.84(7)	N(2)–Ru(1)–N(3)	98.21(7)
N(2)–Ru(1)–N(4)	82.97(8)	N(4)–Ru(1)–N(3)	77.63(7)

Table 3 Selected bond distances (Å) and angles (°) for **2**

Ru(1)–O(1)	2.199(6)	Ru(1)–P(1)	2.289(2)
Ru(1)–N(1)	2.126(6)	Ru(1)–N(2)	2.082(7)
Ru(1)–N(3)	2.018(7)	Ru(1)–N(4)	2.064(7)
O(1)–C(21)	1.403(10)	O(1)–C(39)	1.482(11)
Ru(2)–O(2)	2.200(6)	Ru(2)–P(2)	2.277(2)
Ru(2)–N(5)	2.109(6)	Ru(2)–N(6)	2.092(7)
Ru(2)–N(7)	2.012(7)	Ru(2)–N(8)	2.064(7)
O(2)–C(61)	1.419(10)	O(2)–C(79)	1.460(11)
P(1)–Ru(1)–O(1)	79.48(17)	P(1)–Ru(1)–N(2)	98.25(19)
P(1)–Ru(1)–N(3)	100.7(2)	P(1)–Ru(1)–N(4)	89.0(2)
O(1)–Ru(1)–N(1)	95.5(2)	O(1)–Ru(1)–N(2)	84.3(2)
O(1)–Ru(1)–N(4)	97.9(3)	N(1)–Ru(1)–N(2)	77.7(3)
N(1)–Ru(1)–N(3)	84.5(3)	N(1)–Ru(1)–N(4)	95.2(3)
N(2)–Ru(1)–N(3)	98.8(3)	N(3)–Ru(1)–N(4)	78.8(3)
P(2)–Ru(2)–O(2)	79.41(17)	P(2)–Ru(2)–N(6)	99.0(2)
P(2)–Ru(2)–N(7)	99.6(2)	P(2)–Ru(2)–N(8)	89.3(2)
O(2)–Ru(2)–N(5)	97.4(2)	O(2)–Ru(2)–N(6)	84.9(2)
O(2)–Ru(2)–N(8)	96.7(3)	N(5)–Ru(2)–N(6)	77.7(3)
N(5)–Ru(2)–N(7)	83.8(3)	N(5)–Ru(2)–N(8)	94.0(3)
N(6)–Ru(2)–N(7)	99.1(3)	N(7)–Ru(2)–N(8)	79.4(3)

Table 4 Selected bond distances (Å) and angles (°) for **3**

Ru(1)–O(1)	2.174(3)	Ru(1)–P(1)	2.286(2)
Ru(1)–N(1)	2.098(4)	Ru(1)–N(2)	2.118(4)
Ru(1)–N(3)	2.055(4)	Ru(1)–N(4)	2.029(5)
O(1)–C(34)	1.434(6)	O(1)–C(35)	1.405(7)
P(1)–Ru(1)–O(1)	81.4(1)	P(1)–Ru(1)–N(1)	99.5(1)
P(1)–Ru(1)–N(3)	88.2(1)	P(1)–Ru(1)–N(4)	96.7(1)
O(1)–Ru(1)–N(1)	83.3(1)	O(1)–Ru(1)–N(2)	95.3(2)
O(1)–Ru(1)–N(3)	98.0(2)	N(1)–Ru(1)–N(2)	77.8(2)
N(1)–Ru(1)–N(4)	99.9(2)	N(2)–Ru(1)–N(3)	94.5(2)

Table 5 Summarized results of reactions[a] of Ru(POR) with free POR as determined from ^{31}P NMR spectra[b]

	POMe	POEt	PC2OMe
Ru(POMe) **1**	Dealkylation of Ru(POMe) by POMe	Dealkylation of Ru(POMe) by POMe and POEt Ligand exchange to form Ru(POEt)	Ligand exchange to form Ru(PC2OMe)[c] $Ru(PC2OMe)_2$ formation Dealkylation of Ru(POMe) by POMe and PC2OMe
Ru(POEt) **2**	Ligand exchange to form Ru(POMe) Dealkylation of Ru(POMe) by POEt and POMe	Mostly no reaction Dealkylation of Ru(POEt) by POEt (trace)	Mostly no reaction Ligand exchange to form Ru(PC2OMe) $Ru(PC2OMe)_2$ formation
Ru(PC2OMe) **3**	Mostly no reaction Ligand exchange to form Ru(POMe) (trace) Dealkylation of Ru(POMe) by POMe $Ru(PC2OMe)_2$ formation	Mostly no reaction Ligand exchange to form Ru(POEt) (trace)	$Ru(PC2OMe)_2$ formation

[a] Conditions: 1 : 1 stoichiometry, refluxing acetone solution, 18 h. [b] Spectra obtained in acetone-d_6 after removal of acetone-h_6. Data available in ESI.† [c] 48 h reaction.

(estimated using cone angles: $\theta = 171°$ for POMe, $\theta \approx 141°$ for PC2OMe by comparison to Ph_2PBu^n),[13,27,28] it is not surprising that the PC2OMe–POMe ligand exchange does not proceed towards completion. Any dealkylation that occurs in this case is of **1** formed by ligand exchange; complex **3** is not dealkylated.

To help clarify the importance of the incoming nucleophile, the complexes **1**–**3** were also reacted with free POEt and PC2OMe. The NMR data were interpreted as described above and the complete set of results is presented in Table 5; ^{31}P NMR spectral data are available as electronic supplementary information (ESI).†

Summary of dealkylation results

Not surprisingly, in all the cases where a smaller phosphine reacts with a complex containing a larger phosphine, ligand displacement dominates (*e.g.*, **1** + PC2OMe, **2** + POMe or PC2OMe). This pathway occurs to a lesser extent when a larger phosphine reacts with a complex containing a smaller one (*e.g.*, **1** + POEt, **3** + POMe or POEt). Additionally, **3** reacts with the relatively small PC2OMe to form the bisphosphine complex **5**. In general, dealkylation is the preferred reaction of **1**, and can be effected by free POMe, POEt and PC2OMe, as determined by the observation of the corresponding methylphosphonium salts' resonances in the ^{31}P NMR spectra. Complex **2** is dealkylated to a small extent by POEt, but there is no evidence for dealkylation of **3** by any of the free phosphine-ethers studied. In summary, the aryl ether complexes **1** and **2** are more prone to dealkylation than is the alkyl ether complex **3**. There appears to be little dependence on the nature of the incoming phosphine-ether nucleophile.

A structural study was undertaken to assist in the understanding of these reactivity trends. Surprisingly, the differences in the phosphine-ether ligands do not cause significant differences in the Ru–P or Ru–O bond lengths in **1**–**3**; similarly, the oxidation potential of the metal varies only slightly from **1** to **3** (for **1**, $E_{1/2}(Ru^{III/II}) = 1.56$ V; for **2**, $E_{ox}(Ru^{III/II}) = 1.59$ V; for **3**, $E_{1/2}(Ru^{III/II}) = 1.48$ V *vs.* SCE), although in all three complexes the metal centre is notably electron-deficient. The O–C_α bond that connects the ether's alkyl moiety to the complex is, however, sensitive to the changes in ligand structure. This O–C_α bond length varies as follows: 1.441(3) Å in **1**; 1.482(11) Å and 1.460(11) Å in **2**; and 1.405(7) Å in **3**. The O–C_α bond lengths in the aryl ether complexes **1** and **2** are significantly longer than in the alkyl ether complex **3**, which may be responsible for a difference in C_α electrophilicity that would be consistent with the observed dealkylation reactivities. More importantly, however, the aryl ethers are thermodynamically predisposed to dealkylation because the reaction yields a resonance-stabilized phenoxide. The difference between the two aryl ether complexes' reactivity can be justified simply: complex **2** undergoes less dealkylation than **1** because of the lower electrophilicity of the ethyl group's C_α compared to the methyl group's carbon.

The resistance to dealkylation seen for **3** results from a combination of factors whose relative importance is not clarified by the structural study. The two O–C_α bond lengths are significantly different (O–C(35) 1.405(7) Å *vs.* O–C(34) 1.434(6) Å), but neither C_α is susceptible to nucleophilic attack by free phosphines. Based on bond lengths, one might expect the longer O–C(34) bond to be cleavable. However, attack at this carbon would require a sterically disfavoured approach from inside the chelate ring; moreover, such a reaction is also entropically unfavourable because the resulting phosphonium salt would be tethered to the metal complex. While attack at the methoxy carbon C(35) is both sterically and entropically favoured, this carbon may simply have insufficient electrophilicity to compete with attack of free phosphine directly at the uncrowded and electron-deficient Ru centre in **3**.

Conclusions

Complexes **1** and **2** contain triphenylphosphine derivatives with an ether substituent on one of the phenyl rings. These complexes undergo ligand-assisted *O*-dealkylation by the same weakly basic phosphines, a reaction that is typically observed for complexes containing highly basic phosphines with multiple ether substituents, such as TMPP. The high electron deficiency of the Ru(II) centre in these complexes is likely responsible for the ease with which these complexes are dealkylated to yield the aryloxide complexes. When the phenylene bridge between the phosphorus and oxygen moieties is replaced by an ethylene bridge as in **3**, the complex is not susceptible to ligand-assisted dealkylation. This difference in reactivity is explained primarily by steric arguments, but the lack of resonance stabilization of the hypothetical alkoxide product may also play a role. Dealkylation of ether complexes may provide a synthetic route to aryloxide complexes that contain groups incompatible with phenols and/or phenoxides, such as metal alkyls that are susceptible to protonolysis or ancillary ligands with deprotonatable (*e.g.*, carboxylic acid) or protonatable (*e.g.*, amine) functionalities.

Experimental

Materials and methods

Synthetic manipulations were carried out under an atmosphere of nitrogen unless otherwise specified. Chemicals were used as received from the suppliers (Aldrich, Strem, Alfa Aesar) unless otherwise specified. Deuterated solvents were used as received from Cambridge Isotope Labs. $Ru(bpy)_2Cl_2 \cdot 2H_2O$,[29] 2-meth-

oxyphenyldiphenylphosphine (POMe),[30] 2-ethoxyphenyldiphenylphosphine (POEt),[31] 2-methoxyethyldiphenylphosphine (PC2OMe)[32] were prepared using literature methods. Complex **1** was available from previous studies.[1]

NMR spectra were acquired on Bruker AC-200, Avance 300, Avance 400, AM-400, AMX-500 or Varian XL-300 instruments, using residual solvent peaks as internal ^{1}H reference (*vs.* TMS at δ 0) and 85% H_3PO_4 as external ^{31}P reference (δ 0).

Electrochemical measurements were performed with a Pine Instruments AFCBP1 bipotentiostat using a three-electrode cell (Pt disc working electrode, Pt wire coil counter electrode, Ag wire reference electrode). Decamethylferrocene or ferrocene was used as internal standard. Experiments were done in CH_2Cl_2 solution containing ≈0.1 M *n*-Bu_4NPF_6 supporting electrolyte. Methylene chloride was distilled from calcium hydride immediately before use in electrochemical experiments. *n*-Bu_4NPF_6 was recrystallized three times from methanol, dried *in vacuo* at 110 °C for 3 days, and stored in a dessicator.

Preparation of complexes

[Ru(bpy)$_2$(POEt-*P*,*O*)](PF$_6$)$_2$ 2. Prepared as described for **3** (below) using 2-ethoxyphenyldiphenylphosphine and obtained pure after metathesis to the PF_6 salt (yield 85%). ^{31}P{^{1}H} NMR (81 MHz, 25 °C, CD_2Cl_2): δ 51.1 (s, POEt), −144 (septet, $^1J_{PF}$ = 711 Hz, PF_6). ^{1}H NMR (200 MHz, 25 °C, CD_2Cl_2): δ 8.61–8.54 (m, 2H), 8.31 (d, J = 5.6 Hz, 1H), 8.22–8.08 (m, 3H), 7.96–7.35 (m, 18H), 7.26–7.12 (m, 2H), 6.97–6.88 (m, 2H), 6.42–6.33 (m, 2H), 4.64–4.47 (m, 1H), 4.14–3.97 (m, 1H), 0.72 (t, J = 7.0 Hz, 3H). Elemental analysis: calc. for $C_{40}H_{35}F_{12}N_4OP_3Ru$: C, 47.58; H, 3.49; N, 5.55; found: C, 47.32; H, 3.58; N, 5.49%. $E_{ox}(Ru^{III/II})$ = 1.59 V *vs.* SCE. Crystals suitable for X-ray crystallographic analysis were obtained by slow crystallization from methanol.

[Ru(bpy)$_2$(PC2OMe-*P*,*O*)](PF$_6$)$_2$ 3. A suspension of Ru(bpy)$_2$Cl$_2$·2H$_2$O (0.682 g, 1.31 mmol) in nitrogen-sparged acetone (20 mL) was treated with a solution of $AgBF_4$ (0.510 g, 2.62 mmol) in acetone (30 mL). The mixture was sparged thoroughly with nitrogen, stirred at room temperature for several hours to ensure complete precipitation of AgCl, then filtered through Celite to yield a deep wine-red solution of the solvate complex. To this solution was added 1 equivalent of 2-methoxyethyldiphenylphosphine (0.320 g, 1.31 mmol) as a solution in acetone (20 mL), and the mixture was heated to reflux under nitrogen overnight to yield a reddish orange solution. The cooled reaction mixture was filtered, evaporated to dryness and the residue dissolved in a small volume of acetone and precipitated with aqueous NH_4PF_6. The flocculent orange solid was collected, washed with water and ether, and dried. Crude yield: 85%. Impurities (*ca.* 10% by ^{31}P NMR) removed by recrystallization from hot methanol. ^{31}P{^{1}H} NMR (81 MHz, 25 °C, CD_2Cl_2): δ 50.5 (s, PC2OMe), −144 (septet, $^1J_{PF}$ = 711 Hz, PF_6). ^{1}H NMR (200 MHz, 25 °C, CD_2Cl_2): δ 8.80 (d, J = 5.69 Hz, 1H), 8.59–8.50 (m, 3H), 8.23–7.77 (m, 7H), 7.75–7.32 (m, 10H), 7.19–7.12 (m, 1H), 6.99–6.91 (m, 2H), 6.53–6.45 (m, 2H), 4.46–4.26 (m, 1H), 3.91–3.72 (m, 1H), 3.25–2.85 (m, 2H), 2.97 (s, 3H, OCH_3). Elemental analysis: calc. for $C_{35}H_{32}F_{12}N_4OP_3Ru$: C, 44.36; H, 3.51; N, 5.91; found: C, 44.00; H, 3.63; N, 5.86%. $E_{1/2}(Ru^{III/II})$ = 1.48 V *vs.* SCE. Crystals suitable for X-ray crystallographic analysis were obtained by crystallization from hot methanol.

[Ru(bpy)$_2${Ph$_2$P(*o*-OC$_6$H$_4$)-*P*,*O*}](PF$_6$) 4. Prepared by reacting [Ru(bpy)$_2$(Me$_2$CO)$_2$](BF$_4$)$_2$ with 2 equivalents of POMe in refluxing acetone, or by reacting [Ru(bpy)$_2$(POMe-*P*,*O*)](PF$_6$)$_2$ with one equivalent of POMe in refluxing acetone. Metathesis to the PF_6 salt followed by recrystallization from acetone/ether or hot methanol provides the aryloxide complex as a black powder in good yield. ^{31}P{^{1}H} NMR (81 MHz, 25 °C, CD_2Cl_2): δ 54.0 (s, PPh_2(*o*-OC_6H_4), −144 (septet, $^1J_{PF}$ = 711 Hz, PF_6). ^{1}H NMR (400 MHz, 25 °C, CD_2Cl_2): δ 8.66 (d, J = 8.20 Hz, H), 8.62 (d, J = 7.97 Hz, 1H), 8.51 (d, J = 5.12 Hz, 1H), 8.38–8.34 (m, 2H), 8.27 (d, J = 5.52 Hz, 1H), 8.11–8.05 (m, 2H), 8.00–7.96 (m, 2H), 7.84–7.76 (m, 3H), 7.59–7.40 (m, 8H), 7.16–7.03 (m, 3H), 6.92–6.88 (m, 2H), 6.73 (dd, J_1 = 5.49, J_2 = 5.60 Hz, 1H), 6.65–6.56 (m, 3H). Elemental analysis: calc. for $C_{38}H_{30}F_6N_4OP_2Ru$: C, 54.62; H, 3.62; N, 6.70; found: C, 54.37; H, 3.73; N, 6.72%. $E_{1/2}(Ru^{III/II})$ = 0.63 V *vs.* SCE.

[Ru(bpy)$_2$(PC2OMe-*P*)$_2$](PF$_6$)$_2$ 5. To a solution of [Ru(bpy)$_2$(Me$_2$CO)$_2$](BF$_4$)$_2$ (0.496 mmol) in N_2-sparged acetone (65 mL) was added 2 equivalents of 2-methoxyethyldiphenylphosphine (0.249 g, 1.02 mmol) as a solution in N_2-sparged acetone (35 mL). The mixture was heated to reflux for 3 days, then the clear red solution was filtered through Celite and evaporated to dryness. The residue was converted to the PF_6 salt and the bisphosphine complex was isolated by recrystallization from acetone to yield a bright orange powder. Purified by crystallization from methanol–acetone. Yield: *ca.* 35% by ^{31}P{^{1}H} NMR spectroscopy of the crude product mixture, remainder bidentate *P*,*O* complex and other unidentified products. ^{31}P{^{1}H} NMR (81 MHz, 25 °C, CD_3CN): δ 22.0 (s, PC2OMe), −144 (septet, $^1J_{PF}$ = 711 Hz, PF_6). ^{1}H NMR (200 MHz, 25 °C, CD_3CN): δ 8.84 (d, J = 5.46 Hz, 4H), 7.99 (t, J = 7.73 Hz, 4H), 7.87 (d, J = 7.90 Hz, 4H), 7.56 (dd, J_1 = 5.96, J_2 = 7.38 Hz, 4H), 7.26 (dd, J_1 = 7.34, J_2 = 7.89 Hz, 4H), 6.98 (dd, J_1 = 7.82, J_2 = 7.38 Hz, 8H), 6.41 (m, 8H), 2.75 (s, 6H, MeO), 2.69 (m, 4H), 1.71 (dd, J_1 = 7.27, J_2 = 6.82 Hz, 4H). Elemental analysis: calc. for $C_{50}H_{50}F_{12}N_4O_2P_4Ru$: C, 50.39; H, 4.23; N, 4.70; found: C, 50.58; H, 4.33; N, 4.75%. $E_{1/2}(Ru^{III/II})$ = 1.60 V *vs.* SCE.

Structure determination

Suitable crystals of **1**–**3** grown from methanol were selected and mounted on thin glass fibres. Data were collected at 173(1) K on a Rigaku/ADSC CCD area detector in two sets of scans (ϕ = 0.0 to 190.0°, χ = −90.0°; and ω = −18.0 to 23.0°, χ = −90.0°) using 0.50° oscillations with 19.0, 12.0 and 77.0 second exposures, respectively. ORTEP representations of the solid-state molecular structures of **1**–**3** were prepared using Ortep-3 for Windows.[33]

Complex **2** crystallizes with two salt moieties, related by a pseudo-inversion centre, in the asymmetric unit. This pseudo-inversion centre is located at 0.8756 0.0228 0.8735, or roughly x = 7/8, y = 0. The existence of pseudo-centres in non-centrosymmetric structures has been studied in detail by Marsh *et al.*[34] and usually results in large correlations between refined parameters of each crystallographically independent moiety. In order to obtain reasonable anisotropic displacement parameters, refinements were carried out using restraints that called for equivalent anisotropic displacement parameters for pairs of atoms related by the pseudo-inversion centre.

Complex **3** crystallizes in the non-centrosymmetric space group $P2_12_12_1$. A parallel refinement was carried out on both enantiomers. The enantiomer reported herein was assigned on the basis of the better final residual values.

CCDC reference numbers 153809–153811.

See http://www.rsc.org/suppdata/dt/b0/b008931l/ for crystallographic data in CIF or other electronic format.

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