

Reactivity of New Osmium Dihydrides with Arenediazonium Cations: Preparation and Properties of Bis(aryldiazene) and Mono(aryldiazenido) Complexes. A Comparison with Analogous Iron and Ruthenium Derivatives

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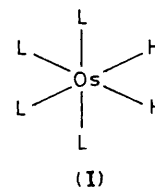
Hydride complexes $[\text{OsH}_2\text{L}_4]$ [$\text{L} = \text{P}(\text{OEt})_3$ or $\text{PPh}(\text{OEt})_2$] were prepared. Their reactions with arenediazonium cations led to the synthesis of $[\text{Os}(\text{RN}=\text{NH})_2\text{L}_4][\text{BPh}_4]_2$ and $[\text{OsH}(\text{RN}=\text{NH})\text{L}_4]\text{BPh}_4$ ($\text{R} = \text{Ph}$, 4-MeC₆H₄, or 4-MeOC₆H₄) complexes which were characterized by ¹H and ³¹P n.m.r. data (with ¹⁵N isotopic substitution). The compounds $[\text{Os}(4\text{-MeC}_6\text{H}_4\text{N}=\text{NH})(4\text{-MeC}_6\text{H}_4\text{NC})\text{L}_4][\text{BPh}_4]_2$ were also prepared. The reaction of the bis(aryldiazene) derivatives with NEt_3 led to new five-co-ordinate aryldiazenido complexes $[\text{Os}(\text{RN}_2)\text{L}_4]\text{BPh}_4$ ($\text{R} = \text{Ph}$ or 4-MeC₆H₄). Protonation of the diazenido compounds with $\text{CF}_3\text{CO}_2\text{H}$ and HBF_4 gave the six-co-ordinate mono(diazene) $[\text{Os}(\text{CF}_3\text{CO}_2)(\text{RN}=\text{NH})\text{L}_4]\text{BPh}_4$ and the five-co-ordinate $[\text{Os}(\text{RN}=\text{NH})\text{L}_4]\text{BPh}_4$ ($\text{R} = 4\text{-MeC}_6\text{H}_4$) derivatives, respectively. Infrared and ¹H and ³¹P n.m.r. data for these complexes are reported.

Investigations of diazene complexes $[\text{M}(\text{RN}=\text{NH})]$ ($\text{R} = \text{aryl}$) formed by the reactions of arenediazonium cations and metal hydrides are of interest because they may provide insights on the initial stages of hydrogenation of nitrosyl, carbonyl, and di-nitrogen ligands. Our interest in this field¹ has recently been devoted to the reactivity of iron and ruthenium dihydrides^{2,3} $[\text{MH}_2\text{L}_4]$ ($\text{L} = \text{P}$ donor) with arenediazonium cations, which led to the synthesis of the first bis(aryldiazene) complexes. We extended our studies of the reactions of RN_2^+ with the osmium hydrides $[\text{OsH}_2\text{L}_4]$ containing phosphite ligands to determine whether the osmium dihydrides show similar properties, to complete the Fe, Ru, Os triad, and to compare the results among the three metals. Since $[\text{OsH}_2\text{L}_4]$ dihydrides with phosphite ligands were unknown, we report the syntheses and characterization of these new complexes. Reactions of the new bis(diazene) $[\text{Os}(\text{RN}=\text{NH})_2\text{L}_4][\text{BPh}_4]_2$ and mono(diazenido) $[\text{Os}(\text{RN}_2)\text{L}_4]\text{BPh}_4$ compounds are also reported.

Results and Discussion

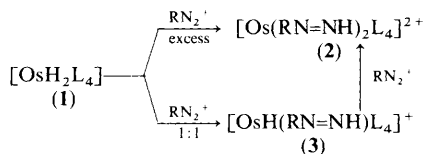
Dihydride $[\text{OsH}_2\text{L}_4]$ Complexes.—Sodium tetrahydroborate reduction of $[\text{NH}_4]_2[\text{OsCl}_6]$ in the presence of phosphite gave the new hydride complexes $[\text{OsH}_2\text{L}_4]$ **(I)**; $\text{L} = \text{P}(\text{OEt})_3$ or $\text{PPh}(\text{OEt})_2$ which were isolated as white stable, diamagnetic solids. Their ³¹P-¹H n.m.r. spectra (between +30 and -80 °C) are A₂B₂ multiplets (Table 1), in accord with the two hydride ligands being in *cis* positions **(I)**. The complicated ¹H n.m.r. multiplet in the hydride region confirms this assignment. In the ν(MH) region the i.r. spectra show only one broad band at 1 950 cm⁻¹ for (a) $\text{L} = \text{P}(\text{OEt})_3$ and at 1 745 cm⁻¹ for (b) $\text{L} = \text{PPh}(\text{OEt})_2$ which disappears in the spectra of the deuteride complexes $[\text{OsD}_2\text{L}_4]$. However, ν(OsD) was not observed, probably owing to masking in the 1 300–1 450 cm⁻¹ region by intense phosphite bands. The assignment of these absorptions to ν(OsH) is therefore plausible, although two bands are to be expected for a *cis* complex. It may be noted that osmium dihydrides of the type $[\text{OsH}_2\text{L}_4]$ have been reported with (uni- and bi-dentate) tertiary phosphine groups,⁴ but not with phosphite ligands.

When the hydride synthesis was carried out at 40–50 °C or when the reaction was stopped after 5–10 min of reflux, a new hydride presumed to be the $[\text{OsH}_4\text{L}_3]$ derivative was present in



the final product (40–50%). Apart from the signals due to $[\text{OsH}_2\text{L}_4]$, the ¹H n.m.r. spectra of the product had a quartet at δ -9.66 with $J(\text{PH})$ 8 Hz [$\text{P}(\text{OEt})_3$] and at δ -9.38 with $J(\text{PH})$ 8 Hz [$\text{PPh}(\text{OEt})_2$], whereas singlets at δ 124.2 and at 135.6 respectively appear in the ³¹P-¹H n.m.r. spectra, which remain unchanged below -80 °C. Similar data had been previously observed for the analogous $[\text{OsH}_4\text{L}_3]$ ($\text{L} = \text{tertiary phosphine}$) derivatives.⁵

Aryldiazene Derivatives.—The reactions of the hydride $[\text{OsH}_2\text{L}_4]$ [$\text{L} = \text{P}(\text{OEt})_3$ or $\text{PPh}(\text{OEt})_2$] with arenediazonium cations give thermally stable mono- and bis(aryldiazene) complexes, as shown in Scheme 1. The complexes which were



$\text{L} = \text{P}(\text{OEt})_3$ or $\text{PPh}(\text{OEt})_2$; $\text{R} = \text{Ph}$, 4-MeC₆H₄, or 4-MeOC₆H₄

Scheme 1.

isolated as yellow BPh_4^- salts are air-stable and diamagnetic. The ¹H n.m.r. spectra of the labelled and unlabelled complexes confirm the presence of the diazene ligand. The broad signal at δ 13.44–14.60 in the spectra of **(2)** and **(3)** ($\text{R} = \text{Ph}$) due to the NH resonance which is substituted by a doublet for the corresponding labelled (PhN=¹⁵NH) complexes [¹J(¹⁵NH) between 68.2 and 60.8 Hz] confirms the presence of the diazene ligand. The signal of the labelled ¹⁵N complexes is not a sharp doublet, but appears as a doublet of multiplets, owing to coupling of the non-aromatic diazene protons with the

Table 1. Infrared and $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. data of selected osmium complexes

Compound ^a	I.r. (cm ⁻¹) ^b	Spin system	$^{31}\text{P}\{-^1\text{H}\}$ n.m.r. ^c
$[\text{OsH}_2\{\text{P}(\text{OEt})_3\}_4]$	(1 950m) v(MH)	A_2B_2	$\delta_{\text{A}} = 123.5, \delta_{\text{B}} = 122.2$ [$J(\text{AB}) = 29.3$]
$[\text{OsH}_2\{\text{PPh}(\text{OEt})_2\}_4]$	(1 745m) v(MH)	A_2B_2	$\delta_{\text{A}} = 133.1, \delta_{\text{B}} = 131.6$ [$J(\text{AB}) = 20.7$]
$[\text{Os}(\text{PhN}=\text{NH})_2\{\text{P}(\text{OEt})_3\}_4]^{2+}$	—	A_2B_2	$\delta_{\text{A}} = 81.2, \delta_{\text{B}} = 76.2$ [$J(\text{AB}) = 44.0$]
$[\text{Os}(\text{PhN}=\text{NH})_2\{\text{P}(\text{OEt})_3\}_4]^{2+}$	—	$\text{A}_2\text{BB}'\text{NN}'$	$\delta_{\text{A}} = 81.0, \delta_{\text{B}} = 76.1$ [$J(\text{AB})=J(\text{AB}') = 44.1, J(\text{AN})=J(\text{AN}') = -4.5,$ $J(\text{BB}') = 65.0, J(\text{BN})=J(\text{B}'\text{N}') = 58.0,$ $J(\text{BN}')=J(\text{B}'\text{N}) = -6.0, J(\text{NN}') = 0.3$]
$[\text{Os}(\text{PhN}=\text{NH})_2\{\text{PPh}(\text{OEt})_2\}_4]^{2+}$	—	A_2B_2	$\delta_{\text{A}} = 108.3, \delta_{\text{B}} = 105.7$ [$J(\text{AB}) = 34.7$]
$[\text{OsH}(\text{PhN}=\text{NH})\{\text{P}(\text{OEt})_3\}_4]^+$	(2 037m) v(MH)	A_2BC	$\delta_{\text{A}} = 102.3, \delta_{\text{B}} = 100.8, \delta_{\text{C}} = 99.9$ [$J(\text{AB}) = 32.0, J(\text{AC}) = 43.0, J(\text{BC}) = 31.7$]
$[\text{OsH}(\text{PhN}=\text{NH})\{\text{P}(\text{OEt})_3\}_4]^+$	(1 970m) v(MH)	A_2BCN	$\delta_{\text{A}} = 102.3, \delta_{\text{B}} = 100.8, \delta_{\text{C}} = 99.9$ [$J(\text{AB}) = 33.0, J(\text{AC}) = 44.0, J(\text{AN}) = -2.0,$ $J(\text{BC}) = 31.7, J(\text{BN}) = -5.5, J(\text{CN}) = 48.0$] 120.7(s)
$[\text{OsH}(\text{PhN}=\text{NH})\{\text{PPh}(\text{OEt})_2\}_4]^+$	(2 020m) v(MH)	—	
$[\text{Os}(4\text{-MeC}_6\text{H}_4\text{N}=\text{NH})(4\text{-MeC}_6\text{H}_4\text{NC})\{\text{P}(\text{OEt})_3\}_4]^{2+}$	2 166s v(CN) (2 163s)	AB_2C	$\delta_{\text{A}} = 80.3, \delta_{\text{B}} = 79.6, \delta_{\text{C}} = 78.3$ [$J(\text{AB}) = 39.0, J(\text{AC}) = 55.0, J(\text{BC}) = 62.0$]
$[\text{Os}(4\text{-MeC}_6\text{H}_4\text{N}=\text{NH})(4\text{-MeC}_6\text{H}_4\text{NC})\{\text{PPh}(\text{OEt})_2\}_4]^{2+}$	2 167s v(CN) (2 165s)	ABC_2	$\delta_{\text{A}} = 111.3, \delta_{\text{B}} = 106.1, \delta_{\text{C}} = 104.8$ [$J(\text{AB}) = 32.2, J(\text{AC}) = 39.5, J(\text{BC}) = 31.0$]
$[\text{Os}(\text{PhN}_2)\{\text{P}(\text{OEt})_3\}_4]^+$	1 645s v(NN) (1 642s)	ABC_2^d	$\delta_{\text{A}} = 104.7, \delta_{\text{B}} = 102.0, \delta_{\text{C}} = 92.8$ [$J(\text{AB}) = 46.1, J(\text{AC}) = 40.0, J(\text{BC}) = 38.0$]
$[\text{Os}(\text{PhN}=\text{N})\{\text{P}(\text{OEt})_3\}_4]^+$	1 626s v(N \equiv ¹⁵ N)	ABC_2N^d	$\delta_{\text{A}} = 104.6, \delta_{\text{B}} = 102.0, \delta_{\text{C}} = 92.8$ [$J(\text{AB}) = 46.7, J(\text{AC}) = 39.8, J(\text{AN}) = 46.0,$ $J(\text{BC}) = 37.8, J(\text{BN}) = 24.0, J(\text{CN}) = 9.5$]
$[\text{Os}(\text{PhN}_2)\{\text{PPh}(\text{OEt})_2\}_4]^+$	1 640s v(NN) (1 641s)	ABC_2^d	$\delta_{\text{A}} = 121.3, \delta_{\text{B}} = 120.3, \delta_{\text{C}} = 110.7$ [$J(\text{AB}) = 25.1, J(\text{AC}) = 25.0, J(\text{BC}) = 30.0$]
$[\text{Os}(\text{CF}_3\text{CO}_2)(4\text{-MeC}_6\text{H}_4\text{N}=\text{NH})\{\text{P}(\text{OEt})_3\}_4]^+$	(1 678s) v(CO ₂)	A_2BC	$\delta_{\text{A}} = 88.1, \delta_{\text{B}} = 85.7, \delta_{\text{C}} = 66.8$ [$J(\text{AB}) = 45.0, J(\text{AC}) = 41.0, J(\text{BC}) = 46.4$]
$[\text{Os}(\text{CF}_3\text{CO}_2)(4\text{-MeC}_6\text{H}_4\text{N}=\text{NH})\{\text{PPh}(\text{OEt})_2\}_4]^+$	(1 675s) v(CO ₂)	A_2BC	$\delta_{\text{A}} = 113.8, \delta_{\text{B}} = 113.4, \delta_{\text{C}} = 97.5$ [$J(\text{AB}) = 60.0, J(\text{AC}) = 32.0, J(\text{BC}) = 32.1$]
$[\text{Os}(4\text{-MeC}_6\text{H}_4\text{N}=\text{NH})\{\text{PPh}(\text{OEt})_2\}_4]^{2+}$	—	AB_2C	$\delta_{\text{A}} = 111.7, \delta_{\text{B}} = 106.9, \delta_{\text{C}} = 100.3$ [$J(\text{AB}) = 38.0, J(\text{AC}) = 30.0, J(\text{BC}) = 28.5$]

^a All cationic compounds are BPh_4^- salts. ^b In CH_2Cl_2 , except those values in parentheses (KBr). ^c At room temperature in CD_2Cl_2 , unless otherwise noted. Positive shift downfield from 85% H_3PO_4 ; J values in Hz. ^d At -65°C .

phosphorus nuclei of the phosphite ligands.* Similar coupling (between ^{15}NH and P) had previously been observed for related ruthenium complexes.³

The $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectra of the bis(diazene) derivatives (**2**) which are A_2B_2 multiplets (between $+30$ and -80°C) confirm the *cis*-geometry (**II**) for the compounds in CD_2Cl_2 solution. In contrast, the ^{31}P n.m.r. spectra of the mono(diazene) complexes (**3**) depend on the nature of the phosphite ligand. While the $\text{P}(\text{OEt})_3$ derivatives show an A_2BC pattern consistent with the *cis* geometry (**II**), the $\text{PPh}(\text{OEt})_2$ complexes give sharp singlets, consistent with the hydride and diazene ligands in mutually *trans* position (**III**).

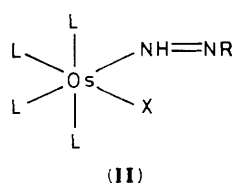
Osmium phosphine dihydrides such as the $[\text{OsH}_2(\text{CO})(\text{PPh}_3)_3]$ were reported to react with arenediazonium cations to insert only one RN_2^+ group to form the mono(diazene) complexes $[\text{OsH}(\text{RN}=\text{NH})(\text{CO})(\text{PPh}_3)_3]$.⁶ As previously observed for iron and ruthenium dihydrides,^{2,3} the presence of phosphite ligands makes the $[\text{OsH}_2\text{L}_4]$ hydride susceptible to the insertion of two arenediazonium groups to yield the bis(diazene) complexes $[\text{Os}(\text{RN}=\text{NH})_2\text{L}_4]^{2+}$.

Studies of the chemical reactions of the diazene compounds indicate that they are relatively robust. Substitution reactions with RNC , CO , and phosphite ligands are very slow. The complexes $[\text{Os}(\text{RN}=\text{NH})(\text{R}'\text{NC})\text{L}_4][\text{BPh}_4]_2$ [**4**; $\text{R} = \text{R}' = 4\text{-MeC}_6\text{H}_4$, $\text{L} = \text{P}(\text{OEt})_3$ or $\text{PPh}(\text{OEt})_2$] could be obtained from (**2**) in pure form after 8 h of reflux in 1,2-dichloroethane with an excess of isocyanide. In contrast a mixture of products con-

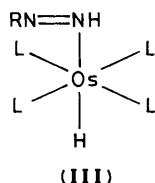
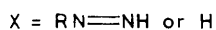
taining both the mono- and bis-(carbonyl) derivatives $[\text{Os}(\text{RN}=\text{NH})(\text{CO})\text{L}_4]^{2+}$ and $[\text{Os}(\text{CO})_2\text{L}_4]^{2+}$ was observed after refluxing (**2**) in acetone solution under 1 atm (101 325 pa) of CO . The $\text{P}(\text{OEt})_3$ ligand also substitutes one diazene in (**2**) to give $[\text{Os}(\text{RN}=\text{NH})\{\text{P}(\text{OEt})_3\}_3][\text{BPh}_4]_2$ (NH at δ 13.7), but the pure complex was not isolated. A mutually *cis* position of the diazene and isocyanide ligands for complexes (**4**) [$\nu(\text{CN})$ at $2\ 166\text{--}2\ 167\ \text{cm}^{-1}$ in CH_2Cl_2] is indicated by the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectra which appear as multiplets (Table 1).

The formation of mono- and bis-(aryldiazene) complexes in the reaction of RN_2^+ with $[\text{OsH}_2\{\text{P}(\text{OEt})_3\}_4]$ is analogous with the reactions of the iron² and ruthenium³ hydride complexes. Differences in the reactions of the $\text{PPh}(\text{OEt})_2$ complexes were observed. Whereas the dihydrides of Os and Ru³ gave only the bis(diazene) complex $[\text{M}(\text{RN}=\text{NH})_2\text{L}_4]^{2+}$ when treated with an excess of RN_2^+ , the bis(aryldiazene) derivatives $[\text{Fe}(\text{RN}_2)_2\text{L}_3]$ were obtained in a complicated reaction sequence. Studies of this reaction⁷ showed that the bis(aryldiazene) complex is formed first and $[\text{Fe}(\text{RN}_2)_2\text{L}_3]^{2+}$ is formed as the final product by further reaction. We therefore

* For example, in the case of the complex $[\text{Os}(\text{PhN}=\text{NH})_2\{\text{P}(\text{OEt})_3\}_4][\text{BPh}_4]_2$, taking into account that the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum is an $\text{A}_2\text{BB}'\text{NN}'$ multiplet (Table 1), the NH pattern at δ 14.54 can be simulated as the X part of an $\text{A}_2\text{BB}'\text{NN}'\text{XX}'$ system ($\text{X} = \text{H}$ of diazene) with the following parameters: $J(\text{AX})=J(\text{AX}')$ 1.4, $J(\text{BX})=J(\text{B}'\text{X}')$ -6 , $J(\text{BX}')=J(\text{B}'\text{X})$ -2.3 , $J(\text{NX})=J(\text{N}'\text{X}')$ 67.8, $J(\text{NX}')=J(\text{N}'\text{X})$ 0.8, and $J(\text{XX}')$ 0.1 Hz.



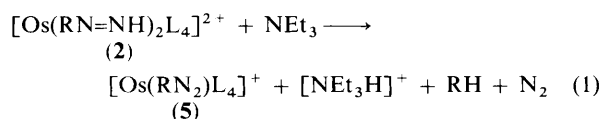
(II)



(III)

conclude that all the $[\text{MH}_2\text{L}_4]$ dihydrides of the iron triad containing these phosphite ligands react with RN_2^+ to give bis(aryldiazene) derivatives.

Mono(aryldiazene) Complexes.—The reactions of the bis(diazene) complexes (2) with triethylamine, in both 1:1 ratio or in excess, proceed in CH_2Cl_2 to give aryldiazene derivatives [5; $\text{L} = \text{P}(\text{OEt})_3$ or $\text{PPh}(\text{OEt})_2$] [equation (1)], which were



isolated and characterized. Instead, the mono(diazene) complexes $[\text{OsH}(\text{RN}=\text{NH})\text{L}_4]\text{BPh}_4$ are unreactive toward bases and the starting compound can be recovered unchanged even after long reaction times with excess of base.

No osmium compounds other than (5) could be detected by following the course of reaction (1) by i.r. and ^1H n.m.r. spectra. Since N_2 and RH are the decomposition products of the free $\text{RN}=\text{NH}$ ligand,⁸ it is likely that the deprotonation of only one diazene ligand in (2) is followed by dissociation and decomposition of the other $\text{RN}=\text{NH}$ group, to give complexes (5) as final products.

Some spectroscopic properties of the new aryldiazene derivatives, which are yellow solids, diamagnetic, and 1:1 electrolytes, are reported in Table 1. The i.r. spectra both in the solid state and in CH_2Cl_2 solution show only one $\nu(\text{NN})$ band at $1\ 630\text{--}1\ 645\ \text{cm}^{-1}$, which is shifted to $1\ 622\text{--}1\ 626\ \text{cm}^{-1}$ for the corresponding ^{15}N -labelled compounds. These values, which compare favourably with data for aryldiazene complexes whose crystal structures are known, such as $[\text{Fe}(4\text{-MeC}_6\text{H}_4\text{N}_2)\{\text{P}(\text{OEt})_3\}_4]\text{BPh}_4$ ¹ and $[\text{OsH}(\text{CO})(\text{PhN}_2)(\text{PPh}_3)_2]$,⁹ indicate a singly bent aryldiazene group in our complexes. This assignment also agrees with the empirical rules proposed by Haymore and Ibers.¹⁰

The $^{31}\text{P}\text{-}\{^1\text{H}\}$ n.m.r. spectra of aryldiazene complexes (5) at room temperature show an ABC_2 multiplet (parameters in Table 1), which remains unchanged between $+34$ and -80°C . A regular trigonal bipyramidal geometry for the complexes, which would be expected to have an A_2B_2 or AB_3 spectrum, can therefore be excluded. The ABC_2 pattern could suggest a square pyramidal structure in solution, however, a trigonal bipyramidal geometry slightly distorted toward square pyramidal geometry would also give an ABC_2 ^{31}P n.m.r. spectrum. As previously observed in the related complex $[\text{Fe}(\text{RN}_2)\{\text{P}(\text{OEt})_3\}_4]\text{BPh}_4$,² such a structure may reasonably be proposed for our derivatives (5).

The aryldiazene complexes do not react with excess of halogenide ions X^- (Cl^- or Br^-) in acetone solution, and the starting materials were recovered unchanged even after 2 h of reflux. This behaviour is different from that shown by the derivatives $[\text{Os}(\text{RN}_2)(\text{CO})_2(\text{PPh}_3)_2]^+$,¹¹ which react with X^- to give the octahedral $[\text{OsX}(\text{RN}_2)(\text{CO})_2(\text{PPh}_3)_2]$ complexes with a presumed doubly bent RN_2 ligand. The five-co-ordinate 18-electron aryldiazene complexes (5) are quite stable towards the formation of octahedral species as well as to the substitution of the phosphite and aryldiazene ligands.

Trifluoroacetic acid reacts in CH_2Cl_2 with the aryldiazene derivatives (5) to give the mono(aryldiazene) complexes $[\text{Os}(\text{CF}_3\text{CO}_2)(\text{RN}=\text{NH})\text{L}_4]\text{BPh}_4$ [6; $\text{R} = 4\text{-MeC}_6\text{H}_4$, $\text{L} = \text{P}(\text{OEt})_3$ or $\text{PPh}(\text{OEt})_2$], which were isolated and characterized. The i.r. spectra show acetate absorptions at $1\ 675\text{--}1\ 678\ \text{cm}^{-1}$, and in the ^1H n.m.r. spectra the NH resonances appear at δ 16.66 [$\text{L} = \text{P}(\text{OEt})_3$] and 16.07 [$\text{L} = \text{PPh}(\text{OEt})_2$], consistent with the proposed formulation. In order to determine the nitrogen atom which is protonated, we studied the reactions of $[\text{Os}(\text{RN}=\text{N}^{15}\text{N})\text{L}_4]^+$ and $[\text{Os}(\text{R}^{15}\text{N}=\text{N})\text{L}_4]^+$ cations with $\text{CF}_3\text{CO}_2\text{H}$, and observed that protonation takes place at the nitrogen atom bonded to Os to give the proposed aryldiazene complexes (6). A mutual *cis* position of the trifluoroacetate and $\text{RN}=\text{NH}$ ligands may be also deduced from the ^{31}P n.m.r. spectra which show A_2BC multiplets between $+34$ and -80°C .

Fluoroboric acid also reacts with the $[\text{Os}(\text{RN}_2)\{\text{PPh}(\text{OEt})_2\}_4]\text{BPh}_4$ to give a yellow-orange diamagnetic solid which was characterized as the five-co-ordinate derivative $[\text{Os}(4\text{-MeC}_6\text{H}_4\text{N}=\text{NH})\{\text{PPh}(\text{OEt})_2\}_4][\text{BPh}_4]_2$ (7). Its ^1H n.m.r. spectrum shows the diazene signal at δ 12.92 and that of the ^{15}N -labelled compound indicates protonation of the nitrogen atom bonded to Os. In the temperature range from $+30$ to -80°C the $^{31}\text{P}\text{-}\{^1\text{H}\}$ n.m.r. spectra display an AB_2C multiplet, which was simulated with the values reported in Table 1. However, these data do not allow an unambiguous geometry to be assigned to the complex in solution, because both a square pyramidal and a distorted trigonal bipyramidal structure should give an AB_2C ^{31}P n.m.r. spectrum.

The three aryldiazene complexes $[\text{M}(\text{RN}_2)\{\text{P}(\text{OEt})_3\}_4]\text{BPh}_4$ ($\text{M} = \text{Fe}, \text{Ru}, \text{or Os}$) which may all easily be obtained by deprotonation of the corresponding bis(diazene) derivatives $[\text{M}(\text{RN}=\text{NH})_2\{\text{P}(\text{OEt})_3\}_4][\text{BPh}_4]_2$ have $\nu(\text{NN})$ frequencies which are lowered from $1\ 668$ to $1\ 640\ \text{cm}^{-1}$ (Table 2) on going from iron to ruthenium to osmium. A singly bent RN_2 ligand seems to be present in all these iron triad compounds. While the ruthenium complex has the regular trigonal bipyramidal geometry in solution, the ABC_2 multiplets in the ^{31}P n.m.r. spectra of the complexes of Fe and Os suggest a distortion from such a structure. Furthermore, the coupling constants of the phosphorus atoms in the aryldiazene complexes are larger with Fe (125–126 Hz) than with Ru and Os (which are comparable), whereas a regular decrease of the chemical shifts is observed from the iron to the osmium derivatives. Lastly, while the iron compounds are unreactive toward protonation, the diazene complexes of Ru and Os are protonated to form mono(diazene) complexes.

In summary, we have shown in this and previous investigations^{2,3} that the hydridophosphite complexes $[\text{MH}_2\text{L}_4]$ ($\text{M} = \text{Fe}, \text{Ru}, \text{or Os}$; $\text{L} = \text{P}(\text{OEt})_3$ or $\text{PPh}(\text{OEt})_2$) react with RN_2^+ to form first the mono(diazene) complexes $[\text{MH}(\text{RN}=\text{NH})\text{L}_4]^+$ and then the *cis*-bis(diazene) complexes $[\text{M}(\text{RN}=\text{NH})_2\text{L}_4]^{2+}$. Mixed bis(diazene) complexes $[\text{M}(\text{RN}=\text{NH})(\text{R}'\text{N}=\text{NH})\text{L}_4]^{2+}$ were prepared by reaction of $[\text{MH}(\text{RN}=\text{NH})\text{L}_4]^+$ and $\text{R}'\text{N}_2^+$. The mono- and bis(diazene) compounds are all thermally stable and undergo substitution relatively slowly.

Experimental

General Comments.—All solvents used were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. The salt $[\text{NH}_4]_2\text{-}[\text{OsCl}_6]$ (Alfa Ventron) was used as supplied. Diethoxyphenylphosphine was prepared by the method of Rabinowitz and Pellon;¹² triethyl phosphite was an Ega Chemie product and was purified by distillation under nitrogen. Diazonium salts were obtained in the usual way, as described in the literature.¹³ The labelled diazonium salts $[\text{PhN}=\text{N}^{15}\text{N}]\text{BF}_4$ and $[\text{Ph}^{15}\text{N}=\text{N}]\text{BF}_4$ were prepared by using the appropriate $\text{Na}^{15}\text{NO}_2$ or $\text{Ph}^{15}\text{NH}_2$

Table 2. Infrared and ^{31}P n.m.r. data for aryldiazenido complexes of Fe, Ru, and Os

Compound ^a	I.r. (cm^{-1}), ^b $\nu(\text{NN})$	Spin system	$^{31}\text{P}\{-^1\text{H}\}$ n.m.r. ^c
$[\text{Fe}(4\text{-MeC}_6\text{H}_4\text{N}_2)\{\text{P}(\text{OEt})_3\}_4]^+$	1 668	ABC_2	$\delta_A = 167.4, \delta_B = 165.5, \delta_C = 152.5$ $[J(\text{AB}) = -4.8, J(\text{AC}) = 126.0, J(\text{BC}) = 125.0]$
$[\text{Ru}(4\text{-MeC}_6\text{H}_4\text{N}_2)\{\text{P}(\text{OEt})_3\}_4]^+$	1 647	A_2B_2	$\delta_A = 146.4, \delta_B = 131.2$ $[J(\text{AB}) = 52.4]$
$[\text{Os}(4\text{-MeC}_6\text{H}_4\text{N}_2)\{\text{P}(\text{OEt})_3\}_4]^+$	1 640	ABC_2	$\delta_A = 104.8, \delta_B = 102.3, \delta_C = 93.2$ $[J(\text{AB}) = 45.4, J(\text{AC}) = 39.8, J(\text{BC}) = 37.8]$

^a All compounds are BPh_4^- salts. ^b In CH_2Cl_2 . ^c In CD_2Cl_2 at -65°C . Positive shift downfield from 85% H_3PO_4 , J values in Hz.

(ICN Stable Isotopes) as reagents. Substituted phenyl isocyanides were obtained by the phosgene method of Ugi *et al.*¹⁴ Other reagents were purchased from commercial sources in the highest available purity and used as received.

Infrared spectra were recorded on a Perkin-Elmer model 683 Spectrometer. Solution ^1H n.m.r. spectra were obtained with Varian EM-390 and Varian FT-80A spectrometers at variable temperatures between -80 and $+34^\circ\text{C}$ unless noted otherwise, and are referred to internal tetramethylsilane. Fourier-mode, proton-noise-decoupled ^{31}P n.m.r. spectra were recorded on a Varian FT-80A spectrometer operating at 32.203 MHz. All chemical shifts are reported with respect to 85% H_3PO_4 , downfield considered positive. Conductivities of 10^{-3} mol dm^{-3} solutions of the complexes at 25°C were measured with a CDM 83 Radiometer in nitromethane as solvent, unless noted otherwise. Solution susceptibilities were determined by the Evans method.¹⁵

Synthesis of Complexes.—All preparative work was performed under an inert atmosphere, using standard Schlenk techniques. Once isolated, the complexes were shown to be stable in air for 1–2 d. The elemental analyses of the compounds are reported in Table 3.

$[\text{OsH}_2\text{L}_4]$ [1; $\text{L} = \text{P}(\text{OEt})_3$ or $\text{PPh}(\text{OEt})_2$]. An excess of the appropriate phosphite (10 mmol) was added to a suspension of $[\text{NH}_4]_2[\text{OsCl}_6]$ (1 mmol, 0.44 g) in ethanol (30 cm^3) and the reaction mixture was warmed to $50\text{--}60^\circ\text{C}$. The slow addition of a solution of NaBH_4 (13 mmol, 0.49 g) in ethanol (10 cm^3) caused the solution to change from red-brown to pale yellow, and a white solid began to separate. The reaction mixture was refluxed for 4 h, filtered, and evaporated under reduced pressure to give a brown oil from which the hydride was extracted with five 10- cm^3 portions of light petroleum (b.p. $30\text{--}50^\circ\text{C}$). The solvent was removed under reduced pressure at 30°C . The resulting oil, dissolved in ethanol (3 cm^3) was crystallized by cooling the solution at -30°C ; yield $\geq 45\%$. $[\text{OsH}_2\{-\text{P}(\text{OEt})_3\}_4]$, m.p. 45°C (decomp.); $\delta_{\text{H}}(\text{C}_6\text{D}_6)$ 4.12 (24 H, m, CH_2), 1.31, 1.26 (36 H, t, CH_3), and -12.17 (2 H, m, hydride). $[\text{OsH}_2\{\text{PPh}(\text{OEt})_2\}]$, m.p. 120°C (decomp.); $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2)$ 7.38, 7.20 (20 H, m, Ph), 3.63, 3.27 (16 H, m, CH_2), 1.06, 1.04 (24 H, t, CH_3), and -11.53 (2 H, m, hydride).

In the same way were prepared $[\text{OsD}_2\text{L}_4]$ using NaBD_4 as reducing agent.

$[\text{Os}(\text{RN}=\text{NH})_2\text{L}_4][\text{BPh}_4]_2$ [2; $\text{L} = \text{P}(\text{OEt})_3$, or $\text{PPh}(\text{OEt})_2$; $\text{R} = \text{Ph}$, 4-Me C_6H_4 , or 4-MeOC $_6\text{H}_4$]. To a solution of $[\text{OsH}_2\text{L}_4]$ (0.1 mmol) in CH_2Cl_2 (10 cm^3) at 0°C an excess of the appropriate diazonium salt was added and the reaction mixture was stirred for 3 h. After filtration to remove the unreacted diazonium salt, the solution was evaporated to dryness, leaving an oil which was treated with ethanol (7 cm^3). Addition of NaBPh_4 (0.2 mmol, 0.07 g) to the resulting solution caused the precipitation of a yellow solid, which was filtered off and crystallized from CH_2Cl_2 (2 cm^3) and ethanol (10–12 cm^3); yield $\geq 85\%$. $[\text{Os}(\text{PhN}=\text{NH})_2\{\text{P}(\text{OEt})_3\}_4][\text{BPh}_4]_2$ m.p. 127°C ;

Λ_{M} 172.3 S cm^2 mol^{-1} (Me_2CO); $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2)$ 14.53 (2 H, br, NH), 7.58, 7.30, 6.95 (50 H, m, Ph), 4.07, 3.85 (24 H, m, CH_2), 1.32 and 1.03 (36 H, t, CH_3). $[\text{Os}(4\text{-MeC}_6\text{H}_4\text{N}=\text{NH})_2\{\text{P}(\text{OEt})_3\}_4][\text{BPh}_4]_2$, m.p. 133°C ; Λ_{M} 170.1 S cm^2 mol^{-1} (Me_2CO); $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2)$ 14.37 (2 H, br, NH), 7.29, 6.95 (48 H, m, Ph), 4.10, 3.87 (24 H, m, CH_2), 2.43 (6 H, s, CH_3), 1.33, 1.05 (36 H, t, CH_3 of phosphite); $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. (CD_2Cl_2) A_2B_2 , $\delta_A = 81.4$ and $\delta_B = 76.6$, $J(\text{AB})$ 43.8 Hz. $[\text{Os}(4\text{-MeOC}_6\text{H}_4\text{N}=\text{NH})_2\{-\text{P}(\text{OEt})_3\}_4][\text{BPh}_4]_2$, m.p. 136°C ; Λ_{M} 119.5 S cm^2 mol^{-1} ; $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2)$ 13.99 (2 H, br, NH), 7.29, 6.94 (48 H, m, Ph), 4.14, 3.87 (24 H, m, CH_2), 3.82 (6 H, s, CH_3), 1.34 and 1.06 (36 H, t, CH_3 of phosphite); $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. (CD_2Cl_2) A_2B_2 , $\delta_A = 81.9$ and $\delta_B = 77.2$, $J(\text{AB})$ 43.8 Hz. $[\text{Os}(\text{PhN}=\text{NH})_2\{\text{PPh}(\text{OEt})_2\}_4][\text{BPh}_4]_2$, m.p. 135°C (decomp.); Λ_{M} 111.5 S cm^2 mol^{-1} ; $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2)$ 13.44 (2 H, br, NH), 7.64, 7.28, 6.93 (70 H, m, Ph), 3.99, 3.54 (16 H, m, CH_2), 1.44 and 0.99 (24 H, t, CH_3). $[\text{Os}(4\text{-MeC}_6\text{H}_4\text{N}=\text{NH})_2\{\text{PPh}(\text{OEt})_2\}_4][\text{BPh}_4]_2$, m.p. 145°C ; Λ_{M} 121.5 S cm^2 mol^{-1} ; $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2)$ 13.26 (2 H, br, NH), 7.63, 7.24, 6.91 (68 H, m, Ph), 3.95, 3.57 (16 H, m, CH_2), 2.40 (6 H, s, CH_3), 1.41 and 0.99 (24 H, t, CH_3 of phosphite); $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. (CD_2Cl_2) A_2B_2 , $\delta_A = 108.5$ and $\delta_B = 105.9$, $J(\text{AB})$ 34.6 Hz. $[\text{Os}(4\text{-MeOC}_6\text{H}_4\text{N}=\text{NH})_2\{\text{PPh}(\text{OEt})_2\}_4][\text{BPh}_4]_2$, m.p. 117°C ; Λ_{M} 121.6 S cm^2 mol^{-1} ; $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2)$ 12.85 (2 H, br, NH), 7.63, 7.29, 6.93 (68 H, m, Ph), 3.83 (16 H, m, CH_2), 3.86 (6 H, s, CH_3), 1.43, 1.04 (24 H, t, CH_3 of phosphite); $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. (CD_2Cl_2) A_2B_2 , $\delta_A = 109.0$ and $\delta_B = 106.4$, $J(\text{AB})$ 34.5 Hz.

$[\text{Os}(\text{PhN}=\text{NH})_2\text{L}_4][\text{BPh}_4]_2$ and $[\text{Os}(\text{Ph}^{15}\text{N}=\text{NH})_2\text{L}_4][\text{BPh}_4]_2$ [$\text{L} = \text{P}(\text{OEt})_3$ or $\text{PPh}(\text{OEt})_2$]. These ^{15}N -labelled complexes were prepared as for the unlabelled ones using the $\text{Ph}^{14}\text{N}=\text{N}^+\text{BF}_4^-$ and $\text{Ph}^{15}\text{N}=\text{N}^+\text{BF}_4^-$ arenediazonium salts, respectively; yield $\geq 85\%$. $[\text{Os}(\text{PhN}=\text{NH})_2\{-\text{P}(\text{OEt})_3\}_4][\text{BPh}_4]_2$, m.p. 132°C ; Λ_{M} 158.0 S cm^2 mol^{-1} (Me_2CO); $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2)$ 14.54 [2 H, d of m, NH, $J(^{15}\text{NH})$ 67.8 Hz], 7.64, 7.29, 6.95 (50 H, m, Ph), 4.10, 3.88 (24 H, m, CH_2), 1.34 and 1.05 (36 H, t, CH_3). $[\text{Os}(\text{Ph}^{15}\text{N}=\text{NH})_2\{-\text{P}(\text{OEt})_3\}_4][\text{BPh}_4]_2$, m.p. 133°C ; Λ_{M} 121.5 S cm^2 mol^{-1} ; $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2)$ 14.54 [2 H, m, $J(^{15}\text{NH})$ 4.1 Hz, NH], 7.63, 7.29, 6.95 (50 H, m, Ph), 4.10, 3.89 (24 H, m, CH_2), 1.34 and 1.05 (36 H, t, CH_3); $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. (CD_2Cl_2) $\text{A}_2\text{BB}'\text{NN}'$, $\delta_A = 81.1$, $\delta_B = \delta_{B'} = 76.2$, $J(\text{AB}) = J(\text{AB}')$ 44.2, $J(\text{AN}) = J(\text{AN}')$ 1.55, $J(\text{BB}')$ 65.0, $J(\text{BN}) = J(\text{B}'\text{N}')$ 6.50, $J(\text{BN}') = J(\text{B}'\text{N})$ 0.64 and $J(\text{NN}')$ 0.1 Hz. $[\text{Os}(\text{PhN}=\text{NH})_2\{\text{PPh}(\text{OEt})_2\}_4][\text{BPh}_4]_2$, m.p. 153°C ; Λ_{M} 117.3 S cm^2 mol^{-1} ; $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2)$ 13.43 [2 H, d of m, $J(^{15}\text{NH})$ 68.2 Hz, NH], 7.63, 7.28, 6.93 (70 H, m, Ph), 3.99, 3.52 (16 H, m, CH_2), 1.43 and 0.99 (24 H, t, CH_3); $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. (CD_2Cl_2) $\text{A}_2\text{BB}'\text{NN}'$, $\delta_A = 108.2$, $\delta_B = \delta_{B'} = 105.6$, $J(\text{AB}) = J(\text{AB}')$ 34.7, $J(\text{AN}) = J(\text{AN}')$ -4.0 , $J(\text{BB}')$ 58.0, $J(\text{BN}) = J(\text{B}'\text{N}')$ 50.0, $J(\text{BN}') = J(\text{B}'\text{N})$ -4.0 , and $J(\text{NN}')$ 0.1 Hz. $[\text{Os}(\text{Ph}^{15}\text{N}=\text{NH})_2\{-\text{PPh}(\text{OEt})_2\}_4][\text{BPh}_4]_2$, m.p. 151°C ; Λ_{M} 115.2 S cm^2 mol^{-1} ; $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2)$ 13.43 [2 H, m, $J(^{15}\text{NH})$ 3.1 Hz, NH], 7.63, 7.28, 6.93 (70 H, m, Ph), 3.99, 3.52 (16 H, m, CH_2), 1.43 and 0.99 (24 H, t, CH_3); $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. (CD_2Cl_2) $\text{A}_2\text{BB}'\text{NN}'$, $\delta_A = 108.2$, $\delta_B = \delta_{B'} = 105.6$, $J(\text{AB}) = J(\text{AB}')$ 34.7, $J(\text{AN}) = J(\text{AN}')$ 1.6, $J(\text{BB}')$ 58.0, $J(\text{BN}) = J(\text{B}'\text{N}')$ 5.5, $J(\text{BN}') = J(\text{B}'\text{N})$ 0.5, and $J(\text{NN}')$ 0.1 Hz.

Table 3. Analytical data for osmium complexes

Compound ^a	Analysis ^b /%		
	C	H	N
[OsH ₂ {P(OEt) ₃ }] ₄	33.45 (33.65)	7.30 (7.30)	—
[OsH ₂ {PPh(OEt) ₂ }] ₄	48.65 (48.75)	6.30 (6.35)	—
[Os(PhN=NH) ₂ {P(OEt) ₃ }] ₄ ²⁺	59.30 (59.15)	6.55 (6.60)	3.10 (3.30)
[Os(PhN=1 ⁵ NH) ₂ {P(OEt) ₃ }] ₄ ²⁺	59.00 (59.10)	6.70 (6.60)	3.15 (3.40)
[Os(Ph ¹⁵ N=NH) ₂ {P(OEt) ₃ }] ₄ ²⁺	59.20 (59.10)	6.70 (6.60)	3.25 (3.40)
[Os(4-MeC ₆ H ₄ N=NH) ₂ {P(OEt) ₃ }] ₄ ²⁺	59.45 (59.60)	6.80 (6.75)	3.00 (3.25)
[Os(4-MeOC ₆ H ₄ N=NH) ₂ {P(OEt) ₃ }] ₄ ²⁺	58.30 (58.50)	6.75 (6.60)	3.05 (3.15)
[Os(4-MeC ₆ H ₄ N=NH)(4-FC ₆ H ₄ N=NH){P(OEt) ₃ }] ₄ ²⁺	57.95 (58.20)	6.65 (6.50)	3.10 (3.20)
[Os(PhN=NH) ₂ {PPh(OEt) ₂ }] ₄ ²⁺	65.60 (65.50)	6.25 (6.15)	3.00 (3.05)
[Os(PhN=1 ⁵ NH) ₂ {PPh(OEt) ₂ }] ₄ ²⁺	65.55 (65.45)	6.20 (6.15)	3.10 (3.15)
[Os(Ph ¹⁵ N=NH) ₂ {PPh(OEt) ₂ }] ₄ ²⁺	65.20 (65.45)	6.20 (6.15)	3.05 (3.15)
[Os(4-MeC ₆ H ₄ N=NH) ₂ {PPh(OEt) ₂ }] ₄ ²⁺	65.15 (65.80)	6.20 (6.30)	2.75 (3.00)
[Os(4-MeOC ₆ H ₄ N=NH) ₂ {PPh(OEt) ₂ }] ₄ ²⁺	64.50 (64.70)	6.20 (6.15)	2.85 (2.95)
[OsH(PhN=NH){P(OEt) ₃ }] ₄ ⁺	50.30 (50.60)	6.95 (6.85)	1.95 (2.20)
[OsH(PhN=1 ⁵ NH){P(OEt) ₃ }] ₄ ⁺	50.45 (50.60)	6.80 (6.85)	2.15 (2.25)
[OsH(4-MeC ₆ H ₄ N=NH){P(OEt) ₃ }] ₄ ⁺	50.85 (51.00)	6.85 (6.95)	2.00 (2.15)
[OsH(PhN=NH){PPh(OEt) ₂ }] ₄ ⁺	59.40 (59.65)	6.10 (6.20)	2.05 (2.00)
[OsH(PhN=1 ⁵ NH){PPh(OEt) ₂ }] ₄ ⁺	59.45 (59.60)	6.20 (6.20)	2.15 (2.05)
[OsH(4-MeC ₆ H ₄ N=NH){PPh(OEt) ₂ }] ₄ ⁺	59.75 (59.90)	6.40 (6.30)	1.80 (1.95)
[Os(4-MeC ₆ H ₄ N=NH)(4-MeC ₆ H ₄ NC){P(OEt) ₃ }] ₄ ²⁺	60.20 (60.40)	6.60 (6.70)	2.40 (2.45)
[Os(4-MeC ₆ H ₄ N=NH)(4-MeC ₆ H ₄ NC){PPh(OEt) ₂ }] ₄ ²⁺	66.60 (66.55)	6.35 (6.25)	2.20 (2.25)
[Os(PhN ₂){P(OEt) ₃ }] ₄ ⁺	50.50 (50.70)	6.55 (6.70)	2.05 (2.20)
[Os(PhN=1 ⁵ N){P(OEt) ₃ }] ₄ ⁺	50.55 (50.65)	6.80 (6.70)	2.10 (2.25)
[Os(4-MeC ₆ H ₄ N ₂){P(OEt) ₃ }] ₄ ⁺	50.95 (51.10)	6.90 (6.80)	2.10 (2.15)
[Os(PhN ₂){PPh(OEt) ₂ }] ₄ ⁺	59.60 (59.75)	6.20 (6.10)	1.90 (2.00)
[Os(PhN=1 ⁵ N){PPh(OEt) ₂ }] ₄ ⁺	59.60 (59.70)	6.15 (6.10)	1.95 (2.05)
[Os(4-MeC ₆ H ₄ N ₂){PPh(OEt) ₂ }] ₄ ⁺	59.75 (60.00)	6.00 (6.15)	1.85 (1.95)
[Os(CF ₃ CO ₂)(4-MeC ₆ H ₄ N=NH){P(OEt) ₃ }] ₄ ⁺	48.50 (48.65)	6.50 (6.30)	1.85 (2.00)
[Os(CF ₃ CO ₂)(4-MeC ₆ H ₄ N=NH){PPh(OEt) ₂ }] ₄ ⁺	56.95 (57.10)	5.80 (5.80)	1.65 (1.80)
[Os(4-MeC ₆ H ₄ N=NH){PPh(OEt) ₂ }] ₄ ²⁺	65.30 (65.50)	6.35 (6.25)	1.50 (1.60)

^a All cationic compounds are BPh₄⁻ salts. ^b Calculated values in parentheses.

[OsH(RN=NH)L₄][BPh₄]⁻ [3; L = P(OEt)₃ or PPh(OEt)₂, R = Ph or 4-MeC₆H₄]. A solution of [OsH₂L₄] (0.1 mmol) in CH₂Cl₂ (10 cm³) was cooled to -20 °C and quickly transferred, at the same temperature, to a reaction flask containing the appropriate diazonium salt (0.1 mmol, ratio 1:1). The temperature of the reaction mixture was brought slowly to 20 °C and the solution was stirred for 2 h. The solvent was removed under reduced pressure, leaving an oil which was treated with ethanol (5 cm³) to give a yellow solution. The addition of NaBPh₄ (0.15 mmol, 0.05 g) afforded a yellow precipitate, which was filtered off and crystallized from ethanol (between +30 and -30 °C); yield ≥ 80%. [OsH(PhN=NH){P(OEt)₃}]₄[BPh₄], m.p. 145 °C; Λ_M 56.1 S cm² mol⁻¹; δ_H(CD₂Cl₂) 14.48 (1 H, br, NH), 7.30, 6.97 (25 H, m, Ph), 4.00 (24 H, m, CH₂), 1.26, 1.25, 1.17 (36 H, t, CH₃), and -8.55 (1 H, m, hydride). [OsH(4-MeC₆H₄N=NH){P(OEt)₃}]₄[BPh₄], m.p. 115 °C; Λ_M 57.6 S cm² mol⁻¹; ν_{max}(MH) 1970 m cm⁻¹ (KBr); δ_H(CD₂Cl₂) 14.33 (1 H, br, NH), 7.27, 6.96 (24 H, m, Ph), 4.00 (24 H, m, CH₂), 2.36 (3 H, s, CH₃), 1.27, 1.25, 1.16 (36 H, t, CH₃ of phosphite), and -8.56 (1 H, m, hydride); ³¹P-{¹H} n.m.r. (CD₂Cl₂) A₂BC, δ_A = 102.5, δ_B = 101.1, and δ_C = 100.0, J(AB) 32.0, J(AC) 44.0, and J(BC) 29.8 Hz. [OsH(PhN=NH){PPh(OEt)₂}]₄[BPh₄], m.p. 107 °C (decomp.); Λ_M 50.5 S cm² mol⁻¹; δ_H(CD₂Cl₂) 14.60 (1 H, br, NH), 7.26, 6.97 (45 H, m, Ph), 3.64 (16 H, m, CH₂), 1.14 (24 H, t, CH₃), and -13.65 [1 H, qnt, J(PH) 19 Hz, hydride]. [OsH(4-MeC₆H₄N=NH){PPh(OEt)₂}]₄[BPh₄], m.p. 113 °C (decomp.); Λ_M 52.6 S cm² mol⁻¹; ν_{max}(MH) 2030 m cm⁻¹ (KBr); δ_H(CD₂Cl₂) 14.42 (1 H, br, NH), 7.25, 6.93 (44 H, m, Ph), 3.63 (16 H, m, CH₂), 2.35 (3 H, s, CH₃), 1.13 (24 H, t, CH₃ of phosphite), and -13.83 [1 H, qnt, J(PH) 18.3 Hz, hydride]; ³¹P-{¹H} n.m.r. (CD₂Cl₂) δ 120.9 (s).

[OsH(PhN=1⁵NH)L₄][BPh₄]⁻ [L = P(OEt)₃, or PPh(OEt)₂].

These complexes were prepared as the non-labelled compounds (3) using the PhN≡1⁵N⁺BF₄⁻ arenediazonium salt; yield ≥ 80%. [OsH(PhN=1⁵NH){P(OEt)₃}]₄[BPh₄], Λ_M 54.3 S cm² mol⁻¹; δ_H(CD₂Cl₂) 14.49 [1 H, d of m, J(¹⁵NH) 66.3 Hz, NH], 7.30, 6.97 (25 H, m, Ph), 3.96 (24 H, m, CH₂), 1.25, 1.17 (36 H, t, CH₃), and -8.55 (1 H, m, hydride). [OsH(PhN=1⁵NH){PPh(OEt)₂}]₄[BPh₄], Λ_M 58.4 S cm² mol⁻¹; ν_{max}(MH) 2020 m cm⁻¹ (KBr); δ_H(CD₂Cl₂) 14.51 [1 H, d of m, J(¹⁵NH) 60.8 Hz, NH], 7.17, 6.88 (45 H, m, Ph), 3.56 (16 H, m, CH₂), 1.06 (24 H, t, CH₃), and -13.74 [1 H, qnt of d, J(PH) 19, J(¹⁵N) 13 Hz, hydride]; ³¹P-{¹H} n.m.r. (CD₂Cl₂) A₄N, δ_A = 120.7, J(AN) 2.0 Hz.

[Os(4-MeOC₆H₄N=NH)(4-FC₆H₄N=NH){P(OEt)₃}]₄[BPh₄]₂. An excess of [4-FC₆H₄N₂][BF₄]⁻ (0.2 mmol, 0.042 g) was added to a solution of [OsH(4-MeOC₆H₄N=NH){P(OEt)₃}]₄[BPh₄] (0.076 mmol, 0.1 g) in CH₂Cl₂ (10 cm³). The reaction mixture was stirred for 2 h and then filtered to remove the unreacted diazonium salt. The solvent was removed leaving a yellow oil which was treated with ethanol containing NaBPh₄ (0.1 mmol, 0.034 g). The yellow solid which separated out after 5–10 min of stirring was crystallized from CH₂Cl₂ (3 cm³) and ethanol (15 cm³); yield ≥ 90%, m.p. 128 °C; Λ_M 117.4 S cm² mol⁻¹; δ_H(CD₂Cl₂) 14.47, 13.88 (2 H, br, NH), 7.29, 6.94 (48 H, m, Ph), 4.13, 3.90 (24 H, m, CH₂), 3.81 (3 H, s, CH₃), 1.34, 1.32, and 1.05 (36 H, t, CH₃ of phosphite); ³¹P-{¹H} n.m.r. (CD₂Cl₂) A₂BC, δ_A = 81.5, δ_B = 77.1, and δ_C = 76.1, J(AB) 42.2, J(AC) 46.2, and J(BC) 41.0 Hz.

[Os(4-MeC₆H₄N=NH)(4-MeC₆H₄NC)L₄][BPh₄]₂ [4; L = P(OEt)₃, or PPh(OEt)₂]. An excess of 4-tolyl isocyanide (0.3 mmol, 35 μl) was added to a 1,2-dichloroethane solution (10 cm³) of [Os(4-MeC₆H₄N=NH)₂L₄][BPh₄]₂ (0.1 mmol) and the reaction mixture was refluxed for 8 h. The solvent was removed under reduced pressure, leaving a brown oil which was

trituated with ethanol (10 cm³) to afford a pale yellow solid after 10–20 min. Crystallization from CH₂Cl₂ (3 cm³) and ethanol (10 cm³) gave pale yellow microcrystals of the complexes; yield ≥80%. [Os(4-MeC₆H₄N=NH)(4-MeC₆H₄NC){P(OEt)₃}₄][BPh₄]₂, m.p. 155 °C; Λ_M 117.1 S cm² mol⁻¹; δ_H(CD₂Cl₂) 13.73 (1 H, m, NH), 7.29, 6.95 (48 H, m, Ph), 4.01 (24 H, m, CH₂), 2.42, 2.41 (6 H, s, CH₃), 1.34, 1.33, and 1.14 (36 H, t, CH₃ of phosphite). [Os(4-MeC₆H₄N=NH)(4-MeC₆H₄NC){PPh(OEt)₂}₄][BPh₄]₂, m.p. 143 °C; Λ_M 109.2 S cm² mol⁻¹; δ_H(CD₂Cl₂) 13.05 (1 H, m, NH), 7.64, 7.28, 6.93 (68 H, m, Ph), 3.79 (16 H, m, CH₂), 2.43, 2.36 (6 H, s, CH₃), 1.43, 1.29, and 0.93 (24 H, t, CH₃ of phosphite).

[Os(RN₂)L₄][BPh₄]₂ [5; L = P(OEt)₃ or PPh(OEt)₂, R = Ph or 4-MeC₆H₄]. Triethylamine (0.2 mmol, 28 μl) was added to a solution of [Os(RN=NH)₂L₄][BPh₄]₂ (0.1 mmol) in CH₂Cl₂ (4 cm³) and the reaction mixture was stirred for 2.5 h. A white precipitate of [NEt₃H]BPh₄ began to separate out after 10–15 min and was later filtered off, and the solution was evaporated to dryness. The oil obtained was treated with ethanol (3 cm³) to give an orange solution, which was allowed to stand overnight at 5 °C. The solid obtained was filtered off, and the remaining solution cooled to -30 °C to give yellow crystals of the aryldiazenido complex; yield ≥75%. [Os(PhN₂){P(OEt)₃}₄][BPh₄], Λ_M 54.5 S cm² mol⁻¹; δ_H(CD₂Cl₂) 7.35, 6.99 (25 H, m, Ph), 4.02 (24 H, m, CH₂), 1.31 and 1.26 (36 H, t, CH₃ of phosphite). [Os(4-MeC₆H₄N₂){P(OEt)₃}₄][BPh₄], m.p. 95 °C (decomp.); Λ_M 58.7 S cm² mol⁻¹; ν_{max}(NN) 1 638s (KBr), 1 640s cm⁻¹ (CH₂Cl₂); δ_H(CD₂Cl₂) 7.31, 6.97 (24 H, m, Ph), 4.05 (24 H, m, CH₂), 2.42 (3 H, s, CH₃), 1.31, 1.15 (36 H, t, CH₃ of phosphite); ³¹P-{¹H} n.m.r. (CD₂Cl₂, at -65 °C) ABC₂, δ_A = 104.8, δ_B = 102.3, and δ_C = 93.2, J(AB) 45.4, J(AC) 39.8, and J(BC) 37.8 Hz. [Os(PhN₂){PPh(OEt)₂}₄][BPh₄], Λ_M 57.2 S cm² mol⁻¹; δ_H(CD₂Cl₂) 7.30, 6.97 (45 H, m, Ph), 3.63 (16 H, m, CH₂), 1.26, 1.14 (24 H, t, CH₃ of phosphite). [Os(4-MeC₆H₄N₂){PPh(OEt)₂}₄][BPh₄], m.p. 78 °C (decomp.); Λ_M 59.2 S cm² mol⁻¹; ν_{max}(NN) 1 630s (KBr), 1 635s cm⁻¹ (CH₂Cl₂); δ_H(CD₂Cl₂) 7.35, 6.99 (44 H, m, Ph), 3.65 (16 H, m, CH₂), 2.45 (3 H, s, CH₃), 1.18, 1.07 (24 H, t, CH₃ of phosphite); ³¹P-{¹H} n.m.r. (CD₂Cl₂, at -65 °C) ABC₂, δ_A = 121.4, δ_B = 120.5, and δ_C = 111.3, J(AB) 45.0, J(AC) 28.0, and J(BC) 32.0 Hz.

[Os(PhN≡¹⁵N)L₄][BPh₄]₂ [L = P(OEt)₃ or PPh(OEt)₂]. These complexes were prepared exactly as for the corresponding unlabelled complexes starting from the [Os(PhN≡¹⁵NH)₂L₄][BPh₄]₂ derivatives. [Os(PhN≡¹⁵N){P(OEt)₃}₄][BPh₄], Λ_M 58.2 S cm² mol⁻¹; δ_H(CD₂Cl₂) 7.31, 6.98 (25 H, m, Ph), 4.06 (24 H, m, CH₂), 1.31 and 1.15 (36 H, t, CH₃). [Os(PhN≡¹⁵N){PPh(OEt)₂}₄][BPh₄], Λ_M 60.0 S cm² mol⁻¹; ν_{max}(N≡¹⁵N) 1 622s cm⁻¹ (CH₂Cl₂); δ_H(CD₂Cl₂) 7.29, 6.98 (45 H, m, Ph), 3.62 (16 H, m, CH₂), 1.28 and 1.19 (24 H, t, CH₃); ³¹P-{¹H} n.m.r. (CD₂Cl₂, at -65 °C) ABC₂N, δ_A = 121.3, δ_B = 120.3, and δ_C = 110.5, J(AB) 25.1, J(AC) 25.0, J(AN) 25.0, J(BC) 30.0, J(BN) 31.0, and J(CN) 7.8 Hz.

[Os(CF₃CO₂)(4-MeC₆H₄N=NH)L₄][BPh₄]₂ [6; L = P(OEt)₃ or PPh(OEt)₂]. Trifluoroacetic acid (0.2 mmol, 15 μl) was added to a dichloromethane solution (10 cm³) of [Os(4-MeC₆H₄N₂)L₄][BPh₄]₂ (0.1 mmol) and the reaction mixture was stirred for 1 h. After removal of the solvent at reduced pressure, the oil obtained was treated with ethanol containing NaBPh₄ (0.1 mmol, 0.034 g) to give a yellow solid which was filtered off and crystallized from CH₂Cl₂ (3 cm³) and diethyl ether; yield ≥85%. [Os(CF₃CO₂)(4-MeC₆H₄N=NH){P(OEt)₃}₄][BPh₄], m.p. 138 °C; Λ_M 66.9 S cm² mol⁻¹; δ_H(CD₂Cl₂) 16.66 (1 H, m, NH), 7.30, 6.97 (24 H, m, Ph), 4.04

(24 H, m, CH₂), 2.40 (3 H, s, CH₃), 1.30, 1.25, and 1.16 (36 H, t, CH₃ of phosphite). [Os(CF₃CO₂)(4-MeC₆H₄N=NH){PPh(OEt)₂}₄][BPh₄], m.p. 139 °C; Λ_M 53.8 S cm² mol⁻¹; δ_H(CD₂Cl₂) 16.07 (1 H, m, NH), 7.48, 7.23, 6.95 (44 H, m, Ph), 3.73 (16 H, m, CH₂), 2.36 (3 H, s, CH₃), 1.33, 1.28, and 1.15 (24 H, t, CH₃ of phosphite).

[Os(4-MeC₆H₄N=NH){PPh(OEt)₂}₄][BPh₄]₂ (7). A slight excess of HBF₄ (30 μl of ca. 54% Et₂O solution, ca. 0.21 mmol) was added to a cooled (-5 °C) solution of [Os(4-MeC₆H₄N₂){PPh(OEt)₂}₄][BPh₄]₂ (0.14 mmol, 0.2 g) in dichloromethane (10 cm³). The reaction mixture was brought to room temperature in 10–15 min, stirred for another 30 min, and then evaporated to dryness. The oil obtained was trituated with ethanol (10 cm³) containing NaBPh₄ (0.28 mmol, 0.096 g) to give an orange solid which was crystallized from CH₂Cl₂ (4 cm³) and ethanol; yield ≥75%; Λ_M 115.6 S cm² mol⁻¹; δ_H(CD₂Cl₂) 12.92 (1 H, m, NH), 7.41, 6.95, 6.35 (64 H, m, Ph), 3.80 (16 H, m, CH₂), 2.31 (3 H, s, CH₃), 1.43, 1.23, and 1.18 (24 H, t, CH₃ of phosphite).

The compound [Os(4-MeC₆H₄N₂){P(OEt)₃}₄][BPh₄]₂ also reacts with HBF₄ in CH₂Cl₂ to give a diazene complex (¹H n.m.r. spectroscopy), but in this case a pure compound was not isolated.

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