Dalton Transactions

PAPER

Cite this: *Dalton Trans.*, 2018, **47**, 11658

Preparation and reactivity of half-sandwich organic azide complexes of osmium†

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Received 31st May 2018,
Accepted 2nd August 2018

DOI: 10.1039/c8dt02230e

rsc.li/dalton

Organic azide complexes $[Os(\eta^5\text{-}C_5H_5)(\kappa^1\text{-}N_3R)(PPh_3)\{P(OR1)_3\}]BPh_4$ (**1**, **2**) [R = $CH_2C_6H_5$ (**a**), $CH_2C_6H_4\text{-}4\text{-}CH_3$ (**b**), $CH(CH_3)C_6H_5$ (**c**), C_6H_5 (**d**); R1 = Me (**1**), Et (**2**)] were prepared by allowing bromo-compounds $[OsBr(\eta^5\text{-}C_5H_5)(PPh_3)\{P(OR1)_3\}]$ to react first with AgOTf and then with an excess of azide in toluene. Benzylazide complexes reacted in solution leading to imine derivatives $[Os(\eta^5\text{-}C_5H_5)\{\kappa^1\text{-}NH{=}C(R2)Ar\}(PPh_3)\{P(OR1)_3\}]BPh_4$ (**3**, **4**) [R2 = H (**a**, **b**), CH_3 (**c**); Ar = C_6H_5, $C_6H_4\text{-}4\text{-}CH_3$; R1 = Me (**3**), Et (**4**)]. Phenylazide, on the other hand, reacted in solution affording the dinuclear dinitrogen complex $[\{Os(\eta^5\text{-}C_5H_5)(PPh_3)[P(OMe)_3]\}_2(\mu\text{-}N_2)](BPh_4)_2$ (**5**). Depending on the nature of the R substituent, the reaction of the *p*-cymene complex $[OsCl_2(\eta^6\text{-}p\text{-cymene})(PPh_3)\{P(OEt)_3\}]$ with RN_3 yielded imine $[OsCl(\eta^6\text{-}p\text{-cymene})\{\kappa^1\text{-}NH{=}C(H)Ar\}\{P(OEt)_3\}]BPh_4$ (**6**) (Ar = $C_6H_4\text{-}4\text{-}CH_3$) and amine derivatives $[OsCl(\eta^6\text{-}p\text{-cymene})(\kappa^1\text{-}NH_2C_6H_5)\{P(OEt)_3\}]BPh_4$ (**7**). The complexes were characterised spectroscopically (IR, ^1H, ^{31}P, ^{15}N NMR) and by the X-ray crystal structure determination of $[\{Os(\eta^5\text{-}C_5H_5)(PPh_3)[P(OMe)_3]\}_2(\mu\text{-}N_2)](BPh_4)_2$ (**5**).

Introduction

Organic azides are reported to react with transition metal complexes to give metal imido derivatives.[1–4] Generally, the interaction of RN_3 with a metal complex leads to a transient M–N_3R species, which subsequently may extrude N_2 to give a terminal M=NR derivative.[2,4] However, in some cases, the metal κ^1-N_3R intermediate results stable and can be isolated as a metal complex and characterised.[5–9] Although there is significant interest in these intermediates, their isolation and characterisation is difficult and stable metal complexes containing organic azide ligands are rare.[5–9] Examples include V(v), Fe(ii), Ta(v) and W(v) mononuclear derivatives[5] containing the bent moiety NNN **[A]** (Chart 1); Cu(i), Ag(i), Pd(ii) and Ir(iii) derivatives[6,7a] with "linear" organoazide ligands **[B]** and **[C]**; and a Ni(0) complex[8] with η^2-coordination of the RN_3 ligand **[E]**. A mixed-metallic Zr(iv)–Ir(iii) complex, containing a bridging PhNNN group **[D]**, is also reported.[9]

We have a long-standing interest in the chemistry of diazo and triazo complexes of transition metals and have previously reported on the synthesis and reactivity of the hydrazine, diazene, diazenide, triazene and diazoalkane derivatives of Mn[10] and Fe[11] triads. More recently, we have also given an account of the first benzylazide complexes of iridium(iii)[7] and osmium(ii)[12] stabilised by phosphites $P(OR)_3$ or mixed-ligand PPh_3-$P(OR)_3$ as the supporting ligands. These studies have now been extended to half-sandwich fragments to test whether stable organic azide complexes can be prepared. The results of these studies, which allowed the preparation of new azide complexes of osmium, are reported here.

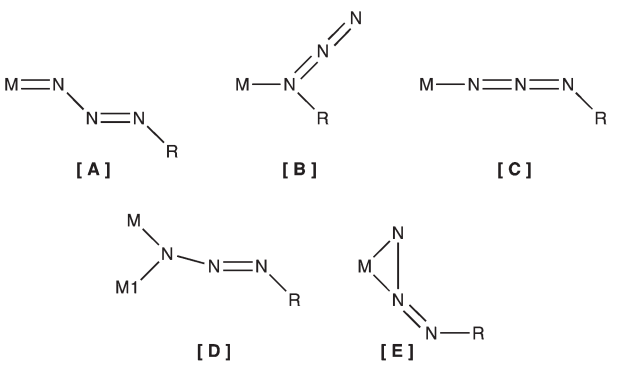

Chart 1

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†Electronic supplementary information (ESI) available. CCDC 1846339. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8dt02230e

Results and discussion

Cyclopentadienyl complexes

Half-sandwich organic azide complexes of osmium $[Os(\eta^5\text{-}C_5H_5)(\kappa^1\text{-}N_3R)(PPh_3)\{P(OR1)_3\}]BPh_4$ (**1**, **2**) were prepared by reacting bromo-compounds $[OsBr(\eta^5\text{-}C_5H_5)(PPh_3)\{P(OR1)_3\}]$ first with AgOTf and then with an excess of the appropriate azide in toluene, as shown in Scheme 1.

The reaction of bromo-compounds $[OsBr(\eta^5\text{-}C_5H_5)(PPh_3)\{P(OR1)_3\}]$ with AgOTf proceeds with the separation of solid AgBr and the formation of triflato complexes $[Os(\kappa^1\text{-}OTf)(\eta^5\text{-}C_5H_5)(PPh_3)\{P(OR1)_3\}]$, which were not separated. The treatment of this species with an excess of organic azide RN_3 afforded azide derivatives $[Os(\eta^5\text{-}C_5H_5)(\kappa^1\text{-}N_3R)(PPh_3)\{P(OR1)_3\}]OTf$, which separated out from their toluene solutions as dark-green gummy products. The related tetraphenylborate salts $[Os(\eta^5\text{-}C_5H_5)(\kappa^1\text{-}N_3R)(PPh_3)\{P(OR1)_3\}]BPh_4$ (**1**, **2**) were obtained as solids by treating the triflate species with an excess of $NaBPh_4$ in ethanol. Also, the related bis(triphenylphosphine) complex $[OsBr(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ does not give any azide complex after treatment first with AgOTf and then with an excess of organic azide and is worth noting. Therefore, it seems that only mixed-ligand fragments $[Os(\eta^5\text{-}C_5H_5)(PPh_3)\{P(OR1)_3\}]$ can stabilise the $[Os]\text{-}\kappa^1\text{-}N_3R$ derivatives.

Azide complexes $[Os(\eta^5\text{-}C_5H_5)(\kappa^1\text{-}N_3R)(PPh_3)\{P(OR1)_3\}]BPh_4$ (**1**, **2**) are green solids stable in air but rather unstable in a solution of polar organic solvents, where they behave as 1 : 1 electrolytes.[13] Analytical and spectroscopic data (IR, ^1H, ^{15}N, ^{31}P NMR) support the proposed formulation.

The IR spectra of complexes **1** and **2** show a medium-intensity band at 2164–2145 cm^{-1}, attributed to ν_{N_3} of the coordinate azide ligand. Support for this attribution comes from the spectra of the labelled compounds $[Os(\eta^5\text{-}C_5H_5)(\kappa^1\text{-}^{15}N_3R)(PPh_3)\{P(OR1)_3\}]BPh_4$ (**1b$_1$**, **2b$_1$**, and **1c$_1$**), which show the $\nu_{^{15}N_3}$ at 2117–2105 cm^{-1} shifted to a lower wavenumber by 30–50 cm^{-1} with respect to unlabelled compounds **1b**, **2b** and **1c** (Fig. 1; ESI, Fig. S1 and S2†).

In addition, the high ν_{N_3} values of our complexes, compared to those of azide complexes, the X-ray structures of which are known,[6,7a] suggest the κ^1-diazoamino coordination mode (Scheme 2) of the azide ligand.

Further support for the coordination of the azide is given by the ^{15}N NMR spectra of the labelled complexes $[Os(\eta^5\text{-}C_5H_5)(\kappa^1\text{-}^{15}N_3R)(PPh_3)\{P(OR1)_3\}]BPh_4$ (**1b$_1$** and **1c$_1$**). These show a multiplet between 139 and 117 ppm and a singlet near 213 ppm, attributed to the Nγ and Nα nitrogen nuclei, respectively, of the coordinate $^{15}N_3R$ group. The ^{31}P NMR of the labelled complexes **1b$_1$**, **2b$_1$** and **1c$_1$** also support the coordination of the azide, showing a multiplet due to coupling with the ^{15}N nuclei of $\kappa^1\text{-}^{15}N_3R$, which can be simulated using an AXN model (A, X = ^{31}P; N = ^{15}N) with the parameters reported in the Experimental section. The good fit between the experimental and calculated spectra further supports the presence of the coordinated azide.

In addition to the resonances of the substituents of the organic azides RN_3, the ^1H NMR spectra of **1**, **2** show the characteristic signals of the ancillary ligands $\eta^5\text{-}C_5H_5$, PPh_3, and $P(OR1)_3$ and of the BPh_4^- anion, in agreement with the half-sandwich geometry shown in Scheme 1.

Transition metal complexes containing organic azides RN_3 as ligands are rare[5–9] and only one example is known for osmium,[12] $[OsCl(\eta^1\text{-}N_3CH_2Ar)(CO)(PPh_3)_2\{P(OR)_3\}]BPh_4$, involving carbonyl and phosphines as the supporting ligands. The use of the half-sandwich fragment $[Os(\eta^5\text{-}C_5H_5)(PPh_3)\{P(OR1)_3\}]^+$

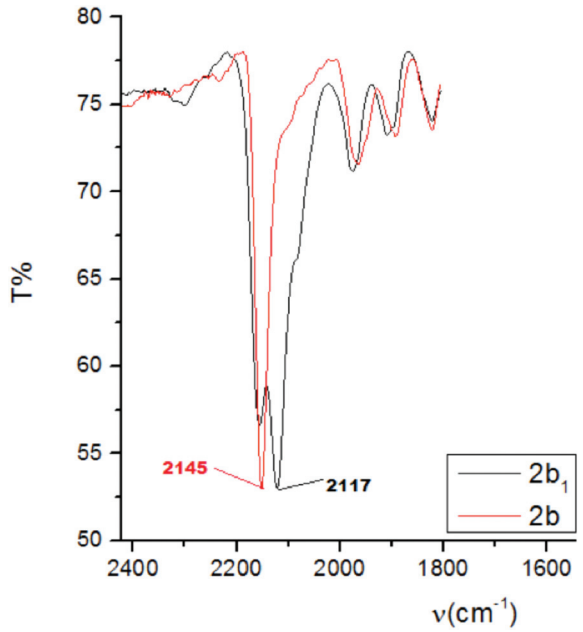
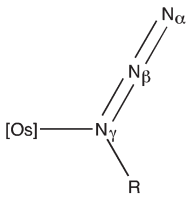
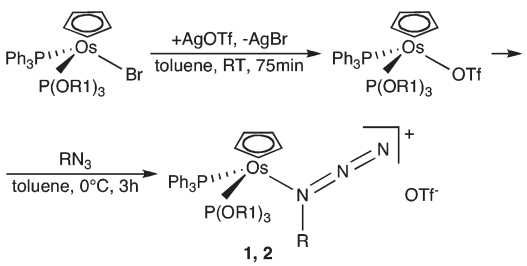


Fig. 1 IR spectra in KBr of the labelled $[Os(\eta^5\text{-}C_5H_5)(\kappa^1\text{-}^{15}N_3CH_2C_6H_4\text{-}4\text{-}CH_3)(PPh_3)\{P(OEt)_3\}]BPh_4$ (**2b$_1$**) and unlabelled compound $[Os(\eta^5\text{-}C_5H_5)(\kappa^1\text{-}N_3CH_2C_6H_4\text{-}4\text{-}CH_3)(PPh_3)\{P(OEt)_3\}]BPh_4$ (**2b**).



Scheme 2



Scheme 1 R = $CH_2C_6H_5$ (**a**), $CH_2C_6H_4\text{-}4\text{-}CH_3$ (**b**), $CH(CH_3)C_6H_5$ (**c**), C_6H_5 (**d**); R1 = Me (**1**), Et (**2**).

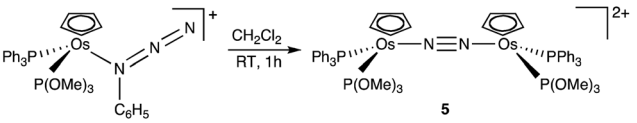
allows new stable organic azide complexes to be prepared. Unfortunately, the bonding mode of the RN_3 in our compounds **1** and **2** could not be established by X-ray determination, owing to their instability in solution, which prevented the preparation of suitable crystals. However, IR data offer information suggesting linear Nγ coordination (Scheme 2). Values for ν_{N_3} (2164–2145 cm^{-1}) higher than those of free RN_3 were found in our complexes **1** and **2** and in those of Ir, Pd, Cu, and Ag, in which Nγ coordination was confirmed by X-ray crystal structure determination. Such coordination through substituted Nγ is favoured by the greater Lewis basicity[14] of the site and is probably the most common type of azide complex with linear NNN geometry.

Azide complexes $[Os(\eta^5\text{-}C_5H_5)(\kappa^1\text{-}N_3CH_2Ar)(PPh_3)\{P(OR1)_3\}]BPh_4$ and $[Os(\eta^5\text{-}C_5H_5)\{\kappa^1\text{-}N_3CH(CH_3)C_6H_5\}(PPh_3)\{P(OR1)_3\}]BPh_4$ (**1a–c**, **2a–c**) are stable as solids but react slowly in solution to give new compounds, characterised as the imine species $[Os(\eta^5\text{-}C_5H_5)\{\kappa^1\text{-}NH{=}C(H)Ar\}(PPh_3)\{P(OR1)_3\}]BPh_4$ and $[Os(\eta^5\text{-}C_5H_5)\{\kappa^1\text{-}NH{=}C(CH_3)C_6H_5\}(PPh_3)\{P(OR1)_3\}]BPh_4$ (**3**, **4**) (Scheme 3).

The extrusion of N_2 in the cooordinated azide complexes **1** and **2** followed by the 1,2-shift of one hydrogen atom may lead to the formation of the imino derivatives **3** and **4**. Both the *cis* and *trans* isomers of the imine ligand are formed in the reaction of (1-azidoethyl)benzene derivatives **1c** and **3c** in approximately a 1 : 4 ratio, whereas, with the benzylazide, only *trans* isomers **3a,b** and **4a,b** are formed.

Surprisingly, the phenylazide complex $[Os(\eta^5\text{-}C_5H_5)(N_3Ph)(PPh_3)\{P(OMe)_3\}]BPh_4$ (**1d**) is also unstable in solution, affording a moderate yield of a blue solid characterised as a dinuclear μ-dinitrogen complex of the type $[\{Os(\eta^5\text{-}C_5H_5)(PPh_3)[P(OMe)_3]\}_2(\mu\text{-}N_2)](BPh_4)_2$ (**5**) (Scheme 4).

The formation of the $\mu\text{-}N_2$ complex is not, in part, unexpected because the decomposition of the coordinated azide with the extrusion of N_2 cannot give an imine owing to the absence of appropriate hydrogen atoms adjacent to the coordinate nitrogen. Therefore, the fragment $[Os(\eta^5\text{-}C_5H_5)(PPh_3)\{P(OMe)_3\}]^+$ does coordinate either C_6H_5N giving imido $[Os]{=}NC_6H_5$, or N_2 affording dinuclear $\mu\text{-}N_2$ (**5**) as the final product. Alternatively, the formation of the dinitrogen complex may be explained on the basis of the mechanism depicted in Scheme 5,[5e] previously proposed for the formation of the nitrene complexes of vanadium.



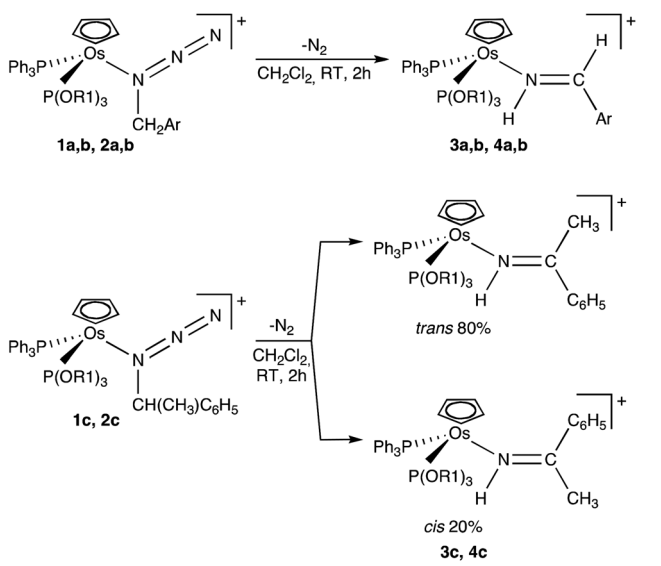
Scheme 4

Loss of nitrene may occur directly from the azide complex **1d** (or an isomer thereof) affording a dinitrogen intermediate (**I**), which then dimerises to give **5**. Also the nitrene fragments thus generated may dimerise to give diazene $C_6H_5N{=}NC_6H_5$ as a final product.

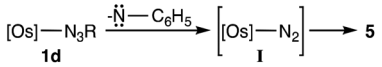
The formation of **5** highlights the greater avidity of the fragment $[Os(\eta^5\text{-}C_5H_5)(PPh_3)\{P(OMe)_3\}]^+$ for the dinitrogen molecule allowing the preparation of new $\mu\text{-}N_2$ complexes. In addition, whatever may be the mechanism, the formation of **5** is interesting and has no precedents in azide derivative reactions.

Both imine complexes $[Os(\eta^5\text{-}C_5H_5)\{\kappa^1\text{-}NH{=}C(H)Ar\}(PPh_3)\{P(OR1)_3\}]BPh_4$ and $[Os(\eta^5\text{-}C_5H_5)\{\kappa^1\text{-}NH{=}C(CH_3)C_6H_5\}(PPh_3)\{P(OR1)_3\}]BPh_4$ (**3**, **4**) and the dinitrogen derivative $[Os(\eta^5\text{-}C_5H_5)(PPh_3)\{P(OMe)_3\}_2(\mu\text{-}N_2)](BPh_4)_2$ (**5**) were separated as green-yellow (**3**, **4**) or blue (**5**) solids, stable in air and in solution of polar organic solvents, where they behave as 1 : 1 (**3**, **4**) or 2 : 1 (**5**) electrolytes.[13] Analytical and spectroscopic data (IR, ^1H, ^{31}P, ^{15}N NMR) support the proposed formulation, which is further confirmed by X-ray crystal structure determination of the $\mu\text{-}N_2$ complex $[\{Os(\eta^5\text{-}C_5H_5)(PPh_3)[P(OMe)_3]\}_2(\mu\text{-}N_2)](BPh_4)_2$ (**5**), the ORTEP[15] of which is shown in Fig. 2.

The asymmetric unit contains a tetraphenylborate anion, a dichloromethane solvent molecule and one half of the osmium cation complex so that the whole cation contains two symmetrically related osmium atoms in a half-sandwich piano-stool coordination. Each is bonded by one cyclopentadienyl (Cp), one $P(OMe)_3$ phosphite, one PPh_3 phosphine and one bridging N–N′-dinitrogen ligand, where the last ligand presents the inversion centre in the middle of the N–N bond. The overall geometry of the half-sandwich piano-stool complex is a slightly distorted octahedral and is marked by the angles between the centroid of the Cp ligand (Ct1) and the legs close



Scheme 3 Ar = C_6H_5 (**a**), 4-$CH_3C_6H_4$ (**b**).



Scheme 5 [Os] = $[Os(\eta^5\text{-}C_5H_5)(PPh_3)\{P(OMe)_3\}]^+$.

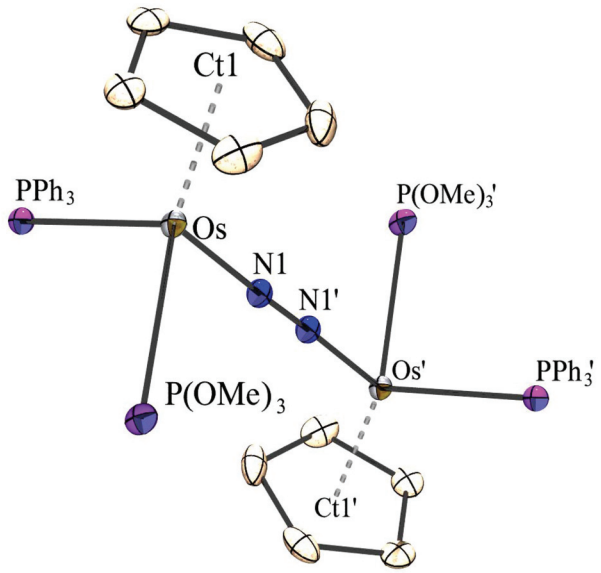


Fig. 2 Molecular structure of **5**.

to the theoretical 125.3°, or by near 90° values for angles formed by the legs of the piano-stool (see Table 1). The two $OsCpP_2$ fragments are rotated about the Os–Os vector by 180°. Coordination of the Cp ligand (ring-slippage, 0.025 Å) with Os–C distances between 2.229(4) and 2.260(4) Å (average, 2.244 Å) do not require further comments as they are similar, for example, to those found in the cation $[CpOs(=C=CH_2)(PPh_3)_2]^+$, Os–C(Cp) 2.25–2.30(2), av. 2.27 Å.[16] The Os–P distances are 2.261(1) and 2.342(1), longer than that of the phosphine ligand, but with less back-bonding than the phosphite ligand. The bond length Os–N(1), 1.957(3) Å, is quite similar to those found for the Os(II) cation $[\{(\mu\text{-}N_2)Cp^*Os(Me_3P)_2\}_2]^{2+}$, 1.959(8) and 1.979(7) Å,[17] and slightly longer than those found in mixed-valence (II + III) CpOs complexes, between 1.883(6) and 1.895(5) Å.[18] The N–N bond length, 1.116(6) Å is, however, shorter than those found in the above-mentioned compounds and, namely, between 1.135(6) and 1.165(8) Å. Conversely, the Os–N–N angle, 177.2(4)°, is more linear than the one found in the above-mentioned complexes (around 170°) or even in the ruthenium analogous complex $[\{(\mu\text{-}N_2)CpRu(PEt_3)_2\}_2]^{2+}$.[19]

Table 1 Selected bond lengths [Å] and angles [°] for **5**

Os–CT1	1.8918(3)	Os–P(1)	2.3416(10)
Os–P(2)	2.2611(10)	Os–N(1)	1.957(3)
Os–C(1)	2.235(4)	Os–C(2)	2.236(4)
Os–C(4)	2.262(4)	Os–C(3)	2.229(4)
Os–C(5)	2.260(4)	Os–C_{av}	2.244(4)
N(1)–N(1^i)	1.116(6)		
CT1–Os–N(1)	126.05(9)	CT1–Os–P(2)	123.98(3)
N(1)–Os–P(2)	88.26(9)	CT1–Os–P(1)	123.31(2)
N(1)–Os–P(1)	89.76(9)	P(2)–Os–P(1)	95.43(3)
N(1^i)–N(1)–Os	177.2(4)		

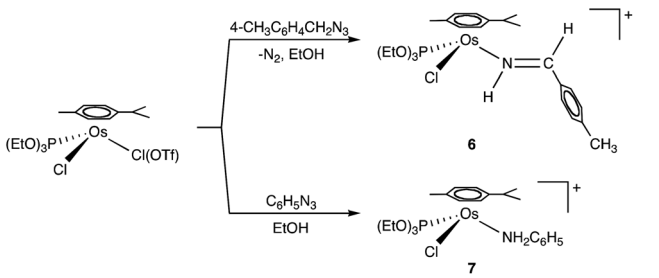
Symmetry transformations used to generate equivalent atoms: i: $1-x$; $1-y$, $2-z$.

The IR spectra of the imine complexes **3** and **4** show a medium-intensity band at 3260–3282 cm^{-1}, attributed to the ν_{NH} of the imine ligand. Its presence is confirmed by ^1H NMR spectra which, in monosubstituted species [Os]–NH=C(H)Ar (**3a**, **3b**, **4a**, **4b**), show a slightly broad doublet between 10.16 and 10.79 ppm, attributed to the NH imine resonance. This attribution is supported by the spectra of the labelled complexes [Os]–^{15}NH=C(H)Ar (**3b$_1$**, **4b$_1$**) (ESI, Fig. S3†), which show a doublet of multiplets due to the coupling of the H imine with the =C(H) proton and the ^{31}P and the ^{15}N nuclei.

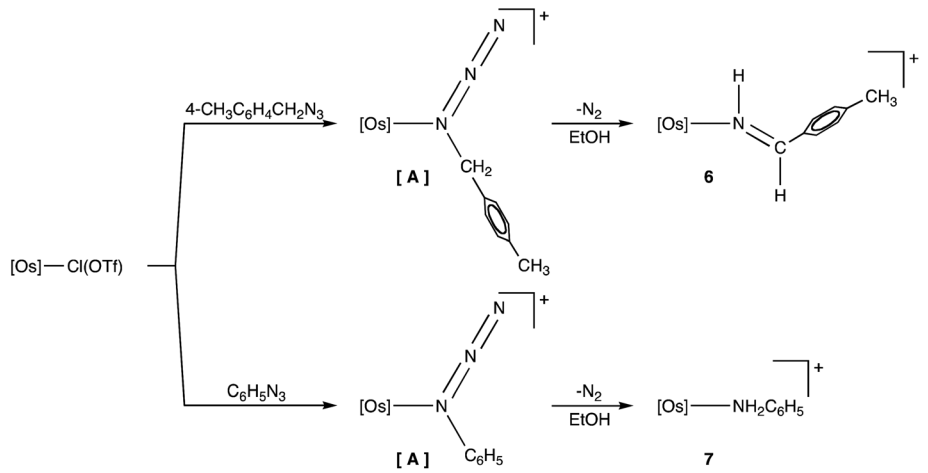
These spectra may be simulated using an AXNYZ model (A, X = ^{31}P; N = ^{15}N; Y, Z = ^1H) with the parameters reported in the Experimental section and a good fit between the calculated and experimental spectra (ESI, Fig. S3†) strongly supports the proposed attribution. Noticeably, a doublet between 8.41 and 8.80 ppm also appears in the spectra, which is correlated with the doublet at 10.16–10.79 ppm of the NH proton in a COSY experiment and was attributed to the =C(H) of the imine.

In the temperature range between +20 and −80 °C, the ^{31}P NMR spectra of the imine derivatives **3a**, **3b**, **4a** and **4b** are AX quartets, whereas those of the labelled compounds **3b$_1$** and **4b$_1$** appear as AXN multiplets (N = ^{15}N). In addition, the proton-coupled ^{15}N NMR spectra are doublets of multiplets that have been simulated by use of an AXNYZ model with the parameters reported in the Experimental section. The good fit between the calculated and the experimental spectra supports the proposed half-sandwich piano-stool geometry of the type depicted in Scheme 1 for our imine complexes.

The ^1H NMR spectra of the complexes $[Os(\eta^5\text{-}C_5H_5)\{\kappa^1\text{-}NH{=}C(CH_3)C_6H_5\}(PPh_3)\{P(OR1)_3\}]BPh_4$ (**3c**, **4c**) show two broad signals between 10.46 and 9.98 ppm, which may be attributed to the NH imine protons of the two isomers *cis* and *trans* (Scheme 3) present in the sample. This attribution is supported by the ^1H NMR spectra of the labelled complexes $[Ru(\eta^5\text{-}C_5H_5)\{\kappa^1\text{-}^{15}NH{=}C(CH_3)C_6H_5\}(PPh_3)\{P(OR1)_3\}]BPh_4$ (**3c$_1$**, **4c$_1$**). These show two multiplets centred on the same chemical shift of the unlabelled species (ESI, Fig. S4†) and may be simulated by the use of two $AXNYZ_3$ models (A, X = ^{31}P; N = ^{15}N; Y, Z = ^1H) (see the Experimental section). The good fit between the experimental and calculated spectra strongly supports the presence of the two species having either *cis*-imine or *trans*-imine as a ligand. NOESY and COSY experiments are used to attribute the geometry of the two isomers.



Scheme 6



Scheme 7 [Os] = [OsCl(η^6-*p*-cymene){P(OEt)$_3$}]$^+$.

The proton-coupled ^{15}N NMR spectra of the two complexes **3c$_1$** and **4c$_1$** show two doublets of multiplets (ESI, Fig. S5†), as well as those of ^{31}P{^{1}H}, which fit the proposed formulation for the complexes.

p-Cymene derivatives

The results obtained from the reaction of the cyclopentadienyl complexes of Os with the organic azide prompted us to extend our study to other half-sandwich derivatives such as [OsBr(η^5-C$_5$Me$_5$)(PPh$_3$){P(OR1)$_3$}] and [OsCl$_2$(η^6-*p*-cymene)(PPh$_3$){P(OEt)$_3$}]. While the reaction of pentamethylcyclopentadienyl derivatives with the organic azide does not give any clear and reproducible results, *p*-cymene complexes quickly react with the organic azide, but do not afford κ^1-azide derivatives (Scheme 6).

Depending on the nature of the substituents, the reaction of both dichloro and chloro-triflate *p*-cymene derivatives [OsCl$_2$(η^6-*p*-cymene)(PPh$_3$){P(OEt)$_3$}] and [OsCl(κ^1-OTf)(η^6-*p*-cymene)(PPh$_3$){P(OEt)$_3$}] with organic azides affords the κ^1-imine complex [OsCl(η^6-*p*-cymene){κ^1-NH=C(H)C$_6$H$_4$-4-CH$_3$}{P(OEt)$_3$}]BPh$_4$ (**6**) and κ^1-amine derivative [OsCl(η^6-*p*-cymene)(κ^1-NH$_2$C$_6$H$_5$){P(OEt)$_3$}]BPh$_4$ (**7**). In any case, no evidence of the formation of κ^1-azide complexes was detected with the *p*-cymene derivatives. However, based on our previous results, we can hypothesise that organic azide RN$_3$ substitutes the Cl$^-$ or OTf$^-$ ligand in the *p*-cymene precursors, affording the κ^1-azide derivative [OsCl(η^6-*p*-cymene)(κ^1-N$_3$R){P(OEt)$_3$}]BPh$_4$ **[A]** (Scheme 7). This intermediate is probably unstable and can give, in the case of *p*-tolylbenzylazide, the κ^1-imine derivative **6**.

Instead, in the presence of ethanol, decomposition of the phenylazide intermediate **[A]** affords the aniline derivative **7**, which was isolated in good yield and characterised. Its formation is not unexpected because it is well known[20] that an azide can be reduced to an amine by an alcohol and the reaction is catalysed by transition metal complexes. As phenylazide cannot give an imine after the extrusion of N$_2$ and the fragment [OsCl(η^6-*p*-cymene){P(OEt)$_3$}]$^+$ does not bind N$_2$, reduction by alcohol of the coordinate C$_6$H$_5$N$_3$ is the easiest reaction of the intermediate **[A]** giving **7**.

Good analytical data were obtained for the *p*-cymene complexes **6** and **7**, which were separated as yellow solids stable both in air and in solution of polar organic solvents, where they behave as 1 : 1 electrolytes.[13] Infrared and NMR spectra support the proposed formulation. In particular, the ^{1}H NMR spectrum of the imine complex [OsCl(η^6-*p*-cymene){κ^1-NH=C(H)C$_6$H$_4$-4-CH$_3$}{P(OEt)$_3$}]BPh$_4$ (**6**) shows a broad doublet at 10.99 ppm, attributed to the iminic NH proton. Besides the signals of the ancillary ligands *p*-cymene and P(OEt)$_3$ and of anion BPh$_4$, the proton spectra also show another doublet at 8.68 ppm, which, in a COSY experiment, is correlated with the broad doublet at 10.99 ppm and is attributed to the =CH proton of the imine ligand. The ^{31}P{^{1}H} NMR spectrum is a sharp singlet at 67.51 ppm and fits the proposed formulation for the complex.

The IR spectrum of the amine complex [OsCl(η^6-*p*-cymene)(κ^1-NH$_2$Ph){P(OEt)$_3$}]BPh$_4$ (**7**) shows two medium-intensity bands at 3286 and 3226 cm^{-1}, attributed to the ν_{NH} of the aniline ligand. Its presence is confirmed using the ^{1}H NMR spectrum, which shows two broad signals at 5.52 and 5.81 ppm, attributed to the NH$_2$ protons of the coordinate aniline. The presence of the two signals is due to the fact that the osmium atom is a chiral centre in the molecule. Signals of the supporting ligands are also present in the spectra, whereas the ^{31}P spectrum is a singlet at 68.29 ppm, in agreement with the proposed formulation for the complex.

Conclusions

In this paper we report that the half-sandwich fragment [Os(η^5-C$_5$H$_5$)(PPh$_3$){P(OR1)$_3$}]$^+$ can stabilise organic azide complexes [Os(η^5-C$_5$H$_5$)(κ^1-N$_3$R)(PPh$_3$){P(OR1)$_3$}]BPh$_4$. Spectroscopic data suggest the κ^1-diazoamino coordination mode of the azide ligand. Also, imine derivatives [Os(η^5-C$_5$H$_5$)

$\{\kappa^1$-NH=C(R2)Ar$\}(PPh_3)\{P(OR1)_3\}]BPh_4$ (R2 = H, CH_3) were also obtained from benzylazide complexes. Instead, the dinuclear dinitrogen derivative $[Os(\eta^5\text{-}C_5H_5)(PPh_3)\{P(OMe)_3\}_2(\mu\text{-}N_2)](BPh_4)_2$ was prepared from phenylazide PhN_3 compounds. Imine $[OsCl(\eta^6\text{-}p\text{-cymene})\{\kappa^1\text{-NH=C(H)R2}\}\{P(OR1)_3\}]BPh_4$ and amine complexes $[OsCl(\eta^6\text{-}p\text{-cymene})(\kappa^1\text{-}NH_2Ph)\{P(OR1)_3\}]BPh_4$ stabilised by the *p*-cymene fragment were also prepared.

Experimental

Materials and physical measurements

All reactions were carried out in an inert atmosphere (argon) by means of standard Schlenk techniques or in an inert-atmosphere glove box. Once isolated, the complexes were found to be relatively stable in air, but were stored under nitrogen at −25 °C. All solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. OsO_4 was a Pressure Chemical Co. (USA) product, used as received. The phosphites $P(OMe)_3$ and $P(OEt)_3$ were Aldrich products, purified by distillation under nitrogen. Benzyl[21] and phenyl[22] azides were prepared following methods previously reported. The labelled benzylazides $4\text{-}CH_3C_6H_4CH_2{}^{15}N_3$ and $C_6H_5CH(CH_3){}^{15}N_3$ were prepared by following the same method,[19] by reacting $Na[^{15}NNN]$ (98% enriched, CIL) with either 4-methylbenzylbromide $4\text{-}CH_3C_6H_4CH_2Br$ or (1-bromoethyl)benzene $C_6H_5CH(CH_3)Br$. Equimolar mixtures of $4\text{-}CH_3C_6H_4CH_2{}^{15}NNN$ and $4\text{-}CH_3C_6H_4CH_2NN{}^{15}N$ and of $C_6H_5CH(CH_3){}^{15}NNN$ and $C_6H_5CH(CH_3)NN{}^{15}N$ were obtained. Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on a Perkin Elmer Spectrum-One FT-IR spectrophotometer. NMR spectra (^1H, ^{31}P, ^{15}N) were obtained on an AVANCE 300 Bruker spectrometer at temperatures between −90 and +30 °C, unless otherwise noted. ^1H spectra are referred to internal tetramethylsilane; $^{31}P\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4, whereas ^{15}N shifts with respect to $CH_3{}^{15}NO_2$; in both cases, downfield shifts are considered positive. COSY, HMQC and HMBC NMR experiments were performed with standard programs. The iNMR software package[23] was used to process NMR data. The conductivity of 10^{-3} mol dm^{-3} solutions of the complexes in CH_3NO_2 at 25 °C was measured on a Radiometer CDM 83. Elemental analyses were determined in the Microanalytical Laboratory of the Dipartimento di Scienze Farmaceutiche, University of Padova (Italy).

Synthesis of the complexes

The complexes $[OsBr(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ and $[OsCl_2(\eta^6\text{-}p\text{-cymene})\{P(OEt)_3\}]$ were prepared following the methods previously reported.[24,25]

$[OsBr(\eta^5\text{-}C_5H_5)(PPh_3)\{P(OR1)_3\}]$ [R1 = Me, Et]. An excess of the appropriate phosphite $P(OR1)_3$ (8 mmol) was added to a solution of $[OsBr(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ (1.72 g, 2 mmol) in 50 mL of toluene and the reaction mixture was refluxed for 1 h. The solvent was removed under reduced pressure to leave an oil, which was triturated at 0 °C with ethanol (2 mL). A yellow solid slowly separated out, which was filtered and dried under vacuum; yield ≥80%.

R1 = Me. ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.52, 7.32 (m, 15H, Ph), 4.65 (s, 5H, Cp), 3.41 (d, 9H, CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 100.45, δ_X 6.55, J_{AX} = 41.4; anal. calcd for $C_{26}H_{29}BrO_3OsP_2$ (721.59): C, 43.28; H, 4.05; Br, 11.07; found: C, 43.41; H, 3.96; Br, 11.28%.

R1 = Et. ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.54, 7.37 (m, 15H, Ph), 4.64 (s, 5H, Cp), 3.87 (m, 6H, CH_2), 1.10 (t, 9H, CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 94.80, δ_X 7.96, J_{AX} = 42.4; anal. calcd for $C_{29}H_{35}BrO_3OsP_2$ (763.67): C, 45.61; H, 4.62; Br, 10.46; found: C, 45.39; H, 4.55; Br, 10.32%.

$[Os(\eta^5\text{-}C_5H_5)(\kappa^1\text{-}N_3R)(PPh_3)\{P(OR1)_3\}]BPh_4$ (1, 2) [R = $CH_2C_6H_5$ (a), $CH_2C_6H_4\text{-}4\text{-}CH_3$ (b), $CH(CH_3)C_6H_5$ (c); R1 = Me (1), Et (2)]. In a 25 mL three-necked round-bottomed flask were placed 0.14 mmol of the appropriate complex $[OsBr(\eta^5\text{-}C_5H_5)(PPh_3)\{P(OR1)_3\}]$, a slight excess of AgOTf (0.15 mmol, 39 mg) and 5 mL of toluene. The reaction mixture was stirred in the dark for 75 min and then filtered to remove the AgBr formed. An excess of the appropriate azide RN_3 (0.18 mmol) was added to the resulting solution, which was stirred at 0 °C for 3 h. The triflate complex $[Os(\eta^5\text{-}C_5H_5)(\kappa^1\text{-}N_3R)(PPh_3)\{P(OR1)_3\}]OTf$ slowly separated out as a dark-green gummy material. The solvent was removed under reduced pressure to give an oil, which was triturated at 0 °C with ethanol (1 mL) containing an excess of $NaBPh_4$ (0.28 mmol, 96 mg). A green solid slowly separated out, which was filtered and crystallised at 0 °C from CH_2Cl_2 and ethanol; yield ≥80%.

1a: IR (KBr, cm^{-1}) ν_{NNN} 2147 (m); ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.85–6.87 (m, 40H, Ph), 4.97 (s, 5H, Cp), 4.86 (s, 2H, CH_2), 3.40 (d, 9H, CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 87.70, δ_X 4.43, J_{AX} = 37.25; Anal. calcd for $C_{57}H_{56}BN_3O_3OsP_2$ (1094.06): C, 62.58; H, 5.16; N, 3.84; found: C, 62.34; H, 5.27; N, 3.72%; Λ_M = 52.3 Ω^{-1} mol^{-1} cm^2.

1b: IR (KBr, cm^{-1}) ν_{NNN} 2164 (m); ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.60–6.88 (m, 39H, Ph), 4.99 (s, 5H, Cp), 4.85 (s, 2H, CH_2), 3.47 (d, 9H, CH_3 phos), 2.37 (s, 3H, CH_3 *p*-tolyl); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 87.79, δ_X 4.69, J_{AX} = 37.79; anal. calcd for $C_{58}H_{58}BN_3O_3OsP_2$ (1108.09): C, 62.87; H, 5.28; N, 3.79; found: C, 62.66; H, 5.20; N, 3.88%; Λ_M = 52.8 Ω^{-1} mol^{-1} cm^2.

1c: IR (KBr, cm^{-1}) ν_{NNN} 2146 (m); ^1H NMR [$(CD_3)_2CO$, 20 °C] δ: 7.65–6.87 (m, 40H, Ph), 5.39 (s, 5H, Cp), 3.52 (q, 1H, CHN), 3.48 (d, 9H, CH_3 phos), 1.75 (d, 3H, CH_3-CHN); $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, 20 °C] δ: AX spin syst, δ_A 89.40, δ_X 5.34, J_{AX} = 37.55; anal. calcd for $C_{58}H_{58}BN_3O_3OsP_2$ (1108.09): C, 62.87; H, 5.28; N, 3.79; found: C, 62.64; H, 5.38; N, 3.70%; Λ_M = 53.4 Ω^{-1} mol^{-1} cm^2.

2a: IR (KBr, cm^{-1}) ν_{NNN} 2147 (m); ^1H NMR [$(CD_3)_2CO$, 20 °C] δ: 7.55–6.77 (m, 40H, Ph), 3.57 (s, 5H, Cp), 4.97 (s, 2H, CH_2N), 3.55 (m, 6H, CH_2 phos), 1.12 (t, 9H, CH_3); $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, 20 °C] δ: AX spin syst, δ_A 82.98, δ_X 5.88, J_{AX} = 37.25; anal. calcd for $C_{60}H_{62}BN_3O_3OsP_2$ (1136.14): C, 63.43; H, 5.50; N, 3.70; found: C, 63.24; H, 5.41; N, 3.79%; Λ_M = 52.8 Ω^{-1} mol^{-1} cm^2.

2b: IR (KBr, cm^{-1}) ν_{NNN} 2145 (m); ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.60–6.87 (m, 39H, Ph), 4.96 (s, 5H, Cp), 4.80 (s, 2H, CH_2N), 3.86 (m, 6H, CH_2 phos), 2.37 (s, 3H, CH_3 *p*-tolyl), 1.16 (t, 9H, CH_3 phos); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 81.73, δ_X 5.36, J_{AX} = 37.79; anal. calcd for $C_{61}H_{64}BN_3O_3OsP_2$ (1150.17): C, 63.70; H, 5.61; N, 3.65; found: C, 63.47; H, 5.52; N, 3.76%; Λ_M = 52.5 Ω^{-1} mol^{-1} cm^2.

2c: IR (KBr, cm^{-1}) ν_{NNN} 2146 (m); ^1H NMR [$(CD_3)_2CO$, 20 °C] δ: 7.50–6.77 (m, 40H, Ph), 5.39 (s, 5H, Cp), 4.03 (m, 6H, CH_2 phos), 3.56 (q, 1H, CHN), 1.77 (d, 3H, CH_3-CHN), 1.18 (t, 9H, CH_3 phos); $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, 20 °C] δ: AX spin syst, δ_A 83.05, δ_X 5.98, J_{AX} = 37.90; anal. calcd for $C_{61}H_{64}BN_3O_3OsP_2$ (1150.17): C, 63.70; H, 5.61; N, 3.65; found: C, 63.51; H, 5.73; N, 6.54%; Λ_M = 53.1 Ω^{-1} mol^{-1} cm^2.

[Os(η⁵-C_5H_5)(κ¹-N_3Ph)(PPh_3){P($OMe)_3$}]BPh_4 (1d). In a 25 mL three-necked round-bottomed flask were placed [OsBr(η⁵-C_5H_5)(PPh_3){P($OMe)_3$}] (0.14 mmol, 100 mg), a slight excess of AgOTf (0.15 mmol, 39 mg) and 5 mL of toluene. The reaction mixture was stirred in the dark for 75 min and then filtered to remove the AgBr formed. An excess of phenylazide $C_6H_5N_3$ (0.18 mmol, 21.5 μL) was added to the resulting solution, cooled to −196 °C. The reaction mixture was left to reach 0 °C and then stirred at this temperature for 1 h. The azide complex [Os(η⁵-C_5H_5)(κ¹-$N_3C_6H_5$)(PPh_3){P($OMe)_3$}]OTf separated out from the solution as an oil. The solvent was removed under reduced pressure leaving an oil, which was triturated at 0 °C with ethanol (1 mL) containing an excess of $NaBPh_4$ (0.28 mmol, 95 mg). A green solid slowly separated out, which was filtered and crystallised at 0 °C from CH_2Cl_2 and ethanol; yield ≥65%. IR (KBr, cm^{-1}) ν_{NNN} 2164 (m); ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.70–6.88 (m, 40H, Ph), 4.98 (s, 5H, Cp), 3.48 (d, 9H, CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 89.73, δ_X 5.99, J_{AX} = 38.90; anal. calcd for $C_{56}H_{54}BN_3O_3OsP_2$ (1080.03): C, 62.28; H, 5.04; N, 3.89; found: C, 62.08; H, 5.13; N, 3.98%; Λ_M = 51.9 Ω^{-1} mol^{-1} cm^2.

[Os(η⁵-C_5H_5)(κ¹-$^{15}N_3CH_2C_6H_4$-4-CH_3)(PPh_3){P($OR)_3$}]BPh_4 ($\mathbf{1b_1}$, $\mathbf{2b_1}$) and [Ru(η⁵-C_5H_5){$^{15}N_3C$(H)(CH_3)C_6H_5}(PPh_3){P($OMe)_3$}]BPh_4 ($\mathbf{1c_1}$). These complexes were prepared exactly like the related unlabelled derivatives **1b**, **2b** and **1c**, using labelled azides 4-$CH_3C_6H_4CH_2{}^{15}N_3$ and $C_6H_5C(H)(CH_3){}^{15}N_3$ as reagents.

$\mathbf{1b_1}$: IR (KBr, cm^{-1}) $\nu_{^{15}NNN}$ 2114 (m); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AXN spin syst, δ_A 88.20, δ_X 5.10, J_{AX} = 37.7, J_{AN} = 3.5, J_{XN} = 2.0; ^{15}N NMR (CD_2Cl_2, 20 °C) δ: 213.6 (s, Nα), 139.4 (m, Nγ).

$\mathbf{1c_1}$: IR (KBr, cm^{-1}) $\nu_{^{15}NNN}$ 2105 (m); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AXN spin syst, δ_A 88.21, δ_X 5.01, J_{AX} = 38.8, J_{AN} = 4.0, J_{XN} = 1.5; ^{15}N NMR (CD_2Cl_2, 20 °C) δ: 213.4 (s, Nα), 117.9 (m, Nγ).

$\mathbf{2b_1}$: IR (KBr, cm^{-1}) $\nu_{^{15}NNN}$ 2117 (m); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AXN spin syst, δ_A 82.16, δ_X 5.72, J_{AX} = 38.0, J_{AN} = 4.0, J_{XN} = 1.5.

[Os(η⁵-C_5H_5){κ¹-NH=C(H)Ar}(PPh_3){P($OR1)_3$}]BPh_4 (3, 4) [Ar = C_6H_5 (a), 4-$CH_3C_6H_4$ (b); R1 = Me (3), Et (4)] and [Os(η⁵-C_5H_5){κ¹-NH=C(CH_3)C_6H_5}(PPh_3){P($OR1)_3$}]BPh_4 (3c, 4c). *Method 1*: A solution of the appropriate azide complex [Os(η⁵-C_5H_5)(κ¹-N_3R)(PPh_3){P($OR1)_3$}]BPh_4 (**1**, **2**) (0.1 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature for 2 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (1 mL). A yellow-green solid slowly separated out, which was filtered and crystallised from CH_2Cl_2 and ethanol; yield ≥85%.

Method 2: In a 25 mL three-necked round-bottomed flask were placed 0.14 mmol of the appropriate complex [OsBr(η⁵-C_5H_5)(PPh_3){P($OR1)_3$}], a slight excess of AgOTf (0.15 mmol, 39 mg) and 5 mL of toluene. The reaction mixture was stirred in the dark for 75 min and then filtered to remove the AgBr formed. An excess of the appropriate azide (0.18 mmol) in 5 mL of CH_2Cl_2 was added to the resulting solution, which was stirred at room temperature for 4 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (1 mL) containing an excess of $NaBPh_4$ (0.28 mmol, 96 mg). A yellow-green solid slowly separated out, which was filtered and crystallised from CH_2Cl_2 and ethanol; yield ≥75%.

3a: IR (KBr, cm^{-1}) ν_{NH} 3266 (m); ^1H NMR (CD_2Cl_2, 20 °C) δ: 10.16 (d br, 1H, NH), 8.49 (d, 1H, =CH), 7.75–6.87 (m, 40H, Ph), 4.99 (s, 5H, Cp), 3.46 (d, 9H, CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 94.90, δ_X 13.69, J_{AX} = 38.2; anal. calcd for $C_{57}H_{56}BNO_3OsP_2$ (1066.05): C, 64.22; H, 5.29; N, 1.31; found: C, 64.03; H, 5.19; N, 1.37%; Λ_M = 52.6 Ω^{-1} mol^{-1} cm^2.

3b: IR (KBr, cm^{-1}) ν_{NH} 3271 (m); ^1H NMR (CD_2Cl_2, 20 °C) δ: 10.30 (d br, 1H, NH), 8.41 (d, 1H, =CH), 7.75–6.87 (m, 39H, Ph), 5.08 (s, 5H, Cp), 3.46 (q, 9H, CH_3 phos), 2.36 (s, 3H, CH_3 *p*-tolyl); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 95.36, δ_X 13.87, J_{AX} = 38.15; anal. calcd for $C_{58}H_{58}BNO_3OsP_2$ (1080.07): C, 64.50; H, 5.41; N, 1.30; found: C, 64.34; H, 5.30; N, 1.38%; Λ_M = 51.4 Ω^{-1} mol^{-1} cm^2.

3c: IR (KBr, cm^{-1}) ν_{NH} 3275 (m); ^1H NMR [$(CD_3)_2CO$, 20 °C] δ: 10.33, 9.98 (s br, 1H, NH), 7.61–6.87 (m, 40H, Ph), 5.22 (s, 5H, Cp), 3.58 (d, 9H, CH_3 phos), 2.37 (br, 3H, CH_3C=); $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, 20 °C] δ: AX spin syst, δ_A 93.45, δ_X 14.97, J_{AX} = 38.40; anal. calcd for $C_{58}H_{58}BNO_3OsP_2$ (1080.07): C, 64.50; H, 5.41; N, 1.30; found: C, 64.28; H, 5.46; N, 1.41%; Λ_M = 53.3 Ω^{-1} mol^{-1} cm^2.

4a: IR (KBr, cm^{-1}) ν_{NH} 3260 (m); ^1H NMR [$(CD_3)_2CO$, 20 °C] δ: 10.79 (d br, 1H, NH), 8.88 (d, 1H, =CH), 7.60–6.78 (m, 40H, Ph), 5.20 (s, 5H, Cp), 3.98 (m, 6H, CH_2), 1.14 (t, 9H, CH_3); $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, 20 °C] δ: AX spin syst, δ_A 90.46, δ_X 14.26, J_{AX} = 37.41; anal. calcd for $C_{60}H_{62}BNO_3OsP_2$ (1108.13): C, 65.03; H, 5.64; N, 1.26; found: C, 64.86; H, 5.71; N, 1.19%; Λ_M = 52.8 Ω^{-1} mol^{-1} cm^2.

4b: IR (KBr, cm^{-1}) ν_{NH} 3265 (m); ^1H NMR (CD_2Cl_2, 20 °C) δ: 10.39 (d br, 1H, NH), 8.44 (d, 1H, =CH), 7.65–6.88 (m, 39H, Ph), 4.90 (s, 5H, Cp), 3.84 (m, 6H, CH_2), 2.36 (s, 3H, CH_3 *p*-tolyl), 1.14 (t, 9H, CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 88.46, δ_X 13.72, J_{AX} = 37.91; anal. calcd for $C_{61}H_{64}BNO_3OsP_2$ (1122.15): C, 65.29; H, 5.75; N, 1.25; found: C, 65.12; H, 5.84; N, 1.17%; Λ_M = 53.5 Ω^{-1} mol^{-1} cm^2.

4c: IR (KBr, cm^{-1}) ν_{NH} 3282 (m); ^1H NMR [$(CD_3)_2CO$, 20 °C] δ: 10.46, 10.15 (s br, 1H, NH), 7.56–6.78 (m, 40H, Ph), 5.16 (s, 5H, Cp), 3.98 (m, 6H, CH_2), 1.10 (t, 9H, CH_3 phos), 2.43 (br, 3H, CH_3C=); $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, 20 °C] δ: AX spin syst,

δ_A 87.47, δ_X 14.45, J_{AX} = 38.64; anal. calcd for $C_{61}H_{64}BNO_3OsP_2$ (1122.15): C, 65.29; H, 5.75; N, 1.25; found: C, 65.13; H, 5.80; N, 1.18%; Λ_M = 52.0 Ω^{-1} mol^{-1} cm^2.

[Os(η^5-C_5H_5){κ^1-^{15}NH═C(H)C_6H_4-4-CH_3}(PPh$_3$){P(OR1)$_3$}]BPh$_4$ (3b$_1$, 4b$_1$) and [Os(η^5-C_5H_5){κ^1-^{15}NH═C(CH_3)C_6H_5}(PPh$_3$){P(OR1)$_3$}]BPh$_4$ (3c$_1$, 4c$_1$) [R1 = Me (3), Et (4)]. These complexes were prepared exactly like the related unlabelled derivatives **3b**, **4b**, **3c** and **4c**, using the labelled azides 4-$CH_3C_6H_4CH_2{}^{15}N_3$ and $C_6H_5C(H)(CH_3){}^{15}N_3$ as reagents; yield ≥65%.

3b$_1$: IR (KBr, cm^{-1}) $\nu_{^{15}NH}$ 3272 (m); ^{1}H NMR (CD_2Cl_2, 20 °C) δ: AXNYZ spin syst (Y, Z = ^{1}H; N = ^{15}N), δ_Y 10.40, δ_Z 8.38, J_{AN} = 3.5, J_{AY} = 3.8, J_{AZ} = 0.1, J_{XN} = 2.6, J_{XY} = 1.8, J_{XZ} = 0.1, J_{NY} = 72.8, J_{NZ} = 3.0, J_{YZ} = 21.3; ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C) δ: AXN spin syst, δ_A 97.02, δ_X 14.54, J_{AX} = 38.0, J_{AN} = 4.0, J_{XN} = 2.6; ^{15}N NMR (CD_2Cl_2, 20 °C) δ: AXNYZ spin syst, δ_N 161.7, J_{AX} = 38.0, J_{AN} = 4.0, J_{AY} = 4.3, J_{AZ} = 0.1, J_{XN} = 2.6, J_{XY} = 1.8, J_{XZ} = 0.1, J_{NY} = 72.6, J_{NZ} = 3.0, J_{YZ} = 21.3.

3c$_1$: ^{1}H NMR (CD_2Cl_2, 20 °C) δ: AXNYZ$_3$ spin syst (Y, Z = ^{1}H; N = ^{15}N), δ_Y 10.24, δ_Z 2.36, J_{AN} = 4.0, J_{AY} = 4.55, J_{AZ} = 0.05, J_{XN} = 2.0, J_{XY} = 0.9, J_{XZ} = 1.0, J_{NY} = 71.6, J_{NZ} = 1.65, J_{YZ} = 2.00; AXNYZ$_3$ spin syst, δ_Y 9.59, δ_Z 2.16, J_{AX} = 4.65, J_{AY} = 4.15, J_{AZ} = 0.05, J_{XN} = 1.9, J_{XY} = 1.65, J_{XZ} = 1.0, J_{NY} = 70.95, J_{NZ} = 1.5, J_{YZ} = 2.00; ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C) δ: AXN spin syst, δ_A 92.56, δ_X 14.80, J_{AX} = 38.0, J_{AN} = 4.0, J_{XN} = 2.0; AXN spin syst, δ_A 93.01, δ_X 15.05, J_{AX} = 38.5, J_{AN} = 4.0, J_{XN} = 2.0; ^{15}N NMR (CD_2Cl_2, 20 °C) δ: AXNYZ$_3$ spin syst, δ_N 173.46, J_{AN} = 4.4, J_{XN} = 2.0; AXNYZ$_3$ spin syst, δ_N 182.27, J_{AN} = 4.0, J_{XN} = 2.0.

4b$_1$: IR (KBr, cm^{-1}) $\nu_{^{15}NH}$ 3266 (m); ^{1}H NMR (CD_2Cl_2, 20 °C) δ: AXNYZ spin syst (Y, Z = ^{1}H; N = ^{15}N), δ_Y 10.52, δ_Z 8.51, J_{AN} = 4.2, J_{AY} = 3.8, J_{AZ} = 0.1, J_{XN} = 2.6, J_{XY} = 1.8, J_{XZ} = 0.1, J_{NY} = 72.4, J_{NZ} = 3.0, J_{YZ} = 21.2; ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C) δ: AXN spin syst, δ_A 90.35, δ_X 14.47, J_{AX} = 38.0, J_{AN} = 4.2, J_{XN} = 2.6; ^{15}N NMR (CD_2Cl_2, 20 °C) δ: AXNYZ spin syst, δ_N 163.7, J_{AN} = 4.2, J_{XN} = 2.6.

4c$_1$: IR (KBr, cm^{-1}) $\nu_{^{15}NH}$ 3275 (m); ^{1}H NMR (CD_2Cl_2, 20 °C) δ: AXNYZ$_3$ spin syst (Y, Z = ^{1}H; N = ^{15}N), δ_Y 10.38, δ_Z 2.33, J_{AN} = 4.4, J_{AY} = 4.65, J_{AZ} = 0.05, J_{XN} = 2.0, J_{XY} = 0.90, J_{XZ} = 1.00, J_{NY} = 71.65, J_{NZ} = 1.65, J_{YZ} = 2.00; AXNYZ$_3$ spin syst, δ_Y 10.07, δ_Z 2.22, J_{AN} = 4.0, J_{AY} = 4.15, J_{AZ} = 0.05, J_{XN} = 2.0, J_{XY} = 1.65, J_{XZ} = 1.00, J_{NY} = 70.96, J_{NZ} = 1.65, J_{YZ} = 2.00; ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C) δ: AXN spin syst, δ_A 86.90, δ_X 14.15, J_{AX} = 38.4, J_{AN} = 4.4, J_{XN} = 2.0; AXN spin syst, δ_A 88.02, δ_X 14.75, J_{AX} = 39.2, J_{AN} = 4.0, J_{XN} = 2.0; ^{15}N NMR (CD_2Cl_2, 20 °C) δ: AXNYZ$_3$ spin syst, δ_N 174.64, J_{AN} = 4.4, J_{XN} = 2.0; AXNYZ$_3$ spin syst, δ_N 182.99, J_{AN} = 4.0, J_{XN} = 2.0.

[{Os(η^5-C_5H_5)(PPh$_3$)[P(OMe)$_3$]}$_2$(μ-N$_2$)](BPh$_4$)$_2$ (5). *Method 1*: A solution of the phenylazide complex [Os(η^5-C_5H_5)(κ^1-N_3Ph)(PPh$_3$){P(OMe)$_3$}]BPh$_4$ (**1d**) (100 mg, 0.09 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature for 1 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (1 mL). A blue solid slowly separated out, which was filtered and twice crystallised from CH_2Cl_2 and ethanol; yield ≥55%.

Method 2: In a 25 mL three-necked round-bottomed flask were placed 0.14 mmol (100 mg) of the complex [OsBr(η^5-C_5H_5)(PPh$_3$){P(OMe)$_3$}], a slight excess of AgOTf (0.15 mmol, 39 mg) and 5 mL of toluene. The reaction mixture was stirred in the dark for 75 min and then filtered to remove the AgBr formed. An excess of phenylazide (0.18 mmol, 21.5 μL) in 5 mL of dichloromethane was added to the resulting solution, and cooled to −196 °C. The reaction mixture was left to reach room temperature and then stirred for 1 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (1 mL) containing an excess of $NaBPh_4$ (0.28 mmol, 96 mg). A blue solid slowly separated out, which was filtered and twice crystallised from CH_2Cl_2 and ethanol; yield ≥45%. ^{1}H NMR [$(CD_3)_2CO$, 20 °C] δ: 7.61–6.77 (m, 70H, Ph), 5.03 (s, 10H, Cp), 3.61 (d, 18H, CH_3); ^{31}P{^{1}H} NMR [$(CD_3)_2CO$, 20 °C] δ: AX spin syst, δ_A 90.21, δ_X 6.24, J_{AX} = 38.5; anal. calcd for $C_{100}H_{98}B_2N_2O_6Os_2P_4$ (1949.83): C, 61.60; H, 5.07; N, 1.44; found: C, 61.41; H, 5.16; N, 1.33%; Λ_M = 58.8 Ω^{-1} mol^{-1} cm^2.

[OsCl(η^6-*p*-cymene){κ^1-NH═C(H)C_6H_4-4-CH_3}{P(OEt)$_3$}]BPh$_4$ (6). *Method 1*: In a 25 mL three-necked round-bottomed flask were placed 80 mg (0.14 mmol) of [OsCl$_2$(η^6-*p*-cymene){P(OEt)$_3$}], a slight excess of AgOTf (0.15 mmol, 39 mg) and 5 mL of dichloromethane. The reaction mixture was stirred in the dark for 24 h, filtered to remove the AgCl formed, and then an excess of 4-$CH_3C_6H_4CH_2N_3$ (0.42 mmol, 62 μL) added. The reaction mixture was stirred for 6 h and then the solvent was removed under reduced pressure. The oil obtained was triturated with ethanol (1 mL) containing an excess of $NaBPh_4$ (0.28 mmol, 96 mg). A yellow solid slowly separated out from the resulting solution, which was filtered and crystallised from CH_2Cl_2 and ethanol; yield ≥75%.

Method 2: In a 25 mL three-necked round-bottomed flask were placed 80 mg (0.14 mmol) of [OsCl$_2$(η^6-*p*-cymene){P(OEt)$_3$}], an excess of $NaBPh_4$ (0.28 mmol, 96 mg), 5 mL of dichloromethane, and 5 mL of ethanol, and an excess of 4-$CH_3C_6H_4CH_2N_3$ (0.42 mmol, 62 μL) was added. The reaction mixture was stirred for 24 h and then the solvent was removed under reduced pressure. The oil obtained was triturated with ethanol (1 mL) until a yellow solid separated out from the resulting solution, which was filtered and crystallised from CH_2Cl_2 and ethanol; yield ≥70%.

^{1}H NMR (CD_2Cl_2, 20 °C) δ: IR (KBr, cm^{-1}) ν_{NH} 3257 (m); 10.99 (d br, 1H, NH), 8.68 (d, 1H, ═CH), 7.31–6.86 (m, 24H, Ph), 5.81, 5.72, 5.60, 5.46 (d, 4H, Ph *p*-cym), 4.11 (qnt, 6H, CH_2), 2.65 (m, 1H, CH *p*-cym), 2.38 (s, 3H, CH_3 *p*-tolyl), 2.12 (s, 3H, CH_3 *p*-cym), 1.30 (t, 9H, CH_3 phos), 1.27 (m, 6H, CH_3 ^{i}Pr); ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C) δ: A spin syst, 67.51 (s); anal. calcd for $C_{48}H_{58}BClNO_3OsP$ (964.45): C, 59.78; H, 6.06; Cl, 3.68; N, 1.45; found: C, 59.60; H, 5.97; Cl, 3.82; N, 1.36%; Λ_M = 53.0 Ω^{-1} mol^{-1} cm^2.

[OsCl(η^6-*p*-cymene)(κ^1-$NH_2C_6H_5$){P(OEt)$_3$}]BPh$_4$ (7). This complex was prepared exactly like compound **6**, using both *Method 1* and *Method 2*, with $C_6H_5N_3$ as a reagent; yield ≥55%. IR (KBr, cm^{-1}) ν_{NH} 3286, 3226 (m); ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 7.47–6.88 (m, 25H, Ph), 5.81, 5.52 (br, 2H, NH_2), 5.38, 5.25, 5.11, 5.00 (d, 4H, Ph *p*-cym), 4.23 (m, 6H, CH_2), 2.62 (m, 1H, CH *p*-cym), 2.10 (s, 3H, CH_3 *p*-cym), 1.39 (t, 9H, CH_3 phos), 1.18, 1.16 (d, 6H, CH_3 ^{i}Pr); ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C) δ: A spin syst, 68.29 (s); anal. calcd for $C_{46}H_{56}BClNO_3OsP$ (938.41):

C, 58.88; H, 6.01; Cl, 3.78; N, 1.49; found: C, 58.65; H, 5.91; Cl, 3.87; N, 1.39%; Λ_M = 51.8 Ω^{-1} mol^{-1} cm^2.

Crystal structure determinations

Crystallographic data for **5** were collected at CACTI (University of Vigo, Spain) at 100 K (CryoStream 800) using a Bruker D8 Venture Photon 100 CMOS detector and Mo-Kα radiation (λ = 0.71073 Å) generated by a Incoatec high brilliance IμS microsource. The software APEX3[26] was used for collecting frames of data, indexing reflections, and the determination of lattice parameters, SAINT[26] for the integration of the intensities of reflections, and SADABS[26] for scaling and empirical absorption correction. The crystallographic treatment was performed with the Oscail program[27] solved using the SHELXT program.[28] The structure was subsequently refined by a full-matrix least-squares based on F^2, SHELXL program.[29] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions and refined with isotropic displacement parameters. Other details of crystal data and structural refinement are given in Table 2. CCDC 1846339† contains the supplementary crystallographic data for this paper.

Table 2 Crystal data and structure refinement

Compound	**5**
Empirical formula	$C_{102}H_{102}B_2Cl_4N_2O_6Os_2P_4$
Moiety formula	$C_{52}H_{58}N_2O_6Os_2P_4$, 2($C_{24}H_{20}B$), 2($CH_2Cl_2$)
Formula weight	2119.55
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 12.7763(19) Å
	b = 13.497(2) Å
	c = 14.717(2) Å
	α = 63.354(4)°
	β = 86.818(5)°
	γ = 83.617(5)°
Volume	2254.3(6) Å^3
Z	1
Density (calculated)	1.561 Mg m^{-3}
Absorption coefficient	3.062 mm^{-1}
F(000)	1066
Crystal size	0.085 × 0.072 × 0.041 mm
Θ range for data collection	2.222 to 28.356°
Index ranges	$-17 \le h \le 17$
	$-18 \le k \le 18$
	$-19 \le l \le 19$
Reflections collected	85 416
Independent reflections	11 224 [R_{int} = 0.0344]
Reflections observed (>2σ)	10 461
Data completeness	0.997
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.6693
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	11 224/0/553
Goodness-of-fit on F^2	1.094
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0326
	wR_2 = 0.0849
R indices (all data)	R_1 = 0.0364
	wR_2 = 0.0867
Largest diff. peak and hole	3.059 and −2.753 e Å^{-3}

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

The financial support of MIUR (Italy) – PRIN 2016 is gratefully acknowledged. We thank Daniela Baldan, from the Università Ca' Foscari Venezia (Italy), for technical assistance.

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