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New osmium hydrides containing the bulky phosphine 1,2-bis(diisopropylphosphino)ethane (dippe)

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Abstract

A range of hydride complexes of osmium(II) and osmium(IV) containing the bulky chelating phosphine dippe have been prepared and characterized. The cationic dichlorohydridoosmium(IV) [$OsHCl_2$(dippe)$_2$][BPh_4] **1** was obtained by reaction of five-coordinate [OsCl(dippe)$_2$][BPh_4] with HCl in dichloromethane, whereas the trihydride [OsH_3(dippe)$_2$][BPh_4] **2** was prepared by reaction of *cis*-[$OsCl_2$(dippe)$_2$] with $NaBH_4$/$NaBPh_4$ in ethanol. This compound has shown to be a 'classical' trihydride Os^{IV} complex rather than an Os^{II} hydrido(dihydrogen) derivative, being reversibly deprotonated by $KOBu^t$ to yield the neutral dihydride *cis*-[OsH_2(dippe)$_2$] **3**. *cis*-[$OsCl_2$(dippe)$_2$] reacted with Li[$HBEt_3$] in THF affording the chlorohydride *trans*-[OsHCl(dippe)$_2$] **4**. This species dissociates chloride furnishing the 16-electron cationic monohydride [OsH(dippe)$_2$]$^+$, which was detected in solution, but not isolated due to its great tendency to react with traces of oxygen to yield the hydrido(dioxygen) complex *trans*-[OsH(O_2)(dippe)$_2$][BPh_4] **5**, which was fully characterized. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Hydride complexes; Dihydrogen complexes; Dioxygen complexes; Osmium; Phosphine

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1. Introduction

In previous reports, we described the synthesis and properties of the 16-electron monohydride complex [RuH(dippe)$_2$][BPh_4] [1], which was reactive towards both H_2 and O_2 furnishing the corresponding complexes, namely [RuH(H_2)(dippe)$_2$][BPh_4] and [RuH(O_2)(dippe)$_2$][BPh_4]. The preparation of these compounds proved that dioxygen coordination is possible at a dihydrogen binding site, and that the steric bulkiness of the auxiliary ligands plays an important role on the stabilization of dioxygen coordination. Rigo and co-workers have prepared related ruthenium and osmium [2–4] compounds containing 1,2-bis(dicyclohexyl-phosphino)ethane (dcpe), which is even bulkier than dippe, and they have also reported recently the X-ray crystal structure of [OsH(O_2)(dcpe)$_2$][BPh_4] [5]. On the other hand, Morris and co-workers have extensively studied the Ru and Os systems containing 1,2-bis(diethylphosphino)ethane (depe) [6–10], which apparently do not react with O_2 to form stable dioxygen adducts. In order to complete the systematic study of the properties of osmium hydrides containing substituted diphosphines, we recently started to extend the work carried out with ruthenium and dippe to osmium [11]. This has led to the isolation of five-coordinate osmium complexes of the type [OsX(dippe)$_2$][BPh_4] (X = Cl, SPh), as well as the dihydrogen derivative [OsCl(H_2)(dippe)$_2$][BPh_4]. In this paper we conclude the study with the report of the synthesis and properties of a series of new osmium hydrides relevant to the activation of dihydrogen and dioxygen, with emphasis in the dynamic processes which some of these compounds undergo in solution.

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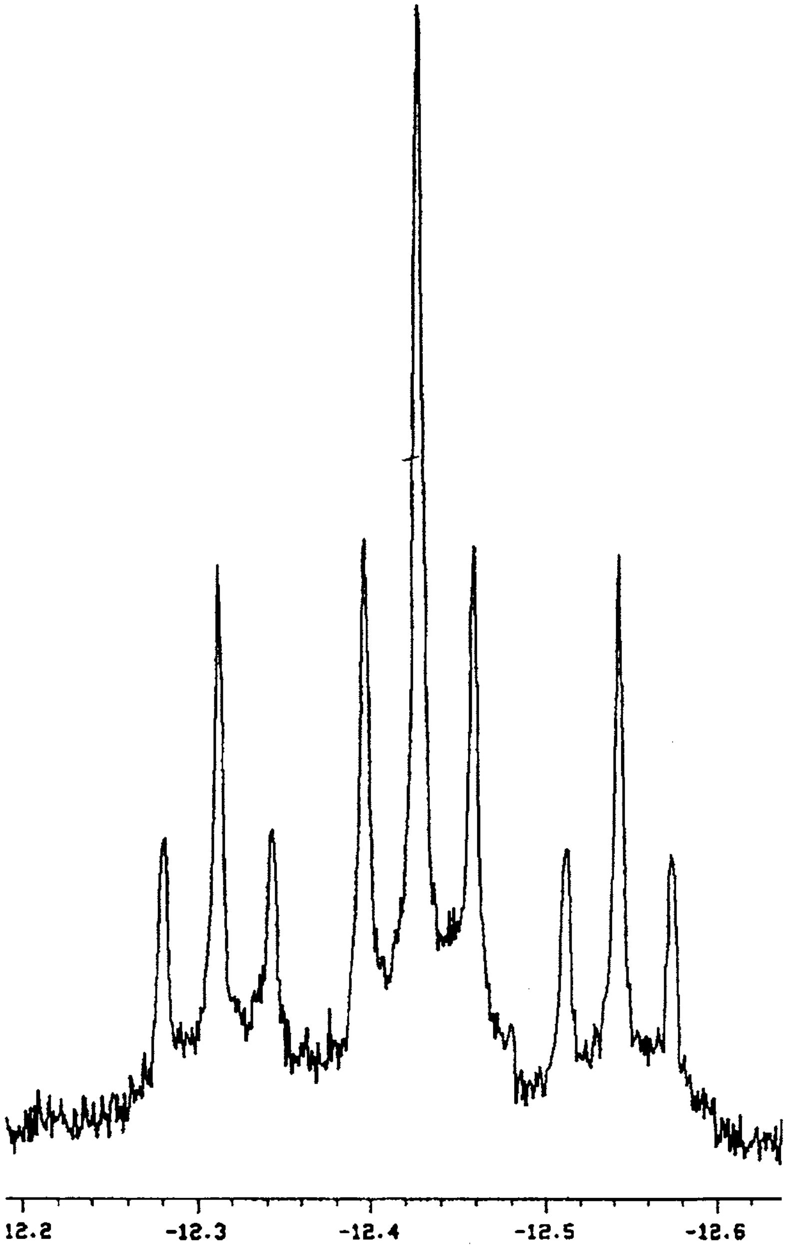


Fig. 1. ^{1}H-NMR spectrum of [OsHCl$_2$(dippe)$_2$][BPh$_4$] (CD$_2$Cl$_2$) in the hydride region at r.t.

2. Results and discussion

The reaction of the five-coordinate complex [OsCl(dippe)$_2$][BPh$_4$] [11] with aqueous HCl in CH$_2$Cl$_2$ leads to a purple solution, from which a purple microcrystalline material was isolated upon concentration and precipitation using petroleum ether. This material is diamagnetic, as inferred from its ^{1}H-NMR spectrum, which shows one hydride resonance centred at -12.43 ppm, apart from the phosphine protons. This signal appears as a triplet of triplets, due to coupling to two sets (two atoms each) of non-equivalent phosphorus atoms. This corresponds to the X part of an A$_2$M$_2$X spin system. Consistent with this, the ^{31}P{^{1}H}-NMR spectrum displays two signals, centred at 27.0 and 16.8 ppm, which, however, do not show any resolved multiplicity due to their relative broadness. Analytical data are consistent with the formulation as [OsHCl$_2$(dippe)$_2$][BPh$_4$] for (Fig. 1) this material (**1**), which appears to be a seven-coordinate Os^{IV} dichlorohydride, formed presumably through an oxidative addition of one HCl molecule to the coordinatively unsaturated complex [OsCl(dippe)$_2$][BPh$_4$]. Despite the fact that seven-coordinate species are very often non-rigid in solution, NMR data suggest that **1** is stereochemically rigid in the NMR time scale. Several possible structures can be proposed for the complex cation, based upon NMR data:

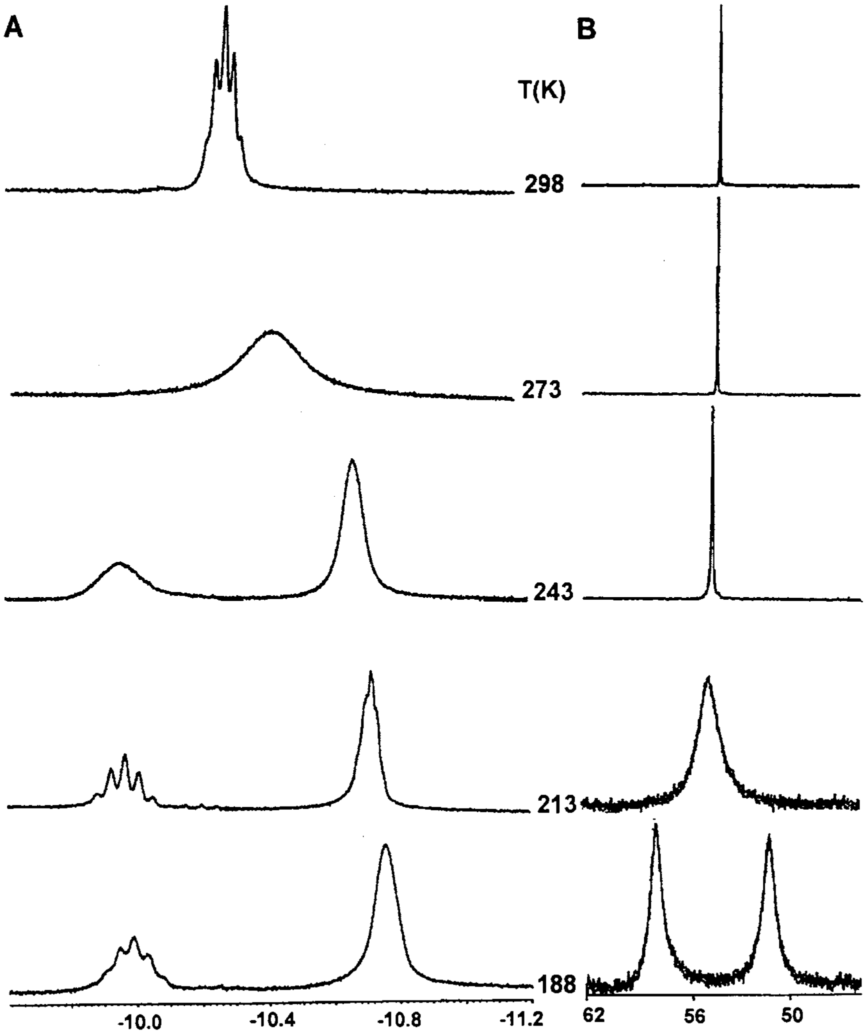
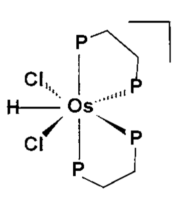
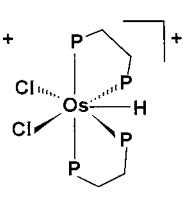


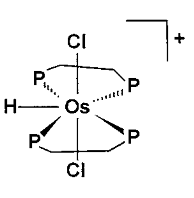
Fig. 2. Variable temperature NMR spectra of $[OsH_3(dippe)_2][BPh_4]$ (acetone-d_6): (a) ^1H in the hydride region; (b) $^{31}P\{^1H\}$.



Ia



Ib



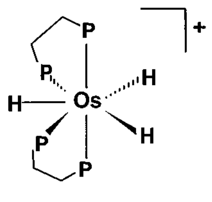
II

Both structures are derived from a pentagonal bipyramid. In structures **Ia** and **Ib**, the phosphines adopt a *cisoid* disposition, with the hydride ligand in between the two chloride ligands (**Ia**) or the two phosphorus atoms lying on the equatorial plane (**Ib**). In structure **II**, the chloride ligands are in axial positions, and the two dippe ligands and the hydride are equatorial. From these two, structures **Ia** and **Ib** seems to be more consistent with the observed NMR data, since they both match an A_2M_2X spin system, whereas with structure **II**, a more complex pattern corresponding to an AA′MM′X spin system, similar to that observed for complexes of the type $[WH(N_2)_2(diphos)_2]^+$ [12], would be expected. The fact that **1** is deprotonated by a strong base such as $KOBu^t$ to yield the neutral dichlorocomplex *cis*-$[OsCl_2(dippe)_2]$ is also in support of a *cisoid* disposition of the phosphine ligands. However, attempts made to obtain **1** from *cis*-$[OsCl_2(dippe)_2]$ by protonation using HBF_4 were unsuccessful, resulting in the formation of paramagnetic species. As far as we are aware, there are no previous reports of other compounds of the type $[OsHCl_2(diphos)_2]^+$ in the literature.

The reaction of *cis*-$[OsCl_2(dippe)_2]$ with $NaBH_4$ in EtOH, in the presence of $NaBPh_4$ afforded $[OsH_3(dippe)_2][BPh_4]$ (**2**) as a white microcrystalline solid which was recrystallized from an acetone/petroleum ether mixture. This material displays one broad ν_{OsH} band centred at 1981 cm^{-1}, and its ^1H-NMR spectrum in acetone-d_6 at room temperature (r.t.) shows one binomial quintet at -10.35 ppm with a coupling constant $J_{HP} = 12$ Hz, indicative of the equivalence at this temperature of the three hydride ligands (Fig. 2). Consistent with this, one sharp singlet appears in the $^{31}P\{^1H\}$-NMR spectrum. As the temperature is lowered, the single hydride resonance in the ^1H-NMR spectrum becomes broad and unresolved, and then splits into two broad signals centred at -9.95 and -10.65 ppm, respectively. The resonance at lower field resolves into one quintet at 213 K, having a coupling constant $J_{HP} = 21$ Hz, whereas the signal at higher field, which has double intensity, remains broad, although it shows signs of a partially resolved coupling to phosphorus with a reduced coupling constant $J_{HP} \cong 7$ Hz. At this temperature, the $^{31}P\{^1H\}$-NMR spectrum consists of one broad signal, which splits into two separate broad resonances at lower temperature (188 K), suggesting that the phosphorus atoms become non-equivalent (Fig. 2). The hydride signals in the ^1H-NMR spectrum become broader at this temperature, although no significant change in the pattern is observed. The fact that two resonances appear for metal-bound protons indicates that there are two different sorts of hydridic sites, and that protons in these sites undergo rapid exchange in the NMR time scale averaging their chemical shifts and J_{HP} coupling constants, as it has been observed for other related complexes of the type $[OsH_3(diphos)_2]^+$ [7]. These osmium derivatives range from hydride(dihydrogen) complexes to 'classical' trihydrides passing through intermediate situations containing an 'elongated' dihydrogen ligand, depending upon the nature of the substituents at the phosphorus atoms of the diphosphine ligands. In some instances, rapid equilibria between the hydride and dihydrogen tautomers has been also observed [13]. In our case, measurements of $(T_1)_{min}$ (minimum longitudinal relaxation time) yielded 289 ms for the quintet, and 182 ms for the broad resonance at higher field (acetone-d$_6$, 400 MHz). These values need to be corrected in order to account for the contribution of the rapid hydride exchange between sites to the overall relaxation [7,13], using the formula:

$$\frac{1}{T_1(H_2)_{obs}} = \frac{1}{T_1(H_2)_{true}} + \frac{1}{T_1(H)_{obs}}$$

This leads to a 'true' $(T_1)_{min}$ value of 492 ms for the OsH_2 resonance, which corresponds to a d_{HH} in the range 1.51–1.90 Å, suggesting that **2** is a 'classical' hydride rather than a dihydrogen complex, and hence should be formulated as an Os^{IV} trihydride, or better as a hydride(dihydride) of the type $[OsH(H)_2(dippe)_2][BPh_4]$. Thus, an increase of the bulk of the substituents at phosphorus favours the hydride tautomer over the dihydrogen form, as inferred from the fact that $[OsH(H...H)(depe)_2]^+$ is an 'elongated' dihydrogen complex [7], whereas **2** and also $[OsH_3(dcpe)_2]^+$ [4] behave as classical trihydrides (or hydride(dihydrides)). $[OsH(H_2)(dppe)_2]^+$ is a hydride(dihydrogen) complex [7], although dppe is a poorer donor than depe, dippe and dcpe. It is interesting to note that the complex $[OsCl(H...H)(dippe)_2][BPh_4]$, recently reported by us [11], contains an 'elongated' dihydrogen ligand ($d_{HH} = 1.0$–1.3 Å). In this sense, the effect of the halide versus hydride on H–H bonding of the *trans*-H_2 ligand in complexes of the type $[MX(H_2)(R_2PCH_2CH_2PR_2)_2]^+$ (M = Ru, Os; X = H, halide) has been subject of detailed studies [6,9,10]. Whereas for Ru complexes a change from halide to hydride involves always a decrease in d_{HH}, for their osmium homologues the change may cause both an increase or a decrease in d_{HH}, depending upon the R substituent on the diphospine. Thus, in our case (R = ^{i}Pr), there is an increase in d_{HH} when changing Cl by H, as it also occurs for R = Cy, although the effect is reversed when R = Et or Ph. The structure proposed for **2**, according to the spectral data, is derived from a pentagonal bipyramid, with all the hydrides lying on the equatorial plane, and the phosphines adopting a *cisoid* disposition, as shown.



This structure involves the non-equivalence of the phosphorus atoms at axial and equatorial positions, although rapid exchange in solution occurs, rendering them equivalent on the NMR time scale. In fact, the $^{31}P\{^1H\}$-NMR spectra of all compounds of the type $[OsH_3(R_2PCH_2CH_2PR_2)_2]^+$ reported in the literature consists of one singlet in the temperature range 200–300 K. However, in the case of **2** the splitting of the $^{31}P\{^1H\}$ resonance has been observed at 183 K (Fig. 2). This has allowed the estimation of the energy barrier responsible for the exchange process from the variable temperature $^{31}P\{^1H\}$-NMR data [14]. Thus, the rate of exchange at 203 K is 2433 s^{-1}. An Eyring plot (Fig. 3) yielded the activation parameters $\Delta H^{\neq} = 8.7 \pm 0.5$ kcal mol^{-1}; $\Delta S^{\neq} = 1 \pm 0.5$ cal K^{-1} mol^{-1}, and $\Delta G^{298} = 8.4 \pm 0.5$ kcal mol^{-1}. This values of ΔG^{298} is coincident with the estimated upper bound for the activation energy of the exchange process in the complexes $[OsH(H_2)(R_2PCH_2CH_2PR_2)_2]^+$ (R = Ph, Et) and $[ReH_3(dppe)_2]$ [7,13], the small value for $\Delta S^{\neq}$ being consistent with an intramolecular mechanism.

Compound **2** is reversibly deprotonated by a strong base such as KOBu^t yielding the neutral dihydride *cis*-$[OsH_2(dippe)_2]$ (**3**). This white, crystalline material is characterized by the presence of a multiplet signal for the hydride protons in the ^1H-NMR spectrum, whereas two sharp singlets are observed in the $^{31}P\{^1H\}$-NMR spectrum, consistent with the *cis*-disposition of the phosphine ligands. The fact that the phosphorus resonances appear as singlets rather than as multiplets, as it would correspond to the expected AA'MM'XX' spin system, is attributed to the cancellation of J_{PP} coupling constants, probably similar in absolute magnitude but opposite in sign.

Reaction of **3** with HBF_4/D_2O yielded a mixture of the isotopomers $[OsH_2D(dippe)_2]^+$ and $[OsHD_2(dippe)_2]^+$, which showed no evidence for H–D coupling in its ^{1}H-NMR spectrum ($J_{HD} \cong 0$ Hz), as expected for a 'classical' hydride complex [13].

At variance with its ruthenium homologue, $[RuH(H_2)(dippe)_2][BPh_4]$ [1], which is a labile dihydrogen complex that dissociates H_2 to give the 16-electron monohydride $[RuH(dippe)_2][BPh_4]$, **2** seems to be remarkably stable towards reductive elimination of H_2. For this reason, we attempted the preparation of $[OsH(dippe)_2][BPh_4]$ starting from the chlorohydride complex *trans*-$[OsHCl(dippe)_2]$ (**4**), which was prepared in moderated yield by reaction of *cis*-$[OsCl_2(dippe)_2]$ with $Li[HBEt_3]$ in THF. This compound, which displays one quintet at -24.14 ppm in its ^{1}H-NMR spectrum, reacted with $NaBPh_4$ in ethanol under dinitrogen or argon to yield a microcrystalline material, which resulted in a mixture of three hydride-containing species, as inferred from its ^{1}H-NMR spectrum. One of the signals corresponds to the trihydride complex **2**, whereas the other two resonances, one quintet at -39.5 ppm, and another quintet at -7.1 ppm, are due to novel compounds. The ratio of the different signals varied depending upon the conditions and reaction times. The signal at very high field is consistent with the presence of a coordinatively unsaturated osmium hydride, and is hence attributed to $[OsH(dippe)_2][BPh_4]$, although all efforts to isolate this compound were unsuccessful. Prolonged reaction times led to the formation of the trihydride **2**, presumably by hydrogen abstraction from the solvent, whereas exposure to oxygen, even at trace level, afforded the hydrido(dioxygen) complex $[OsH(O_2)(dippe)_2][BPh_4]$ (**5**), to which corresponds the observed quintet at -7.1 ppm (Scheme 1). It is clear that $[OsH(dippe)_2]^+$ is a very reactive species having an affinity for O_2 even higher than its ruthenium homologue. The osmium hydrido(dioxygen) complex $[OsH(O_2)(dcpe)_2][BPh_4]$, analogous to **5**, was recently described [5]. As in our case, it was also obtained by addition of O_2 to the corresponding 16-electron osmium monohydride. The NMR properties of **5** match those of its ruthenium homologue. Thus, the spectra are temperature dependent, and the hydride quintet at -7.1 becomes a triplet of triplets as the temperature is lowered (Fig. 4). The $^{31}P\{^1H\}$-NMR spectrum consists of one broad resonance at r.t., which splits into two signals at 213 K. The low temperature spectral data correspond to an A_2M_2X spin system, suggesting that the structure of **5** is essentially identical to that found by X-ray diffraction for its ruthenium homologue [1], and also for $[OsH(O_2)(dcpe)_2][BPh_4]$ [5] (Scheme 1). In fact, the crude molecular skeleton resulting from an X-ray structure analysis made on poor quality crystals of **5** was consistent with this affirmation, although the refinement of the model was not good enough to grant its publication. The dynamic process responsible for the fluxional behaviour of these hydrido(dioxygen) species is thought to be the propeller-like spinning of the dioxygen ligand, similar to that found in dihydrogen complexes [13,15], the rotation energy barrier of **5** having an estimated value $\Delta G^{298} = 13 \pm 1$ kcal mol^{-1} with $\Delta H^{\neq} = 9 \pm 1$ kcal mol^{-1}, and $\Delta S^{\neq} = -15 \pm 1$ cal K^{-1} mol^{-1}, as inferred from the analysis of the variable temperature $^{31}P\{^1H\}$-NMR data (Fig. 5). This calculated energy barrier is similar in value to that measured for the rotation of η^2-alkyne ligands around the metal-alkyne bond [16], and only slightly higher than the that recently reported for the restricted rota-

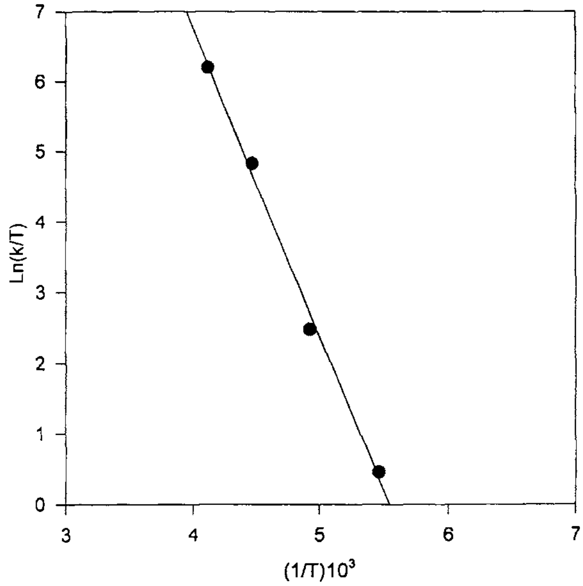
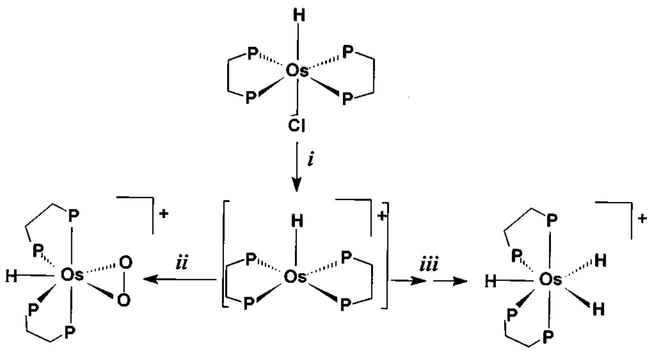


Fig. 3. Plot of Ln(k/T) versus 1/T (K^{-1}) for the phosphorus atom exchange process in $[OsH_3(dippe)_2][BPh_4]$.



Scheme 1. Reagents and conditions: (i) MeOH or EtOH, $NaBPh_4$; (ii) air or traces of oxygen; (iii) H_2 or prolonged stirring in alcohol at r.t.

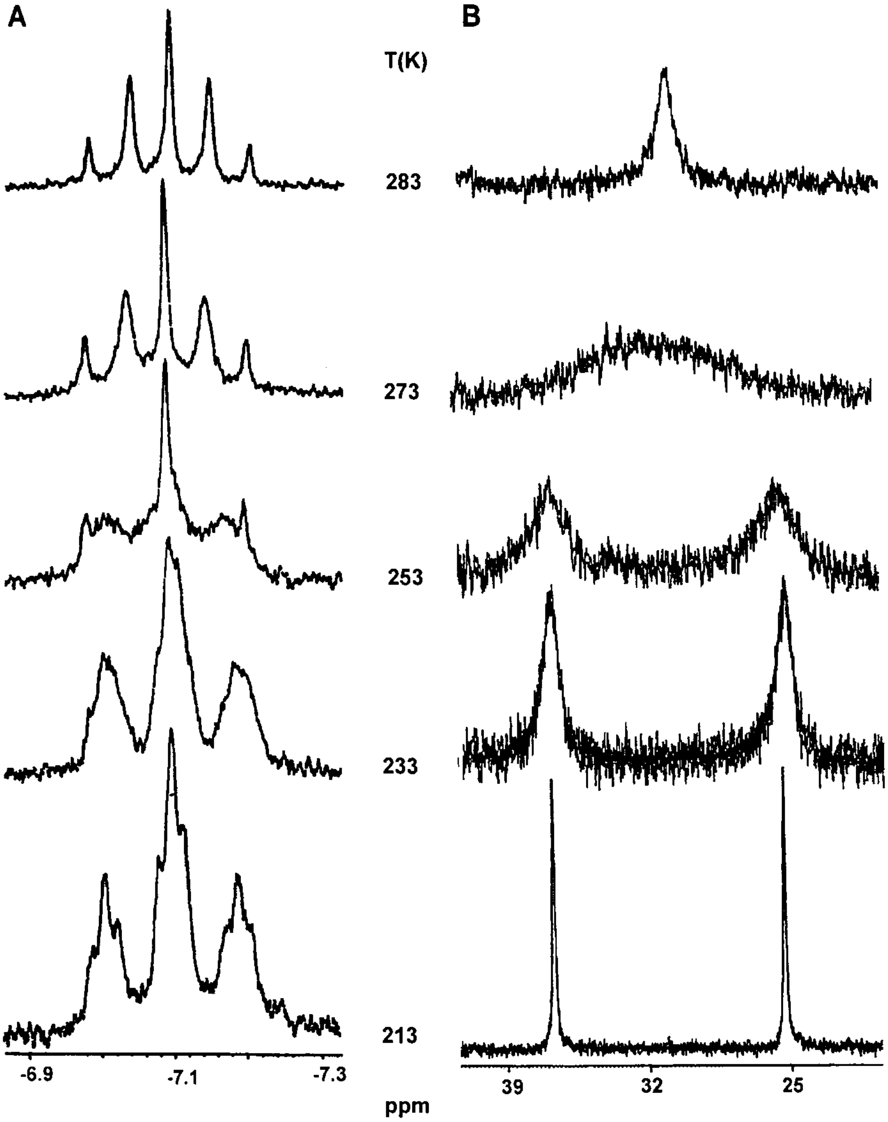


Fig. 4. Variable temperature NMR spectra of $[OsH(O_2)(dippe)_2][BPh_4]$ $(CDCl_3)$: (A) ^1H in the hydride region; (B) $^{31}P\{^1H\}$.

tion of dihydrogen in the complexes $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H_2)(CNR)]^+$ (R = Bu^t, Cy, 2,6-Xylyl) [15], which falls in the range 8.4–9.1 kcal mol^{-1}, being apparently consistent with the affirmation that similar molecular dynamics for the motion of η^2-coordinated dioxygen and other π-ligands such as alkynes or even dihydrogen is expected in their respective complexes.

3. Experimental section

All synthetic operations were performed under a dry dinitrogen or argon atmosphere following conventional Schlenk or drybox techniques. THF, diethylether and petroleum ether (boiling point range 40–60°C) were distilled from the appropriate drying agents. All solvents were deoxygenated immediately before use. $[NH_4]_2[OsCl_6]$ was supplied by Aldrich. 1,2-Bis(diisopropylphosphino)ethane [17], *cis*-$[OsCl_2(dippe)_2]$ and $[OsCl(dippe)_2][BPh_4]$ [11] were prepared according to reported procedures. IR spectra were recorded in Nujol mulls on Perkin Elmer 881 or Perkin Elmer FTIR Spectrum 1000 spectrophotometers. NMR spectra were taken on Varian Unity 400 MHz or Varian Gemini 200 MHz equipments. Chemical shifts are given in ppm from $SiMe_4$ (^1H and $^{13}C\{1H\}$) or 85% H_3PO_4 ($^{31}P\{^1H\}$). The phosphine protons for all compounds appeared in the corresponding ^1H-NMR spectra as a series of overlapping multiplets in the range 0.5–3 ppm, and were not assigned. Microanalysis was by Dr Manuel Arjonilla at the CSIC-Instituto de Ciencias Marinas de Andalucía.

3.1. Preparation of [$OsHCl_2$(dippe)$_2$][BPh_4] (**1**)

To a solution of [OsCl(dippe)$_2$][BPh_4] (0.05 g, ca. 0.064 mmol) in dichloromethane (10 ml), a few drops of concentrated aquous HCl was added. The initially brown solution became purple immediately. The mixture was filtered and then concentrated using reduced pressure. Addition of petroleum ether yielded a precipitate, which was filtered, washed with petroleum ether and dried in vacuo. Yield: 0.04 g, 60%. Anal. Calc. for $C_{52}H_{85}BCl_2OsP_4$ C, 56.5; H, 7.69. Found C, 56.2; H, 8.03. NMR (CD_2Cl_2): ^{1}H δ -12.43 (triplet of triplets, $J_{HP} = 12$ Hz, $J_{HP'} = 44$ Hz, OsHCl$_2$).^{31}P{^{1}H} 27.0 (s, br), 16.8 (s, br).

3.2. [OsH_3(dippe)$_2$][BPh_4] (**2**)

A solution of *cis*-[$OsCl_2$(dippe)$_2$] (0.1 g, *ca.* 0.13 mmol) in ethanol (15 ml), was treated with an excess of solid $NaBPh_4$ followed by solid $NaBH_4$ (excess). The mixture was heated under reflux for 1 h. During this time, a white precipitate was formed. The mixture was allowed to cool down to r.t., and then the white microcrystalline precipitate was filtered off, washed with ethanol and petroleum ether and dried in vacuo. Yield: 0.11 g, 85%. Anal. Calc. for $C_{52}H_{87}BOsP_4$ C, 60.2; H, 8.40. Found C, 60.2; H, 8.68. IR (Nujol): ν_{OsH} 1972 cm^{-1}. NMR (acetone-d$_6$): ^{1}H δ (298 K): -10.32 (q, $J_{HP} = 12$ Hz, $T_1 = 620$ ms, OsH_3); δ (183 K): -9.97 (q, $J_{HP} = 21$ Hz, $T_1 = 289$ ms, OsH(H)$_2$), -10.80 (br, $T_1 = 183$ ms, OsH(H)$_2$); ^{31}P{^{1}H}: δ (298 K): 55.1 s; δ (183 K): 52.1 br, 58.9 br.

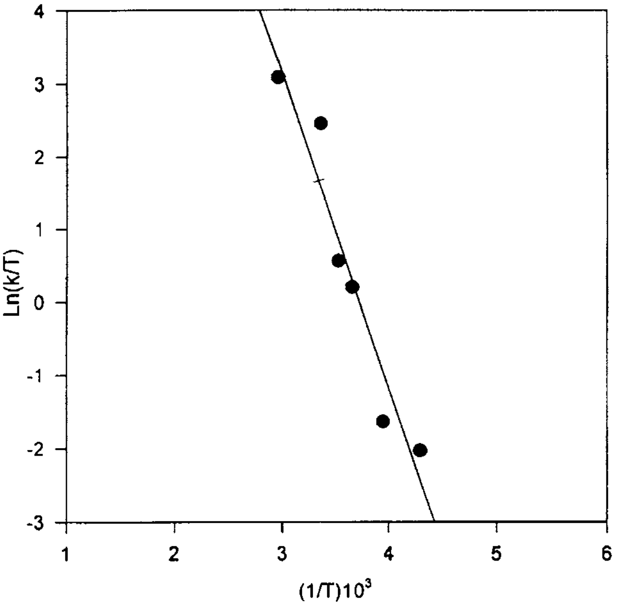


Fig. 5. Plot of Ln(k/T) versus 1/T (K^{-1}) for the phosphorus atom exchange process in [OsH(O_2)(dippe)$_2$][BPh_4].

3.3. *cis*-[OsH_2(dippe)$_2$] (**3**)

To a solution of **2** (0.15 g, ca. 0.14 mmol) in THF (15 ml), an excess of solid KOBu^t was added. The mixture was stirred at r.t. for 30 min. Then, the solvent was removed, and the residue extracted with petroleum ether. Centrifugation or filtration through celite, followed by concentration and cooling to -20°C afforded white crystals, which were filtered off and dried in vacuo. Yield: 0.06 g, 60%. Anal. Calc. for $C_{28}H_{66}OsP_4$ C 46.9; H 9.22. Found C 47.1; H 9.14. IR (Nujol): ν_{OsH} 1951, 1984, 2021 cm^{-1}. NMR (C_6D_6): ^{1}H δ -14.62 (XX′ part of an AA′MM′XX′ spin system, $J_{HA} = 55.3$ Hz, $J_{HA'} \cong J_{HM} = J_{HM'} = 22.8$ Hz, OsH_2). ^{31}P{^{1}H} 42.8 s, 68.4 s (J_{PP} not resolved).

3.4. *trans*-[OsHCl(dippe)$_2$] (**4**)

A solution of *cis*-[$OsCl_2$(dippe)$_2$] (0.1 g, ca. 0.13 mmol) in THF was treated with a slight excess over the equimolar amount of Li[$HBEt_3$] (0.15 ml of a 1 M solution in THF, 0.15 mmol). The mixture was stirred at r.t. for 1 h. At the end of this time, the solvent was removed in vacuo, and the residue extracted with petroleum ether. The resulting yellow solution was filtered through celite or centrifuged. Removal of the solvent afforded a yellow product which was thoroughly dried in vacuo. Yield: 0.07 g, 72%. Anal. Calc. for $C_{28}H_{65}ClOsP_4$ C 44.8, H 8.66. Found C 45.1, H 8.94. IR (Nujol): ν_{OsH} 2119 cm^{-1}. NMR (acetona-d$_6$): ^{1}H δ -24.14 (q, $J_{HP} = 16$ Hz, OsHCl). ^{31}P{^{1}H} 41.1 s.

3.5. [OsH(η^2-O_2)(dippe)$_2$][BPh_4] (**5**)

To a solution of **4** (0.05 g, ca. 0.07 mmol) in ethanol (10 ml), a slight excess of $NaBPh_4$ was added. Upon addition, the initially orange brown clear solution becomes turbid and reddish. The mixture was stirred in the air for 24 h. Dark red microcrystals were obtained, which were filtered off, washed with petroleum ether and dried in vacuo. Another crop of crystals could be obtained by concentration and cooling of the mother liquor. Yield: 0.06 g, 80%. Anal. Calc. for $C_{52}H_{85}BO_2OsP_4$ C 58.5, H 7.97. Found C 58.2, H 8.04. NMR ($CDCl_3$, 298 K): ^{1}H: δ (283 K) -7.10 (q, $J_{HP} = 23.3$ Hz, OsH(O_2)); δ (213 K) -7.10 (triplet of triplets, $J_{HP} = 37.6$ Hz, $J_{HP'} = 6.6$ Hz). ^{31}P{^{1}H} δ (328 K) 33.2 (s br, $\Delta\nu_{\frac{1}{2}} \cong 316$ Hz); δ (213 K) 27.4 (t, $J_{PP'} = 4.8$ Hz), 37.0 (s, br).

Acknowledgements

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