Complex Formation and Rearrangement Reactions of the Phosphine Hydride Anions $[OsH_3(PPh_3)_3]^-$ and $[IrH_2(PPh_3)_3]^-$

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$[OsH_4(PPh_3)_3]$ (**1**) reacts with KH in THF in the presence of 18-crown-6 to form $[K(THF)(18\text{-crown-}6)][OsH_3(PPh_3)_3]$ (**2**), characterized by NMR spectroscopy and X-ray crystallography; cation−anion contact is achieved through three Os−H···K moieties. In contrast, $[IrH_3(PPh_3)_3]$ (**6**) reacts with KH and 18-crown-6 in THF with redistribution of ligands to produce the known bis-phosphine complex $[K(18\text{-crown-}6)][IrH_4(PPh_3)_2]$ (**7**). This reaction has been followed by NMR spectroscopy, and $[IrH_2(PPh_3)_3]^-$ has been identified as a likely intermediate. $K[OsH_3(PPh_3)_3]$ (**3**) reacts with $Bu^n{}_3SnCl$ to form the tin-osmium complex $[OsH_3(SnBu^n{}_3)(PPh_3)_3]$ (**8**), characterized by NMR spectroscopy and X-ray crystallography. The molecule contains a seven-coordinate osmium center, which can be described approximately as a distorted *fac*-$[OsH_3(PPh_3)]$ arrangement, with the $SnBu^n{}_3$ moiety capping the OsH_3 face.

Introduction

Even though transition metal hydrides have been known for over seven decades, they remain highly topical in such diverse fields as organometallic chemistry,[1] bioinorganic chemistry,[2] supramolecular chemistry,[3] and hydrogen storage.[4] Transition metal hydrides have the advantage of containing at least one hydrogen atom with tunable electronic characteristics. This feature enables them to take part in intermolecular noncovalent bonding interactions, including electrostatic and van der Waals interactions, and especially hydrogen bonding. For example, recent elegant work by Morris and co-workers exploited proton−hydride interactions to control the formation of supramolecular structures containing anions such as $[OsH_4(PPr^i{}_3)_2]^-$ and $[IrH_5(PPr^i{}_3)_2]^-$.[5,6] In particular, noncovalent interactions between metal hydrides and either acidic hydrogen (unconventional hydrogen bonding)[7] or other metals[8] have become topical. Morris' work shows that the $M-H\cdots K^+$ interaction is significant and that it may play a role in metal hydride reactivity.

Here we report a study of the coordination chemistry of phosphine polyhydride complexes of Os and Ir and of their conjugate anions stabilized by $[K(18\text{-crown-}6)]^+$. These new materials have electronic and steric properties distinct from those reported by Morris et al.[5,6] We have focused on complexes containing three phosphine ligands instead of two, at the same time using the electronically less basic phosphine PPh_3.

Results and Discussion

Ionic Derivatives of $[OsH_4(PPh_3)_3]$. The complex $[OsH_4(PPh_3)_3]$ (**1**) was synthesized by the literature procedure[9] as an off-white precipitate. Characterization data were in agreement with those previously reported. The yellow, oxygen- and water-sensitive solid $[K(THF)(18\text{-crown-}6)][OsH_3(PPh_3)_3]$ (**2**) was prepared in 62% yield by reacting **1** with an excess of KH in THF in the presence of 18-crown-6. In this reaction, the role of the crown ether is to enhance the solubility of KH in THF and to impart stability to the final complex, but it may also serve as a C−H hydrogen bond donor. This reaction resulted in the formation of only the *fac*-isomer of $[OsH_3(PPh_3)_3]^-$, as evidenced by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy and X-ray crystallography. Complex **2** is very soluble in THF and only sparingly soluble in toluene, and decomposes slowly in chlorinated solvents. The ^1H NMR spectrum (d_8-THF) of **2** shows the distinctive mirror-symmetry patterns characteristic of an $AA'A''XX'X''$ spin system for the octahedrally coordinated anion. This multiplet, centered at −11.3 ppm, clearly differs from the precursor **1** (−8.1 ppm). The singlet observed in the $^{31}P\{^1H\}$ NMR spectrum (d_8-THF) at 24.6 ppm also differs from that of the starting material (23.8 ppm).

The reaction was monitored in a 5 mm NMR tube closed with a Teflon valve, with the hope of identifying any intermediate dihydrogen species. The tube was filled with equimolar amounts of **1** and 18-crown-6 and an excess of KH in d_8-THF and was shaken vigorously, and ^1H and $^{31}P\{^1H\}$ NMR spectra were measured every 30 min at 213 K. However, reaction did

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not commence at this low temperature and had to be encouraged by gentle warming. Once it had clearly started, the mixture was cooled again and its progress was followed by NMR spectroscopy. The spectra revealed a gradual transformation from starting material to product, without any evidence of intermediate species and implying extraction of a hydride from Os by KH in a conventional acid−base reaction.

The osmium complex **2** is extremely sensitive to proton sources, which cleanly and rapidly regenerate [$OsH_4(PPh_3)_3$]. Indeed, in the absence of the stabilizing crown ether, the anion of K[$OsH_3(PPh_3)_3$] (**3**), which is very unstable in solution, easily reverts to the starting tetrahydride complex **1**. The proclivity of anionic [$OsH_3(PPh_3)_3$]$^-$ in complex **2** to react with proton sources was studied by NMR spectroscopy, employing the weak acid $(CF_3)_2CHOH$ (HFIP) as the proton source. Variable-temperature NMR studies of complex **2** in d_8-THF solution showed no evidence of fluxionality over the range 293−180 K. Upon addition of a single equivalent of HFIP, the yellow solution became colorless and the tetrahydride was completely regenerated, even at low temperatures. However, upon addition of 3, 5, 15, 35, and more equivalents of HFIP, the peak at −8.1 ppm assigned to the tetrahydride **1** remained unaltered, and no further species appeared. This observation is remarkable, since addition of an excess of HFIP at low temperature to **1** in CD_2Cl_2 resulted in protonation and led to the formation of [$OsH_5(PPh_3)_3$]$^+$(**4**). This new cationic species was characterized by the appearance of a peak at −5.7 ppm in the ^{1}H NMR spectrum, with a T_1 value of 269 ms at 190 K, much smaller than that of the parent tetrahydride **1** (T_1 = 1738 ms).

Disagreement has arisen in the literature over the formulation of the analogous compound [$OsH_5(PMe_2Ph)_3$]$^+$, either as a nonclassical trihydride-dihydrogen complex[10,11] or as a dodecahedral pentahydride.[12] On the basis of our T_1 measurements for [$OsH_5(PPh_3)_3$]$^+$, we consider it to contain five classical hydride ligands. The short relaxation time for the hydride resonance of **4** relative to the classical tetrahydride complex **1** can be accounted for by the proximity of five fluxional hydride ligands in the cation. The close approach of these hydrides can induce dipole−dipole interactions and may even result in the formation of transient elongated dihydrogen ligands. Such a description accords with the interpretation of Esteruelas and Lledós, who carried out DFT calculations on the model complex [$OsH_5(PH_3)_3$]$^+$.[13] Their optimized geometries revealed that the structures containing nonclassical hydrides are energetically very similar to those that are classical and that their energy is practically independent of the separation between the H atoms involved in the nonclassical interaction. As a consequence, Esteruelas and Lledós described [$OsH_5(PH_3)_3$]$^+$ as a species containing hydrogen atoms moving freely in a wide region within the metal coordination sphere.

In an attempt to study further the reaction between **1** and HFIP, a ^{1}H NMR spectrum was recorded at room temperature 2 days after addition of the acid. Two peaks were observed in the spectrum: the original quartet at −8.1 ppm assigned to **1** along with a quintet at −9.9 ppm. The latter feature was the only one remaining after 5 days: it collapsed to a singlet when phosphorus-decoupled. The same feature was also observed 3 days after addition of HFIP to **2**. This quintet at −9.9 ppm is clearly the known [$OsH_3(PPh_3)_4$]$^+$ (**5**);[14] there was no evidence at this stage of the initially formed pentahydride cation **4**. It is not clear to us why complex **2** is only protonated to the neutral [$OsH_4(PPh_3)_3$] (**1**) in the presence of excess acid, but the rearrangements and ligand exchanges that clearly take place in the formation of **5** from **1** via **4** reveal a complicated series of reactions occurring under acid conditions.

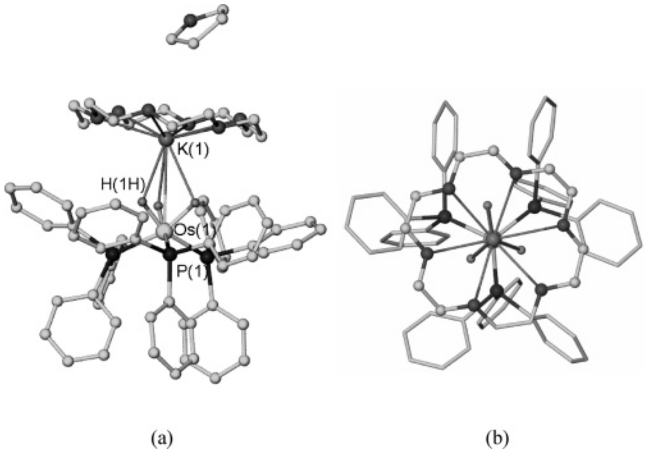

Figure 1. (a) X-ray crystal structure of [K(THF)(18-crown-6)]-[$OsH_3(PPh_3)_3$] (**2**). All non-hydride H atoms are omitted for clarity. Selected average bond lengths (Å): Os−P = 2.3273(13), Os−K = 3.5829(13), Os−H = 1.64(5), K−H = 2.86(5). Selected average angles (deg): P−Os−P = 105.45(5), K−Os−H = 49.7(16), H−Os−H = 83(2). (b) [K(18-crown-6)][$OsH_3(PPh_3)_3$] (**2**) viewed along the Os···K axis. The staggered arrangement of the hydrides with respect to the phosphine ligands is revealed.

Diffraction quality yellow crystals of **2** were obtained by slow diffusion of hexane into a THF solution of the complex under an Ar atmosphere. The complex crystallizes in the triclinic space group $P\bar{1}$, with two molecules per asymmetric unit. The crystal structure reveals the *fac*-configuration deduced spectroscopically for the anion (Figure 1), with the three hydrides pointing toward the potassium cation, which is drawn slightly out of the plane of the crown ether. The ion pair is held together through electrostatic interactions, enhanced by the anionic nature of the metal hydride moieties. The two molecules of the asymmetric unit are well separated, with no unusually short nonbonding intermolecular interactions present, and the two crown ether ligands are displaced away from each other and face in different directions, as can be seen in Figure 2.

The structure adopted by **2** contrasts with that of the crown-ether-free complex K[$OsH_3(PMe_2Ph)_3$],[15] which also contains more basic and sterically less demanding phosphine ligands. This complex adopts a dimeric structure in the crystal, as shown in Figure 3. In this case, the naked potassium ion and the more electron-rich Os−H moieties favor a more ionic arrangement. The two monomers are intimately connected by the interaction of the pyramidal K$^+$ in one monomer with one Os−H moiety from its partner unit, assisted by the encapsulation of K$^+$ by two phenyl rings of the phosphine ligands.

The molecular structure of **2** reveals that the potassium ion does not occupy a direct coordination site at osmium, as indicated by the Os···K distances of 3.54 and 3.63 Å, which are larger than the sum of the covalent radii for K and Os (3.29

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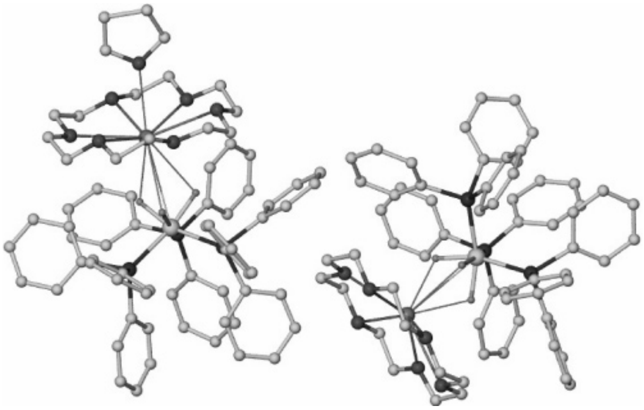

Figure 2. Asymmetric unit of [K(THF)(18-crown-6)][$OsH_3(PPh_3)_3$] (**2**). All non-hydride H atoms are omitted for clarity.

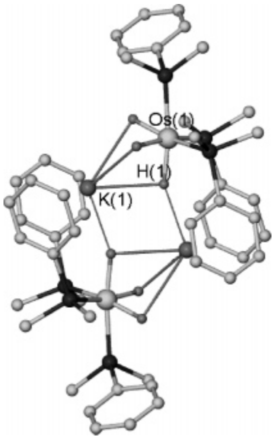

Figure 3. X-ray crystal structure of dimeric $K_2[OsH_3(PMe_2Ph)_3]_2$.[12] All non-hydride H atoms are omitted for clarity.

Å). Generally, as in the highly symmetric complex [K(18-crown-6)]SCN, the crown ether adopts a D_{3d} geometry in which K^+ lies at the center of the crown, with K···O distances of 2.80 Å.[16] In complex **2**, the crown ether ligand also adopts a D_{3d} geometry and K^+ remains equidistant from the six oxygen donor atoms. However, the potassium is attracted out of the plane of the crown and toward the osmium (K−crown centroid = 0.73 Å).

All Os−P distances in **2** are very similar, with an average value of 2.31 Å. The average P−Os−P angle is 105.5°, slightly wider than those in $K[OsH_3(PMe_2Ph)_3]_2$ (97.4°),[15] on account of the larger cone angle of PPh_3.[17] Likewise, all P−Os−K angles are equivalent (113.2°) and slightly smaller than those observed for $K_2[OsH_3(PMe_2Ph)_3]_2$. Average values for the Os−H and K−H distances are 1.64(5) and 2.86(5) Å, respectively, although the former may be in reality somewhat larger and the latter correspondingly smaller on account of the inaccurate location of H atoms by X-ray methods. The average value for the Os−H−K angle (102.3°) shows this moiety to be far from linear, as is the case also with $K[OsH_3(PMe_2Ph)_3]_2$.

The structure we have determined for **2** is in accord with those reported for similar complexes in the literature, viz., [K(18-crown-6)][$RuH_3(PPh_3)_3$],[18] [K(18-crown-6)][$WH_5(PMe_3)_3$],[19] [K(18-crown-6)][$ReH_2(PMe_3)_4$],[19] and [K(18-crown-6)][$IrH_4(PR_3)_2$] (R = Ph or Pr^i).[20] In these other systems, a maximum of three M−H moieties point toward the K^+ ion, although the number of H···K interactions is variable according to the shape and size of the anion, and the H-atom positions are not well defined in some cases. The cation−anion interaction draws the potassium ion out of the plane of the crown ether by 0.7 to 1.2 Å, with M···K distances in the range 3.4−3.8 Å. It is notable also that the [$OsH_3(PPh_3)_3$] anion in **2** bears a striking structural resemblance to the isoeletronic neutral congener *fac*-[$IrH_3(PPh_2Me)_3$], whose structure has been determined by neutron diffraction.[21] Here, the Ir−H bond distances are 1.627(5) Å and the H−Ir−H angles 83.4(2)°. The cation−anion interaction in **2** thus appears to be purely electrostatic and causes a negligible effect on the geometry of the anion.

Ionic Derivatives of [$IrH_3(PPh_3)_3$]. We also investigated the reaction of [$IrH_3(PPh_3)_3$] (**6**) with KH and 18-crown-6, with the aim of forming an iridium analogue of **2**. Complex **6** was prepared in a two-step reaction following the literature method.[22] A mixture of *mer*- and *fac*-isomers of **6** was obtained, as evidenced by ^1H and ^{31}P NMR spectroscopy. This pale yellow complex is quite stable in the solid state, but decomposed gradually in solution.

A mixture of **6**, KH, and 18-crown-6 in THF was warmed to 313 K and stirred for 4 days, during which time the yellow slurry changed through green to deep red in color. Unexpectedly, this produced the known Ir(V) bis-phosphine complex [K(18-crown-6)][$IrH_4(PPh_3)_2$] (**7**) as a white solid, extremely air-sensitive in both the solid state and solution. Complex **7** shows a complicated multiplet pattern at −12.6 ppm (3H) in the hydride region of the ^1H NMR spectrum in d_8-THF and a broad doublet of triplets at −12.9 ppm (1H), revealing two different environments for the hydride ligands. The $^{31}P\{^1H\}$ NMR spectrum also shows two different singlet phosphine resonances, at 26.9 and 12.8 ppm. White crystals were obtained by slow diffusion of hexane into a THF solution of **7**, and X-ray diffraction confirmed these to be [K(18-crown-6)][$IrH_4(PPh_3)_2$] as reported by Morris and co-workers.[20] We note that the ^1H NMR and ^{31}P spectra obtained by us in d_8-THF differ significantly from those described for complex **7** by Morris et al. in d_6-benzene, which showed a triplet of triplets at −11.9 ppm and a multiplet at −12.3 ppm, each integrating to 2H. This difference presumably arises from interference by the basic THF solvent, which can coordinate to the open face of the cation in **7** and lower the symmetry of the hydride ligand environment in the solvated ion pair.

Morris et al. obtained complex **7** and its PPr^i_3 analogue using Ir(III) or Ir(V) precursors with two phosphine ligands, as described in eqs 1 and 2. In contrast, we prepared **7** from an Ir(III) tris-phosphine precursor (eq 3). It is noteworthy that H_2 is added to stabilize the product in eq 1, whereas H_2 is released in eq 2. Our synthesis (eq 3) involved neither addition nor release of H_2 from solution, but instead proceeded through a ligand redistribution process.

$$[IrHCl_2(PPr^i_3)_2] + KH + \text{18-crown-6} \xrightarrow{\text{THF, } H_2} [K(\text{18-crown-6})][IrH_4(PPr^i_3)_2] \quad (1)$$

$$[IrH_5(PPh_3)_2] + KH + \text{18-crown-6} \xrightarrow{\text{THF, } -H_2} [K(\text{18-crown-6})][IrH_4(PPh_3)_2] \quad (2)$$

$$[IrH_3(PPh_3)_3] + KH + \text{18-crown-6} \xrightarrow{\text{THF}} [K(\text{18-crown-6})][IrH_4(PPh_3)_2] \quad (3)$$

In an attempt to characterize intermediates involved in the formation of **7** according to eq 3, we monitored the ^1H NMR

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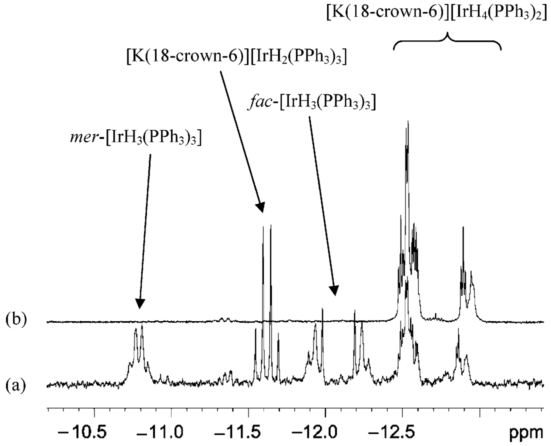

Figure 4. Hydride region of the ^{1}H NMR spectrum for the reaction between [$IrH_3(PPh_3)_3$] (**6**), KH, and [18-crown-6] in d_8-THF. (a) Early stage and (b) later stage, showing the presence of the product [K(18-crown-6)][$IrH_4(PPh_3)_2$] (**7**).

spectrum of the reaction mixture as a function of time, as depicted in Figure 5. The hydride region showed several species to be present. The starting materials *mer*- and *fac*-[$IrH_3(PPh_3)_3$] were evident, as was the product [K(18-crown-6)][$IrH_4(PPh_3)_2$] (**7**), which showed hydride signals in a 3:1 ratio. In addition, a quartet centered at −11.6 ppm ($J_{HP} = 20$ Hz) may be assigned as either [$IrH_2(PPh_3)_3$]$^-$ or [$IrH_4(PPh_3)_3$]$^-$. We prefer the former suggestion on account of the stability of 18-electron five-coordinate complexes of Ir(I).[23]

Accordingly, we propose the following process to explain the formation of **7** through eq 3. The first step involves abstraction of a proton from *mer*- or *fac*-[$IrH_3(PPh_3)_3$] by KH, with the formation of H_2. The resulting tris-phosphine intermediate [K(18-crown-6)][$IrH_2(PPh_3)_3$] is then responsible for the feature at −11.6 ppm in the ^{1}H NMR spectrum, which displays a characteristic quartet ($J_{HP} = 20$ Hz). However, the steric requirements of the crown ether and the three geminal PPh_3 ligands in this intermediate are considerable, and [K(18-crown-6)][$IrH_2(PPh_3)_3$] rapidly loses a phosphine ligand. The newly formed H_2 can now bind to Ir at the vacated coordination site to form [K(18-crown-6)][$IrH_4(PPh_3)_2$] (**7**), possibly via a transient dihydrogen complex.

Covalent Derivatives of [$OsH_4(PPh_3)_3$]. In view of the subtle yet apparently significant influence of the [K(18-crown-6)]$^+$ countercation on the reactivity of polyhydride anions, we decided to explore the effects of replacing this A-metal cation with the much more coordinating and covalent R_3Sn^+ moiety. Monoanionic transition metal complexes react with halides of group 14 forming a wide range of products. Tin-osmium derivatives are of particular interest on account of their catalytic role in important processes such as hydroformylation, olefin hydrogenation, and organic coupling reactions.[24] A THF solution of trihydride **3** reacted with $Bu^n{}_3SnCl$ with elimination of HCl to produce the novel complex [$OsH_3(SnBu^n{}_3)(PPh_3)_3$] (**8**) as a white, air- and water-sensitive crystalline material. The ^{1}H NMR spectrum of **8** in d_8-THF showed a pseudoquartet centered at −11.4 ppm, and the $^{31}P\{^1H\}$ NMR spectrum displayed a singlet at 13.3 ppm. A single crystal of the complex was analyzed by X-ray crystallography.

Complex **8** crystallizes in the monoclinic space group $P2_1/n$. The molecular structure of **8**, shown in Figure 4, consists of a seven-coordinate osmium center with facially disposed phosphines and hydrides approximately occupying the vertexes of an octahedron. The hydride ligands were located in a difference Fourier map, and the positions of two were refined freely while the third was allowed to refine with loose restraints. Description of the nature of the OsH_3Sn moiety is far from clear-cut, and much discussion has arisen around the interpretation of similar moieties in other transition metal hydride complexes.[25] The structure may be considered to contain an Os(III) trihydride center that is covalently bound to the Sn atom. Indeed, the Os−Sn distance of 2.6538(7) Å is slightly less than the sum of the covalent radii (2.66 Å), implying a covalent bond between these two atoms. Alternatively, complex **8** may be described as consisting of the two ionic fragments, [$SnBu^n{}_3$]$^+$ and [$OsH_3(PPh_3)_3$]$^-$. This arrangement then corresponds to Os(II) instead of the more unusual Os(III). A further possibility is to view **8** as a σ-bond complex, in accord with other similar group 8 hydride complexes with group 14 ligands. For example, the tin-iron complex [$FeH_3(PBu^nPh_2)_3(SnPh_3)$] was reported by Schubert et al., who interpreted its NMR spectra in terms of an η^2-HSn moiety that interacts with the metal center of the [$FeH_2(PBu^nPh_2)_3$] fragment.[26] The second-row congener [$RuH_3(SiCl_2Me)(PPh_3)_3$] contains a SiR_3 moiety instead of SnR_3, but otherwise is structurally rather similar to complex **8**.[27] This seven-coordinate Ru complex contains three Ru−H ligands, which engage in secondary interactions with the Si atom only 1.9 Å away, and may be described as [$RuH_2(\eta^2$-$HSiCl_2Me)(PPh_3)_3$], where the Si−H bond is almost fully—albeit not completely—cleaved. In **8**, the average H···Sn distances of 2.3 Å are only 0.1 Å larger than their H···Si counterparts in the Ru analogue. However, we can expect oxidative addition to be more advanced in the Os complex, owing to the more electron-rich metal center and the weaker E−H and stronger M−H bonds involved.

Despite the imprecise location of the H atoms, the geometry of the $OsSnR_3$ moiety of complex **8** affords a diagnosis of the nature of the Os−Sn bond. The angles C−Sn−C [103.2(5)°, 105.0(5)°, and 102.0(5)°] and C−Sn−Os [116.6(4)°, 113.6(3)°, and 114.9(3)°] define a tetrahedral geometry at Sn, and the closest nonbonded C···C distances (3.9 Å) between the phenyl groups on the phosphine ligands and the butyl groups at Sn provide no evidence for steric crowding influencing this geometry. Flattening of the SnC_3 moiety would imply a positive change on Sn and a significant electrostatic component in the bonding between Sn and Os: in the limit [$SnBu^n{}_3$]$^+$ may be expected to be trigonal planar, as has been demonstrated recently for the free silylium cation [Mes_3Si]$^+$.[28] However, the observed

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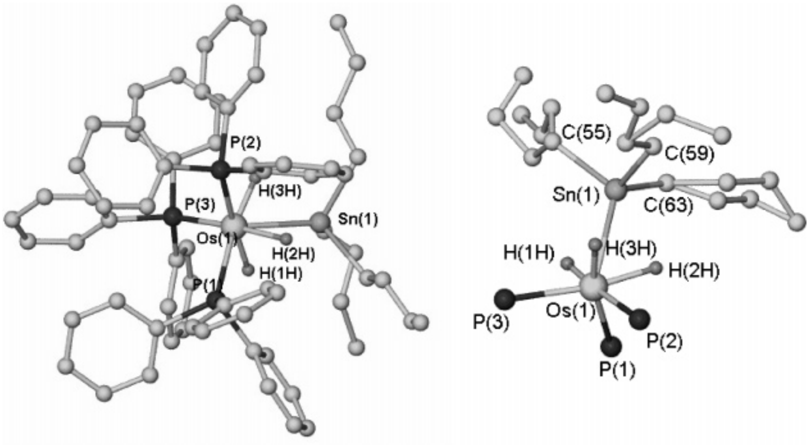

(a) (b)

Figure 5. (a) X-ray crystal structure of [$OsH_3(SnBu^n{}_3)(PPh_3)_3$] (**8**). All non-hydride H atoms are omitted for clarity. Selected bond distances (Å): Os−P 2.375(2), Os−Sn 2.6538(7), Os−H(av) 1.67(7), H···Sn(av) 2.3. Selected angles (deg): P−Os−P(av) 104.87(8), H(1)−Os−H(2) 90.3, H(1)−Os−H(3) 115.5, H(2)−Os−H(3) 90.3, Sn−Os−H(1) 63.5, Sn−Os−H(2) 57.9, Sn−Os−H(1) 60(3), C(55)−Sn−C(59) 103.2(5), C(55)−Sn−C(63) 102.0(5), C(59)−Sn−C(63) 105.0(5), C(55)−Sn−Os 116.6(4), C(59)−Sn−Os 114.9(3), C(55)−Sn−Os 113.6(3). The *n*-butyl groups are disordered, although only one conformation is depicted for clarity. (b) Representation of the skeleton of complex **8**, which contains the disordered *n*-butyl groups.

angles show the Sn−Os bond to be covalent in character, albeit with a certain degree of polarity, and complex **8** is best described as seven-coordinate [$OsH_3(SnBu^n{}_3)(PPh_3)_3$].

Summary

The hydrido tris-phosphine complex [$OsH_4(PPh_3)_3$] (**1**) reacts with KH in THF in the presence of 18-crown-6 to form [K(THF)(18-crown-6)][$OsH_3(PPh_3)_3$] (**2**). The structure of **2**, determined by X-ray crystallography, shows three hydrides to point toward the potassium cation, in an arrangement similar to that reported by Morris et al. for the hydrido bis-phosphine complex [K(18-crown-6)][$IrH_4(PPh_3)_2$] (**7**).[29] In contrast, attempts to prepare an Ir analogue of **2** from [$IrH_4(PPh_3)_3$] (**6**) resulted instead in ligand redistribution and the unexpected formation of **7**. A study of this reaction by NMR spectroscopy identified [$IrH_2(PPh_3)_3$]$^-$ as a likely intermediate in this process.

The tin-osmium complex [$OsH_3(SnBu^n{}_3)(PPh_3)_3$] (**8**) was prepared by reaction of $KOsH_3(PPh_3)_3$ with $Bu^n{}_3SnCl$. Complex **8** possesses a covalent Sn−Os bond in a seven-coordinate environment at osmium, which is best described as a distorted *fac*-[$OsH_3(PPh_3)$] arrangement with the $SnBu^n{}_3$ moiety capping the OsH_3 face, rather than as a σ-bond complex containing an Os(η^2-HSn) moiety.

The results we report here show that the stability and reactivity of anionic phosphine polyhydride complexes depends strongly on the nature and steric bulk of the countercation, as well as on that of the phosphine ligands. Under appropriate circumstances, both phosphine and hydride ligands can be labile, and complex rearrangements can occur. Loss of a phosphine ligand is a common first step in many transition-metal-mediated catalytic processes,[23] but reversible binding and release of H_2 is a less common phenomenon. These results have wider implications in areas such as hydrogenation catalysis and the mechanistic study of H_2 activation.[30]

Experimental Section

General Procedures. Unless otherwise stated, all operations were carried out under strictly inert atmosphere conditions using standard Schlenk and glovebox techniques. All solvents were distilled under an Ar atmosphere, employing as drying agents CaH_2 (pentane, hexane), Na/benzophenone (Et_2O, THF, toluene), or Mg turnings/I_2 (MeOH, EtOH). After distillation, solvents were degassed to completion by vigorous passage of Ar and stored over activated molecular sieves. Deuterated solvents were degassed, then stored over sodium (d_6-benzene, d_8-toluene, d_8-THF). KH was purchased as an oil suspension: before use, it was washed several times with pentane, thoroughly dried in vacuo, and stored in a glovebox. Crown ethers were thoroughly dried before used by dissolving them in THF over dried molecular sieves and were stored in a glovebox. Elemental analyses were performed at Birkbeck College and the University of North London (London, UK) or by Galbraith Laboratories, (Knoxville, TN). All quoted yields are for products obtained as crystalline material.

FT-IR spectra were recorded using a Perkin-Elmer Spectrum One spectrometer with a beam-condensing accessory and employing a diamond compression cell. Spectra were recorded for a neat sample of solid material contained between the diamond optics. Routine ^1H and ^{31}P NMR spectra were recorded using a Bruker AV360 spectrometer operating at 360 and 145 MHz, respectively, a Bruker AV400 spectrometer (400 and 162 MHz), or a Bruker DRX500 spectrometer (500 and 202.5 MHz). Complex **8** was characterized using a Varian Oxford300 spectrometer operating at 300 (^1H), 121 (^{31}P), and 112 (^{119}Sn) MHz. Maestre and XWin-Plot programs were used for graphical representations.

For spin−lattice relaxation time (T_1) measurements, 5 mm NMR tubes were loaded in a glovebox and transferred to a Schlenk line, where the appropriate volume of the corresponding deuterated solvent was added. Acid reagents were added by syringe at 195 K, and the NMR tube was rapidly inserted into the probe of the spectrometer, which had been precooled to ca. 180 K. Samples were allowed at least 10 min to equilibrate at each temperature. The conventional inversion−recovery method (180−τ−90) was used to determine the T_1 relaxation time as a function of temperature. Relaxation times were calculated by using a nonlinear three-parameter fitting routine. The pulses were calibrated at each temperature. In each experiment, the waiting period was much longer than the expected relaxation time, and 16 variable delays were employed.

[$Na_2OsCl_6 \cdot xH_2O$] and $(NH_4)_2IrCl_6$ were purchased from Strem. All other starting materials were purchased from Sigma-Aldrich. The complexes [$OsH_4(PPh_3)_3$],[23] [$IrHCl_2(PPh_3)_3$],[22a] and [$IrH_3(PPh_3)_3$][22b] were each prepared by literature methods.

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Synthesis and Characterization. [K(THF)(18-crown-6)][OsH_3(PPh$_3$)$_3$] (2). A mixture of [$OsH_4(PPh_3)_3$] (1.12 g, 1.15 mmol), THF (12 mL), KH (0.23 g, 5.75 mmol), and 18-crown-6 (0.46 g, 1.73 mmol) was stirred for 5 days under an Ar atmosphere. During this time, the brown slurry became yellow. All solids were removed by filtration, and the yellow product was crystallized from the filtrate by slow diffusion of hexane at 233 K. Yield: 62% (0.96 g, 0.71 mmol). Anal. Calc for $C_{70}H_{80}OsP_3O_7K$: C, 62.02; H, 5.95. Found: C, 62.12; H, 6.28. IR (solid, cm^{-1}): ν_{OsH} 1920 (s). ^{1}H NMR (d_8-THF): δ 7.70−6.70 (m, 45H, phenyl H), 3.45 (s, 24H, crown), −11.27 (m, 3H, OsH). ^{31}P{^{1}H} NMR (d_8-THF): δ 24.55 (s).

K[$OsH_3(PPh_3)_3$] (3). A mixture of [$OsH_4(PPh_3)_3$] (0.24 g, 0.24 mmol) and KH (0.08 g, 1.96 mmol) in THF (7 mL) was stirred for 12 h under an Ar atmosphere, during which time the brown slurry became yellow. All solids were removed by filtration, and the yellow solution was removed in vacuo to leave a very unstable yellow solid, which was washed with hexane. Yield: 80% (0.2 g, 0.20 mmol). Anal. Calc for $C_{54}H_{48}OsP_3K$: C, 63.64; H, 4.75. Found: C, 63.83; H, 4.94. IR (solid, cm^{-1}): ν_{OsH} 1913 (s). The product was identified by ^{1}H and ^{31}P NMR spectroscopy, which revealed a mixture of complexes **3** and **1**, because **3** is unstable in solution. ^{1}H NMR (d_8-THF): δ 7.80−6.70 (m, 45H, phenyl H), −11.45 (m, 3H, OsH). ^{31}P{^{1}H} NMR (d_8-THF): δ 25.71 (s, 2P), 24.53 (s, 1P).

[K(18-crown-6)][$IrH_4(PPh_3)_2$] (7). A mixture of [$IrH_3(PPh_3)_3$] (0.48 g, 0.49 mmol), THF (10 mL), KH (0.1 g, 2.45 mmol), and 18-crown-6 (0.19 g, 0.73 mmol) was gently warmed and stirred for 4 days under an Ar atmosphere. The pale yellow slurry became green and finally deep red. The solution was filtered, and hexane was layered above. This solution was kept at 233 K for 7 days, during which time it turned green and small colorless crystals appeared. Yield: 45% (0.13 g, 0.22 mmol). Anal. Calc for $C_{48}H_{58}IrO_6P_2K$: C, 56.29; H, 5.71. Found: C, 56.46; H, 5.92. IR (solid, cm^{-1}): 1992 (m), ν_{IrH}; 1717 (m), ν_{IrH}. ^{1}H NMR (d_8-THF): δ 7.60−6.90 (m, 30H, phenyl H), 3.82 (s, 24H, crown H), −12.56 (t of t, $^2J_{HH}$ = 5.1 Hz, $^2J_{HP}$ = 13.3 Hz, 3H, H_A of AA′A″BXX′), −12.89 (d of t, 1H, H_B). ^{31}P{^{1}H} NMR (d_8-THF): δ 26.94 (s, 1P, P_X), 12.84 (s, 1P, P_X′).

[$OsH_3(Bu^n{}_3Sn)(PPh_3)_3$] (8). A mixture of [$OsH_4(PPh_3)_3$] (0.25 g, 0.26 mmol) and KH (0.05 g, 1.27 mmol) in THF (10 mL) was stirred at 303 K for 1 day. The resulting yellow solution was filtered into a Schlenk vessel, and Bu_3SnCl (0.07 mL, 0.26 mmol) was added via a syringe. The solution was stirred for 12 h, whereupon it changed from yellow to brown. The brown oily product obtained after removal of solvent in vacuo was extracted with 15 mL of light petroleum, resulting in a clear yellow solution. This solution was kept at 233 K, and white crystals were obtained after 3 days. Yield: 56% (0.18 g, 0.14 mmol). Anal. Calc for $C_{66}H_{75}OsP_3Sn$: C, 62.41; H, 5.95. Found: C, 62.68; H, 6.10. ^{1}H NMR (d_8-THF): δ 7.68−6.89 (m, 45 H, phenyl H), 2.46−0.79 (m, 27H, butyl H), −11.48 (q, 3H, J_{HP} = 27). ^{31}P{^{1}H} NMR (d_8-THF): δ 13.3 (s). ^{119}Sn{^{1}H} (d_8-THF): δ −41.4 (s).

Reactions Monitored by NMR Spectroscopy. Reaction between [$OsH_4(PPh_3)_3$], KH, and 18-crown-6. [$OsH_4(PPh_3)_3$] (0.04 g, 41 μmol), KH (8.2 mg, 0.21 mmol), and 18-crown-6 (16.1 mg, 61.2 μmol) were placed in a 5 mm NMR tube with 1 mL of THF-d_8. The solution was warmed slightly with a water bath and transferred rapidly to the spectrometer probe precooled to 200 K. ^{1}H NMR spectra were recorded at 200, 230, 270, and 293 K and again after 24 h at 293 K, which revealed the direct conversion of **1** into **2** (simultaneous disappearance of the peak at −8.10 and growth of the peak at −11.27 ppm).

Reaction between [$OsH_4(PPh_3)_3$] and $(CF_3)_2CHOH$. A 5 mm NMR tube was charged with [$OsH_4(PPh_3)_3$] (13 mg, 13.3 μmol) and 0.7 mL of CD_2Cl_2. ^{1}H NMR spectra were recorded at 190 K, as was the relaxation time T_1 (1738 ms). Further spectra were recorded at 230, 260, and 293 K. Subsequently, the NMR tube was cooled to 195 K and HFIP (1.37 μL, 13.3 μmol) was added via a syringe. ^{1}H NMR spectra were recorded at 180, 190 (T_1 (269 ms), 230, 260, and 293 K. This reaction was also studied in d_8-THF because [$OsH_4(PPh_3)_3$] decomposes slowly in CD_2Cl_2. In the hydride region of the ^{1}H NMR spectrum peaks were visible at −8.10 (**1**) and −5.74 ppm, assigned to the OsH_5 moiety of [$OsH_5(PPh_3)_3$]$^+$ (**4**). After 3 days ^{1}H, ^{1}H{^{31}P}, and ^{31}P{^{1}H} NMR spectra (d_8-THF) were measured at 293 K, showing a quintet at −9.90, a singlet at −9.90, and a singlet at 37.83 ppm, respectively.

Reaction between [K(THF)(18-crown-6)][$OsH_3(PPh_3)_3$] and [$(CF_3)_2CHOH$]. A 5 mm NMR tube was charged with [K(THF)-(18-crown-6)][$OsH_3(PPh_3)_3$] (13 mg, 10.1 μmol) and 0.7 mL of d_8-THF. HFIP (1.26 μL, 12.2 μmol) was added via a syringe to the precooled tube, and the ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded at 200 K. These revealed the transformation of **2** (^{1}H −11.27; ^{31}P 24.55) into **1** (^{1}H −8.07; ^{31}P 23.80). Subsequent aliquots of HFIP (1.58, 5.25, 14.07, 35.7, and 52.5 μL) were added, and the spectra re-recorded at 200 K, but no further change was observed in the hydride region. After 3 days ^{1}H and ^{31}P{^{1}H} NMR spectra (d_8-THF) were recorded at 298 K, showing a quintet at −9.90 ppm and a singlet at 37.83 ppm, respectively.

X-ray Structural Determinations. Air-sensitive crystals were transferred in a glovebox into a vessel containing perfluoropolyalkyl ether. Crystals were mounted on a thin glass fiber and cooled on the diffractometer to 100−120 K using an Oxford Cryostream Liquid N_2 device. Approximate unit cell dimensions were determined by the Nonius Collect program[31] from five index frames of width 2° in ϕ using a Nonius KappaCCD diffractometer (graphite monochromatic Mo Kα radiation, λ = 0.71073 Å), with a detector-to-crystal distance of 30 mm. The Collect program was then used to calculate a data collection strategy to 99.5% completeness for θ = 27.5° using a combination of 0.5−2° ϕ and ω scans of 10−60 s deg^{-1} exposure time (depending on crystal quality). Crystals were indexed using the DENZO-SMN package,[32] and positional data were refined along with diffractometer constants to give the final unit cell parameters. Integration and scaling (DENZO-SMN, Scalepack[32]) resulted in unique data sets corrected for Lorentz and polarization effects and for the effects of crystal decay and absorption, by a combination of averaging of equivalent reflections and an overall volume and scaling correction. Structures were solved using SHELXS-97[33] and developed via alternating least-squares cycles and difference Fourier synthesis (SHELXL-97) with the aid of the program XSeed.[34] In general, unless stated, all non-hydrogen atoms were modeled anisotropically, while hydrogen atoms were assigned an isotropic thermal parameter 1.2 times that of the parent atom (1.5 for terminal atoms) and allowed to ride. POV-Ray was used for the molecular graphics.

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Supporting Information Available: X-ray crystallographic files in CIF format for complexes **2** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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