Sigma-bond activation reactions induced by unsaturated Os(IV)-hydride complexes

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Abstract

Unsaturated osmium(IV)-hydride complexes are diamagnetic six-coordinate d^4 species, which undergo distortion from the octahedral geometry to form unusual D_{4d} or C_{2v} geometries. They display a notable ability to activate H-H, B-H, C-H, C-C, C-O, C-Br, Si-H, Sn-H, N-H, or O-H bonds of a wide range of inorganic, organic, and organometallic molecules, including: molecular hydrogen, boranes, phosphines, heterocycles, olefins, dienes, enynes, allenes, allenedienes, ynamides, alkylhalides, silanes, stannanes, diamines, oximes, metal-nucleosides, or molecular oxygen. The activations yield, among other organometallic derivatives, dihydrogen, borane, borinium, alkylidene, alkylidyne, vinylidene, NHC, silylene, stannyl, osmafuran, osmaisobenzofuran, osmabenzimidazolium, or azavinylidene complexes. A characteristic of these activation processes is that do not result in an increase of the formal oxidation state of the metal center. Given the wide range of σ-bond activations promoted by these compounds and the wide variety of complexes formed future interesting applications for them can be anticipated.

Keywords

Osmium; hydride; sigma-bond; bond activation; dihydrogen

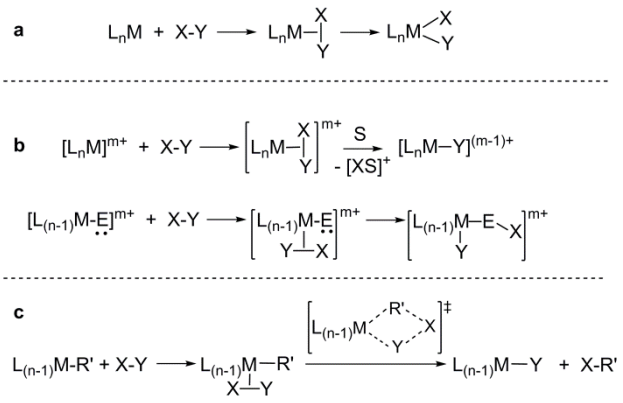
Contents

1. Introduction

The σ-bond activation reactions promoted by transition metal complexes can be grouped in three classes: oxidative addition also denoted as homolytic cleavage, heterolytic cleavage, and σ-bond metathesis The first step for all them is the coordination of that bond to the transition metal, to form a $L_nM(\eta^2$-X-Y) σ-complex (Scheme1). Because the interaction between the σ-bond and the metal center is usually weak, the starting complex must be unsaturated. Saturated species prevent the σ-bond activation processes. The coordination implies σ-donation from the σ(XY) orbital to empty orbitals of the metal and back bonding from the metal to the σ*(XY) orbital.[1] Basic metal centers increase the back-donation, favoring the oxidative addition of the X-Y bond (**a**), while acidic metal centers enhance the σ-donation to the metal for promoting the heterolytic cleavage of the X-Y bond (**b**). The cation acceptor can be an external base or a group with free electron pairs in the sphere of the metal center.[2] This latter case is denoted as activation via "*metal-ligand cooperation*" by some authors, which have proposed it as a fundamental step in relevant catalytic reactions,[3-8] although recent results from DFT calculations are challenging the proposal.[9-16] The third form of cleavage, the σ-bond metathesis, is described as a concerted process via a four-center, four-electron transition state (**c**).[17,18] In contrast to **a**, activations **b** and **c** avoid the formal 2-e oxidation of the metal.

[Insert Scheme 1]

Scheme 1 Modes of σ-bond activation reactions.

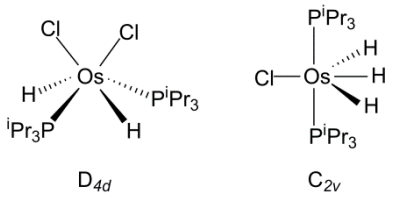


Unsaturated osmium(IV)-hydride complexes are six-coordinate d^4 species, which bear at least a π-donor ligand and are generally stabilized by bulky phosphines. They undergo distortion from the octahedral geometry to destabilize one orbital from the t_{2g} set and simultaneously to stabilize some occupied orbital. Thus, they prefer to be

diamagnetic.[19,20] The distortions mainly give rise to two geometries type (Chart 1). The structures of complexes $OsH_2Cl_2(P^iPr_3)_2$ and $OsH_3Cl(P^iPr_3)_2$ are the main representatives of them. In the beginning, the structure of $OsH_2Cl_2(P^iPr_3)_2$ was viewed as a distorted square antiprism of ideal D_{4d} symmetry with two vacant coordination sites.[21] Later, it was described as a bicapped tetrahedron and as a trigonal prism.[22] The structure of $OsH_3Cl(P^iPr_3)_2$ has essentially C_{2v} symmetry.[23] This distortion partially cancels the electron deficiency at the metal center, which receives electron density through the σ-bonds with the hydride ligands and additionally from a lone pair of the halide via a π bond.[24]

[Insert Chart 1]

Chart 1 Geometries of unsaturated osmium(IV)-hydride complexes.



These osmium(IV) compounds induce the activation of H-H, H-B, C-H, Si-H, N-H, or C-X (X = Cl, Br, I) among other σ-bonds and some multiple bonds such as that of molecular oxygen. The induction occurs because they promote the cleavage of the bond by themselves or because lose H_2 or HCl to generate 14-valence electrons transitory osmium(II) intermediates ($OsCl_2(PR_3)_2$ or $OsHX(PR_3)_2$), which are in many cases the real active species. In this context, the choice of the solvent of the reaction is crucial in the planning of the activation.[25] The reaction solvent determines the stability of the precursor and decides the formation of the osmium(II) intermediate, which governs the activation.

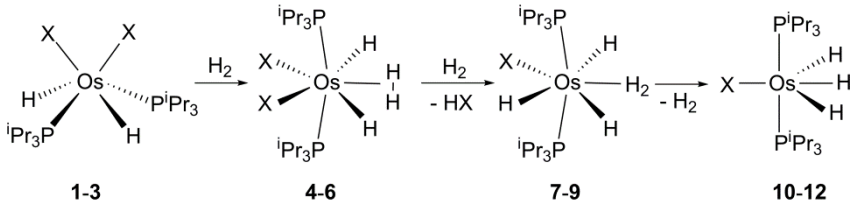
The relevance of the σ-bond cleavage in the modern chemistry along with the electronic (fairly acidic metal center) and structural (unusual geometries among the platinum group metal derivatives) peculiarities of the unsaturated osmium(IV)-hydride complexes converts the reactions of σ-bond activation, induced by these compounds, in a fascinating subject in organometallics. This review contextualizes the reactions of this class performed between 1991 and 2019.

2. H-H bond activation

Complexes $OsH_2X_2(P^iPr_3)_2$ (X = Cl (**1**), Br (**2**), I (**3**)) coordinate a hydrogen molecule in dichloromethane, to give the dihydride-elongated dihydrogen derivatives $OsH_2X_2(\eta^2\text{-}H_2)(P^iPr_3)_2$ (X = Cl (**4**), Br (**5**), I (**6**)).[26] Crystallographic and spectroscopic evidence suggest that the donor atoms around the metal center form a dodecahedron. One of the perpendicular trapezoidal planes is formed by the phosphorous atoms of the phosphines and the hydrogen molecule, whereas the halides and the hydride ligands lie in the other one.[27] In agreement with the acidity of the metal center in these compounds, the coordinated hydrogen molecule undergoes heterolytic cleavage releasing HX, to give the related polyhydrides $OsH_3X(\eta^2\text{-}H_2)(P^iPr_3)_2$ (X = Cl (**7**), Br (**8**), I (**9**)), under hydrogen atmosphere.[23,26] The replacement of a halide by hydride reduces the back-donation power of the metal center to the σ* orbital of the coordinated hydrogen molecule. As a consequence, the later forms a Kubas type dihydrogen ligand in **7-9**. Its dissociation leads to the unsaturated trihydrides $OsH_3X(P^iPr_3)_2$ (X = Cl (**10**), Br (**11**), I (**12**)), according to Scheme 2. The hydride ligands of **10-12** display quantum exchange coupling in addition to thermal exchange.[23]

[Insert Scheme 2]

Scheme 2 Reactions of **1-3** with molecular dihydrogen.



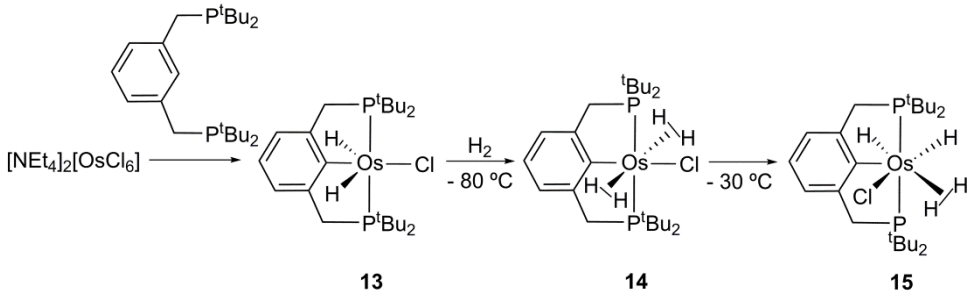
X = Cl (**1**, **4**, **7**, **10**), Br (**2**, **5**, **8**, **11**), I (**3**, **6**, **9**, **12**)

Pincer ligands also stabilize unsaturated osmium(IV)-hydride complexes, which activate molecular hydrogen. Reaction of $[Et_4N]_2OsCl_6$ with the diphosphine 2,6-$(CH_2P^tBu_2)_2C_6H_4$, in 2-propanol, at 100 ºC, under hydrogen atmosphere leads to the dihydride derivative $OsH_2Cl\{\kappa^3\text{-}P,C,P\text{-}[2,6\text{-}(CH_2P^tBu_2)_2C_6H_3]\}$ (**13**) in 76% yield. This compound, which displays a similar structure to that of the trihydride **10**, reacts with hydrogen in methylcyclohexane-d_{14} to afford two complexes (Scheme 3). The kinetic bis(elongated dihydrogen) product $OsCl(\eta^2\text{-}H_2)_2\{\kappa^3\text{-}P,C,P\text{-}[2,6\text{-}(CH_2P^tBu_2)_2C_6H_3]\}$ (**14**) is formed below -70 ºC. On warming to -30 ºC, one of the coordinated hydrogen molecules undergoes homolytic cleavage to give the *cis*-dihydride-elongated dihydrogen derivative $OsH_2Cl(\eta^2\text{-}H_2)\{\kappa^3\text{-}P,C,P\text{-}[2,6\text{-}(CH_2P^tBu_2)_2C_6H_3]\}$ (**15**). Although

for this compound two different pentagonal bipyramidal structures can be considered, H_2 *trans* to Cl and H_2 *trans* to phenyl, it is more likely that the hydrogen molecule is situated *trans* to the ligand possessing the strongest *trans*-influence, while the dihydride unit is more likely to be *trans* to the ligand of weak *trans*-influence and good π-donor chloride.[28]

[Insert Scheme 3]

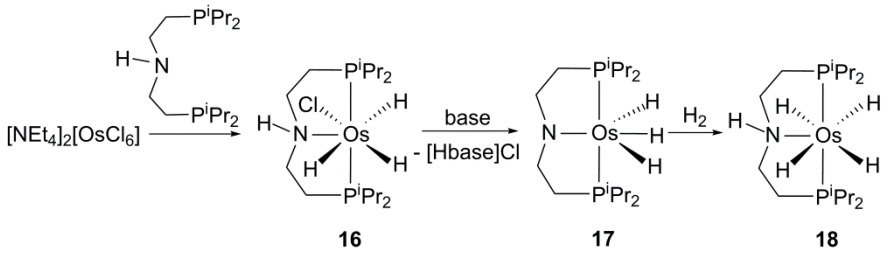
Scheme 3 Reaction of the P,C,P-pincer complex **14** with molecular hydrogen.



Salt $[Et_4N]_2OsCl_6$ also reacts with the aminediphosphine $HN(C_2H_4P^iPr_2)_2$ (Scheme 4). The reaction gives the trihydride derivative $OsH_3Cl\{\kappa^3$-P,N,P-$[HN(C_2H_4P^iPr_2)_2]\}$ (**16**), in 2-propanol or 2-pentanol. Upon treatment with K^tBuO or $NaN(SiMe_3)_2$, complex **16** undergoes dehydrochlorination to afford the P,N,P-pincer counterpart of **10** $OsH_3\{\kappa^3$-P,N,P-$[N(C_2H_4P^iPr_2)_2]\}$ (**17**), which heterolytically activates molecular hydrogen. The activation leads to the tetrahydride $OsH_4\{\kappa^3$-P,N,P-$[HN(C_2H_4P^iPr_2)_2]\}$ (**18**). The latter is an efficient catalyst for the hydrogen transfer from alcohols to ketones, the acceptorless dehydrogenative coupling of primary alcohols to esters and the monoalkylation of primary amines with primary alcohols.[29]

[Insert Scheme 4]

Scheme 4 Preparation of the P,N,P-pincer complex **17** and its reaction with molecular hydrogen.

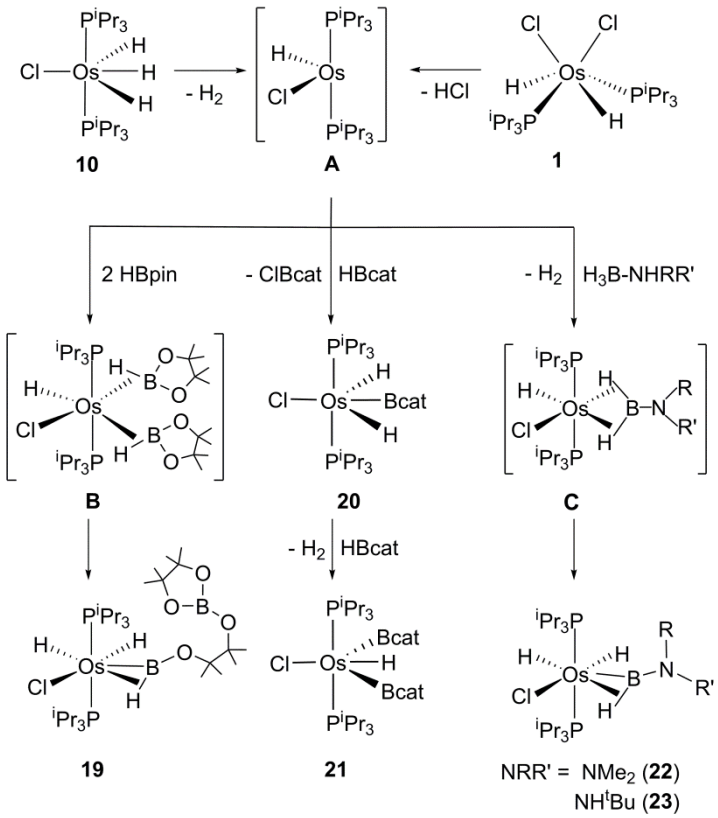


3. B-H bond activation

Trihydride **10** shows a marked tendency to release H_2 to afford the 14-valence electrons species $OsHCl(P^iPr_3)_2$ (**A**), which is also formed from the dihydride-dichloride $OsH_2Cl_2(P^iPr_3)_2$ (**1**) by reductive loss of HCl. This unsaturated species is the tool used by **10** and **1** to activating the B-H bond of boranes and amine-boranes (Scheme 5).

[Insert Scheme 5]

Scheme 5 B-H bond activation reactions promoted by **1** and **10**.



The reaction of **A** with pinacolborane (HBpin) yields the borinium derivative $OsH_2Cl(\eta^2\text{-H-BOCMe}_2\text{CMe}_2\text{OBpin})(P^iPr_3)_2$ (**19**);[30] its formation appears to take place via intermediate $OsHCl(HBpin)_2(P^iPr_3)_2$ (**B**), which can be generated by coordination of the B-H bonds of two molecules of HBpin to the osmium atom of **A**. Once coordinated the boranes, the heterolytic B-H bond activation of one of them gives **19**, using an oxygen atom of the other one as an external base. In contrast to HBpin, catecholborane (HBcat) affords boryl derivatives. The dihydride compound $OsH_2Cl(Bcat)(P^iPr_3)_2$ (**20**) is initially formed, as a result of the homolytic addition of the B-H bond to the osmium atom of **A.** Complex **20** reacts with a second molecule oh HBcat to give the hydride-

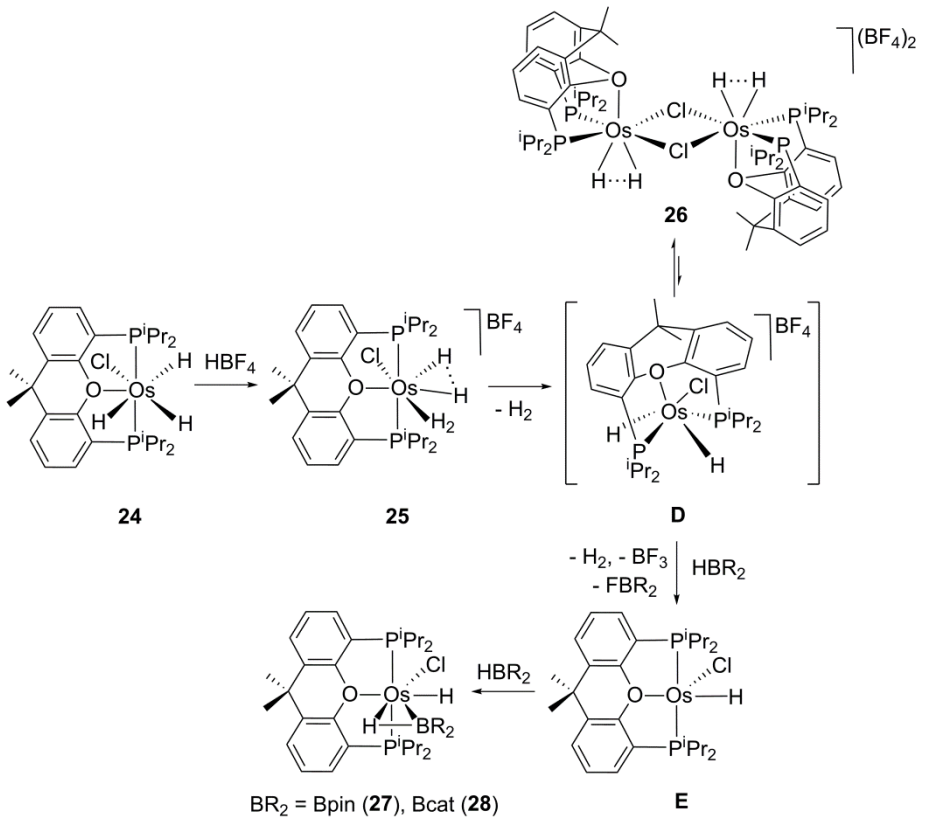
bis(boryl) derivative $OsHCl(Bcat)_2(P^iPr_3)_2$ (**21**) and molecular hydrogen.[31] Amine-boranes undergo dehydrogenation in the presence of **A** to form aminoboranes. The hydride transfer from the aminoboranes to its metal center leads to the aminoborinium compounds $OsH_2Cl(\eta^2\text{-H-BNRR'})(P^iPr_3)_2$ (NRR' = NMe_2 (**22**), NH^tBu (**23**)),[30] most probably via the bis(σ-B-H) intermediates $OsH_2Cl(\eta^2,\eta^2\text{-}H_2BNRR')(P^iPr_3)_2$ (**C**).

DFT calculations suggest that the major contribution to the interaction between the metal fragment and the borinium ligands is electrostatic (57%). This reveals a high degree of polarization for the osmium-borinium bond, which agrees well with the high electronegativity of the osmium atom and suggests a significant positive partial charge on the ligand in a consistent manner with the borinium denomination and the calculated hybridization at the boron atom ($sp^{1.3\text{-}1.6}$). The orbital term of the interaction is the result of three contributions: two σ-interactions and a π-interaction. The most important σ-interaction, the 61% of the total ΔE_{orb} value, involves a charge flow from the metal center to the boron atom; the other one is a donor-acceptor interaction from the doubly occupied σ(B-H) orbital to the metal fragment (about the 10% of ΔE_{orb}). The π-interaction is also significant. Its associated energy for the deformation density corresponds to about 21% of the total orbital attractions.[32]

The activation of HBpin and HBcat promoted by an unsaturated cationic osmium(IV)-dihydride generated *in situ* has been also reported (Scheme 6). Trihydride $OsH_3Cl\{\kappa^3\text{-P,O,P-[xant}(P^iPr_2)_2]\}$ (**24**; $xant(P^iPr_2)_2$ = 9,9-dimethyl-4,5-bis(diisopropylphosphine)xanthene) adds the proton of HBF_4 to afford the compressed dihydride-dihydrogen complex $[OsH_2(\eta^2\text{-}H_2)Cl\{\kappa^3\text{-P,O,P-[xant}(P^iPr_2)_2]\}]BF_4$ (**25**), which is stable under hydrogen atmosphere. Under argon, it dissociates the coordinated hydrogen molecule to afford the 16-valence electrons osmium(IV)-dihydride $[OsH_2Cl\{\kappa^3\text{-P,O,P-[xant}(P^iPr_2)_2]\}]BF_4$ (**D**), which rapidly reaches an equilibrium with the dimer $[(OsH_2\{\kappa^3\text{-P,O,P-[xant}(P^iPr_2)_2]\})_2(\mu\text{-}Cl)_2](BF_4)_2$ (**26**). The unsaturated dihydride **D** heterolytically activates the B-H bond of HBpin and HBcat using the $[BF_4]^-$ anion as an external base. The release of molecular hydrogen generates a square-planar pyramidal metal fragment $OsHCl\{\kappa^3\text{-P,O,P-[xant}(P^iPr_2)_2]\}$ (**E**), which coordinates the B-H bond of a second molecule of borane to yield $OsHCl(\eta^2\text{-H-}BR_2)\{\kappa^3\text{-P,O,P-[xant}(P^iPr_2)_2]\}$ (BR_2 = Bpin (**27**), Bcat (**28**)).[33]

[Insert Scheme 6]

Scheme 6 B-H bond activation of boranes promoted by a P,O,P-pincer system.



The interaction between the metal center and the coordinated B-H bond in **27** and **28** has been analyzed, from X-ray diffraction and theoretical points of view, and compared with that in the dihydrides $OsH_2(\eta^2\text{-H-BR}_2)\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ (BR_2 = Bpin (**29**), Bcat (**30**)). X-ray diffraction analysis and DFT-optimized structures of **27** and **28** reveal distances between the coordinated B and H atoms of the borane in the range of 1.6-1.7 Å, which support an elongated σ-borane character for these compounds. Atoms in molecules (AIM) analysis displays a triangular topology for the OsHB unit involving Os-B, Os-H, and B-H bond critical points and a ring critical point.[34] In contrast to **27** and **28**, the structures of the dihydrides **29** and **30** show distances between the atoms of the coordinated B-H bond in the range of 1.4-1.5 Å, which indicate character of σ-borane derivatives. In agreement with this, the AIM analysis for the OsHB unit only displays Os-B and B-H bond critical points; i.e., they lack a similar topology.[33,34] The electron withdrawing ability of the chloride ligand increases the donation from the σ(B-H) orbital to the osmium atom, whereas its π-donor power favors the *d*(Os)-to-σ*(B-H) back-donation.

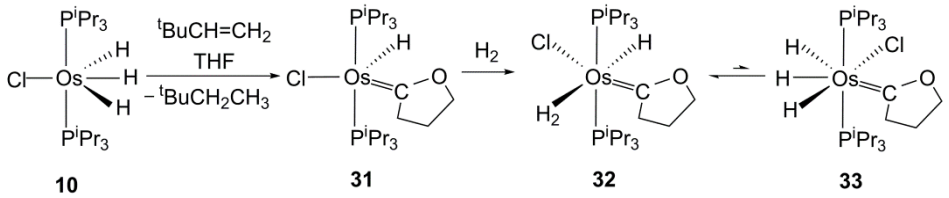
4. C-H bond activation

4.1 C(sp^3)-H bond activation of saturated heterocycles[35]

Trihydride complex **10** doubly dehydrogenates a carbon α to the oxygen atom of tetrahydrofuran, in the presence of *tert*-butylethylene, to afford the carbene derivative $OsHCl[=CO(CH_2)_3](P^iPr_3)_2$ (**31**) and the alkane. In benzene, under 1 atm of hydrogen, complex **31** gives the *trans*-hydride-dihydrogen $OsHCl(\eta^2\text{-}H_2)[=CO(CH_2)_3](P^iPr_3)_2$ (**32**) in equilibrium with the trihydride $OsH_3Cl[=CO(CH_2)_3](P^iPr_3)_2$ (**33**). The relative population of these species (95:5) at 20 ºC indicates a thermodynamic preference for the *trans*-hydride-dihydrogen redox isomer (Scheme 7).

[Insert Scheme 7]

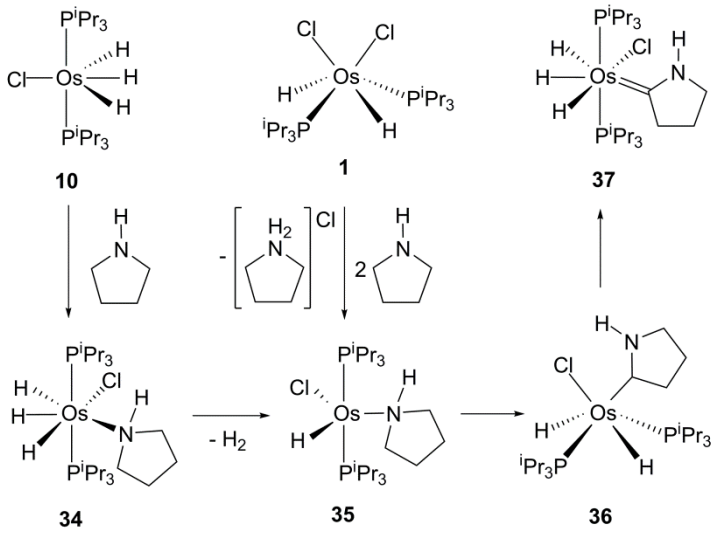
Scheme 7 C(sp^3)-H bond activation of tetrahydrofuran promoted by **10**.



Trihydride **10** also reacts with pyrrolidine (Scheme 8). However, there are significant differences between this activation and that shown in Scheme 7. In contrast to tetrahydrofuran, pyrrolidine initially coordinates to the metal center as amine to yield the saturated trihydride $OsH_3Cl(NHC_4H_8)(P^iPr_3)_2$ (**34**). The latter slowly loses molecular hydrogen to give the 16-valence electrons intermediate $OsHCl(NHC_4H_8)(P^iPr_3)_2$ (**35**), which can be also formed by dehydrochlorination of **1** with 2 equiv of the heterocycle. The metal center of this intermediate promotes a double C_α-H bond activation of the coordinated pyrrolidine, which in a sequential manner generates complexes $OsH_2Cl[CH(NH)C_3H_6](P^iPr_3)_2$ (**36**) and $OsH_3Cl[=CNH(CH_2)_3](P^iPr_3)_2$ (**37**).

[Insert Scheme 8]

Scheme 8 C(sp^3)-H bond activation of pyrrolidine promoted by **10** and **1**.



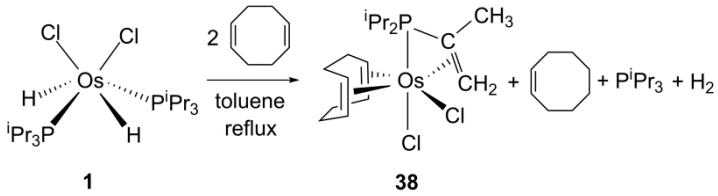
4.2 Cycloolefin-promoted C(sp^3)-H bond activation of phosphines

1,5-Cyclooctadiene (COD), 2,5-norbornadiene (NBD), and tetrafluorobenzobarrelene (TFB) promote the dehydrogenation of a phosphine of **1**. The C(sp^3)-H activations are accompanied by C-C bond activation and C-C and C-P bond formation reactions, depending upon the experimental conditions and the diolefin.[36]

Complex **1** reacts with 2 equiv of COD, in refluxing toluene, to give the isopropenylphosphine derivative $OsCl_2(\eta^4\text{-COD})\{\eta^3\text{-P}[C(CH_3)=CH_2]^iPr_2\}$ (**38**), as a consequence the hydrogen transfer from an isopropyl substituent of a phosphine to an equivalent of diolefin, which yields cyclooctene. In addition, the coordination of the other equivalent of diene and the release of the other triisopropylphosphine and molecular hydrogen take place (Scheme 9).

[Insert Scheme 9]

Scheme 9 C(sp^3)-H bond activation of triisopropylphosphine promoted by 1,5-cyclooctadiene.

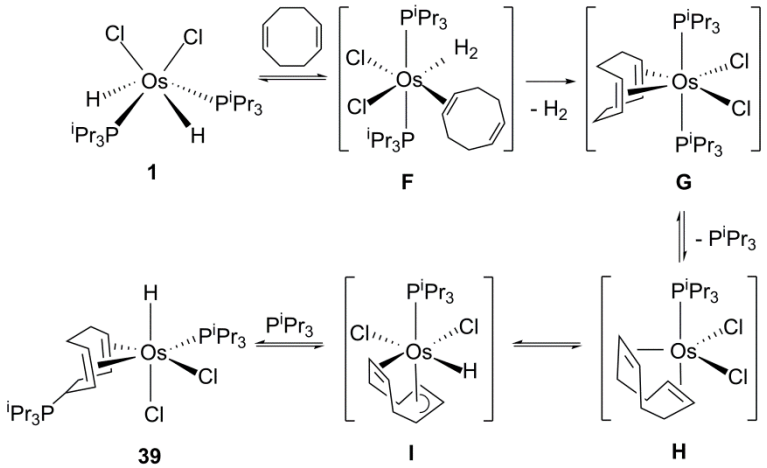


The C(sp^3)-H bond activation of the diene is favored with regard to that of the phosphine at lower temperature. Thus, at 85 ºC, treatment of toluene solutions of **1** with

COD leads to a mixture of **38** and a new compound, $OsHCl_2(\eta^4\text{-}C_8H_{11}P^iPr_3)(P^iPr_3)$ (**39**), in a 30:65 molar ratio. The formation of **39** has been rationalized according to Scheme 10. The initial η^2-coordination of the diene to the osmium atom of **1** affords the dihydrogen intermediate $OsCl_2(\eta^2\text{-}H_2)(\eta^2\text{-}COD)(P^iPr_3)_2$ (**F**), which dissociates the coordinated hydrogen molecule to give $OsCl_2(\eta^4\text{-}COD)(P^iPr_3)_2$ (**G**). The subsequent dissociation of a phosphine from **G** leads to the 16-valence electrons species $OsCl_2(\eta^4\text{-}COD)(P^iPr_3)$ (**H**), which generates the hydride complex $OsHCl_2(\eta^3\text{-}C_8H_{11})(P^iPr_3)$ (**I**) by a $C(sp^3)$-H bond activation reaction on the C^4H_2 group of the coordinated diolefin. The addition of the phosphine, released in the formation of **H**, to one of the terminal carbon atoms of the allyl unit of **I** leads to the reaction product.

[Insert Scheme 10]

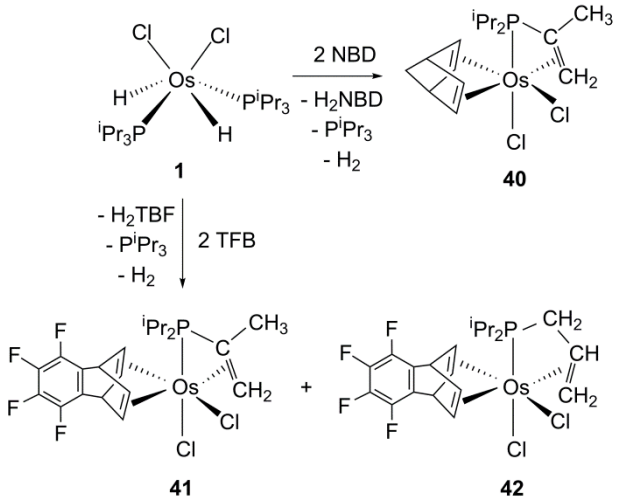
Scheme 10 Mechanism for the formation of complex **39**.



2,5-Norbornadiene is not activated at 85 ºC, in toluene. However, it promotes the dehydrogenation of the phosphine to afford the NBD-counterpart of **38**, $OsCl_2(\eta^4\text{-}NBD)\{\eta^3\text{-}P[C(CH_3)=CH_2]^iPr_2\}$ (**40**). Tetrafluorobenzobarrelene is not C-H activated either. In this case, the dehydrogenation of the phosphine leads to the mixture of the propenylphosphine isomers $OsCl_2(\eta^4\text{-}TFB)\{\eta^3\text{-}P[C(CH_3)=CH_2]^iPr_2\}$ and $OsCl_2(\eta^4\text{-}TFB)\{\eta^3\text{-}P(CH_2CH=CH_2)^iPr_2\}$(**41** and **42**, respectively, in Scheme 11).

[Insert Scheme 11]

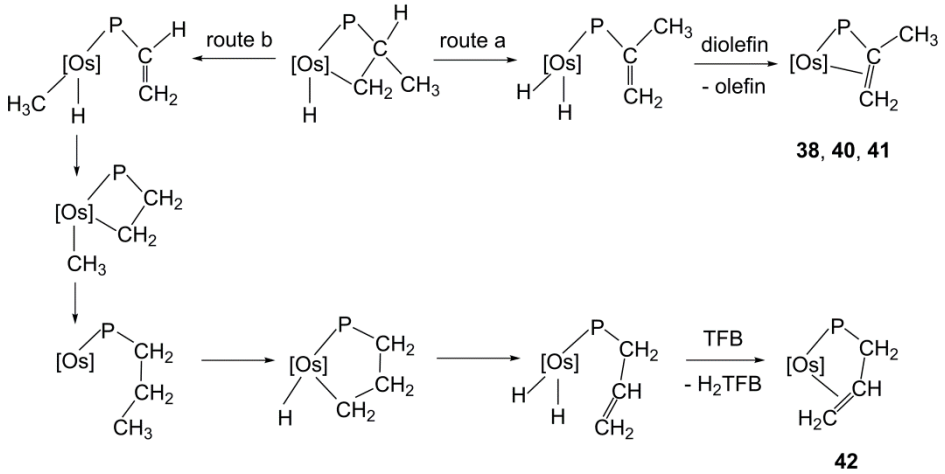
Scheme 11 $C(sp^3)$-H bond activation of triisopropylphosphine promoted by norbornadiene and tetrafluorobenzobarrelene.



The formation of the isopropenylphosphine complexes **38**, **40**, and **41** and the allylphosphine derivative **42** can be understood as two competitive *β*-elimination processes on the metalated group of a metalated triisopropylphosphine ligand (Scheme 12). The *β*-elimination of hydrogen leads to **38**, **40**, and **41** (route a), while the *β*-elimination of the methyl group (route b) gives rise to **42**.

[Insert Scheme 12]

Scheme 12 Rationalization of the formation of **38** and **40**-**42**.



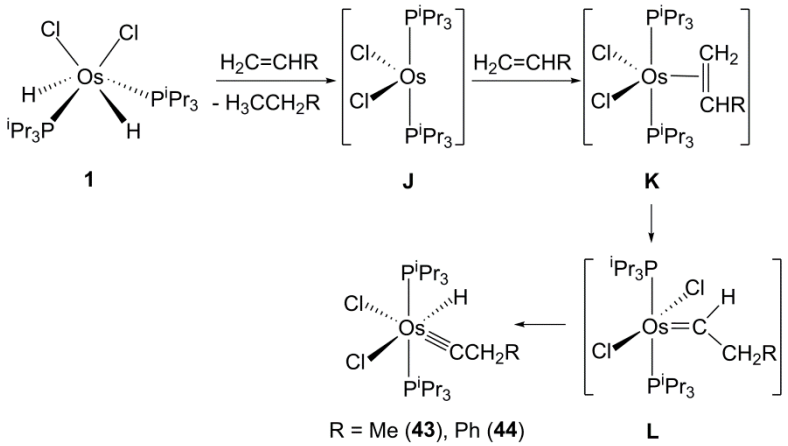
4.3 C(sp^2)-H bond activation of olefins, enynes, acyclic dienes, allenes, and allenedienes

Dihydride-dichloride **1** reacts with propylene and styrene to give equimolecular amounts of the alkylidyne derivatives $OsHCl_2(\equiv CCH_2R)(P^iPr_3)_2$ (R = Me (**43**), Ph (**44**)) and the hydrogenated olefin.[37] The reactions can be rationalized according to Scheme

13. Complex **1** is initially dehydrogenated by the olefin, which yields the alkane. The resulting 14-valence electrons species $OsCl_2(P^iPr_3)_2$ (**J**) coordinates a second equiv of olefin to afford the π-olefin intermediates $OsCl_2(\eta^2\text{-}CH_2{=}CHR)(P^iPr_3)_2$ (**K**), which undergo a M(olefin)-to-M(alkylidene) rearrangement. The latter leads to compounds $OsCl_2(=CHCH_2R)(P^iPr_3)_2$ (**L**). The 1,2-hydrogen shift from the C_α atom of the alkylidene to the metal center gives the reaction products **43** and **44.**

[Insert Scheme 13]

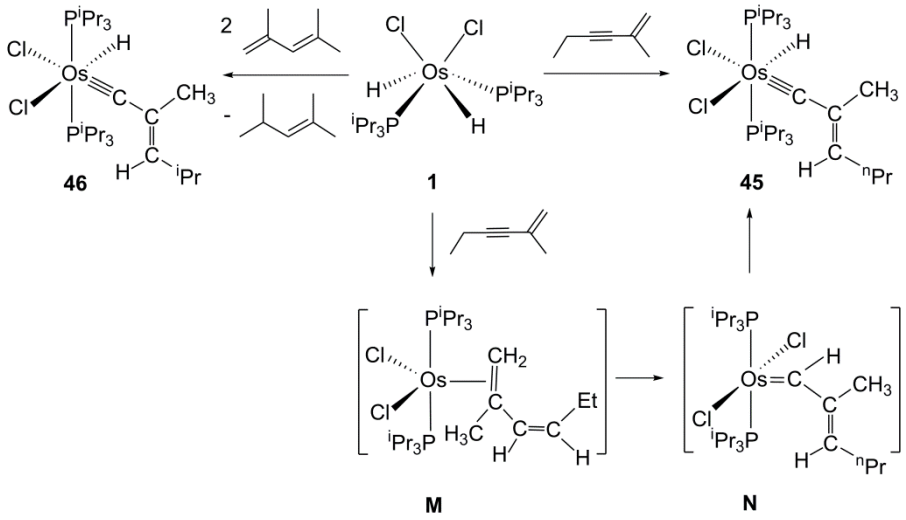
Scheme 13 Reactions of **1** with olefins.



Complex **1** also reacts with 2-methyl-1-hexen-3-yne. In this case, the reaction leads to the hydride-alkenylalkylidyne $OsHCl_2\{\equiv CC(Me){=}CH^nPr\}(P^iPr_3)_2$ (**45**). Its formation has been rationalized according to Scheme 14, on the basis of DFT calculations. The reduction of the C-C triple bond of the enyne affords the η^2-diolefin intermediate $OsCl_2\{\eta^2\text{-}CH_2{=}C(Me)CH{=}CHEt\}(P^iPr_3)_2$ (**M**), which undergoes the activation of both terminal $C(sp^2)$-H bonds. One of the hydrogen atoms migrates to the CHEt-carbon atom, through the metal, to give the alkenylalkylidene species $OsCl_2\{=CHC(Me){=}CH^nPr\}(P^iPr_3)_2$ (**N**). The other one goes to the metal center via a C_α-to-Os 1,2-hydrogen shift on **N**. In agreement with this, the treatment of **1** with 2 equiv of 2,4-dimethyl-1,3-pentadiene gives rise to the hydrogenation of 1 equiv of diene and the formation of $OsHCl_2\{\equiv CC(Me){=}CH^iPr\}(P^iPr_3)_2$ (**46**).[38]

[Insert Scheme 14]

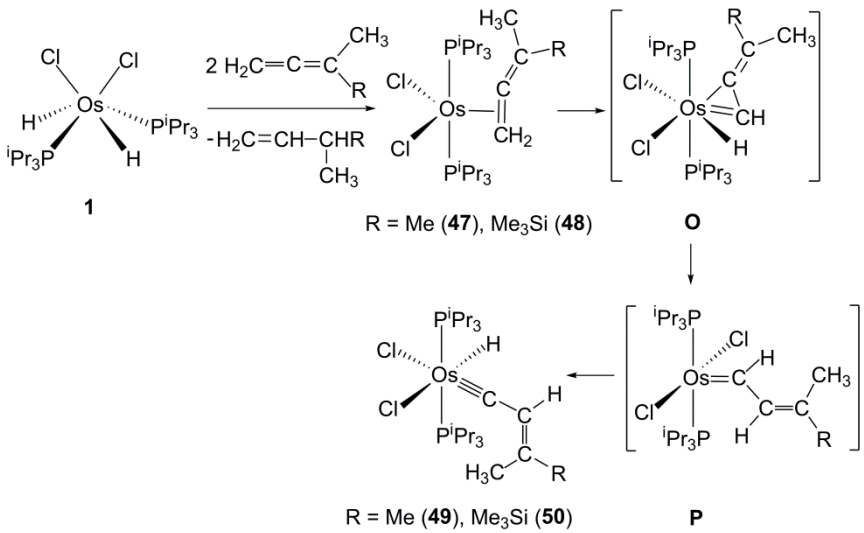
Scheme 14 Reactions of **1** with enynes and acyclic dienes.



Allenes react in a similar manner to olefins, enynes, and acyclic dienes. Reactions of **1** with 1,1-dimethylallene and 1-methyl-1-(trimethylsilyl)allene initially give 1 equiv of olefin and the π-allene derivatives $OsCl_2\{\eta^2\text{-}CH_2{=}C{=}C(Me)R\}(P^iPr_3)_2$ (R = Me (**47**), Me_3Si (**48**)), which evolve into the respective hydride-alkenylalkylidynes $OsHCl_2\{{\equiv}CCH{=}C(Me)R\}(P^iPr_3)_2$ (R = Me (**49**), Me_3Si (**50**)). The transformation involves two different 1,2-hydrogen shifts, as a consequence of two $C(sp^2)$-H bond activations (Scheme 15). The first 1,2-hydrogen shift has an activation energy higher than the second one and takes place through the hydride-osmacyclopropene intermediates **O**, which evolve to the alkenylalkylidenes $OsCl_2\{{=}CHCH{=}C(Me)R\}(P^iPr_3)_2$ (**P**). Intermediates **P**, like **N**, undergo an *α*-hydrogen elimination to yield the hydride-alkenylalkylidyne reaction products.[39]

[Insert Scheme 15]

Scheme 15 Reactions of **1** with allenes.

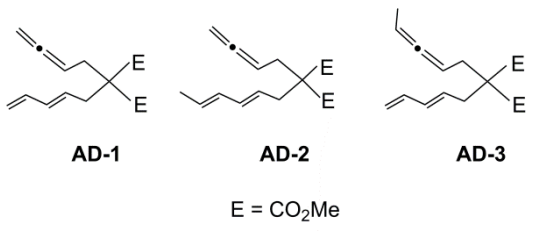


Kinetic studies[40] and DFT calculations[41] have demonstrated that these transformations from alkylidene to hydride-alkylidyne follow the same electronic pattern as the oxidative additions from d^8 to d^6; i.e., π-donor halides destabilize the monosubstituted alkylidene and favor the hydride-alkylidyne form. For example, the sequential replacement of the chloride ligands of complexes $OsHCl_2\{\equiv CCH=CR_2\}(P^iPr_3)_2$ by acetonitrile molecules produces a sequential decrease of the activation energy for the hydride migration from the metal center to the alkylidyne carbon atom, as a consequence of the gradual decrease of the electron richness of the metal center. The control of the position of this redox equilibrium has allowed performing sequential C-C coupling reactions on the coordination sphere of the metal center, to build a variety of interesting organic fragments.[42]

The reactions of the allenedienes collected in Chart 2 with **1** have been also studied. The results uncovered an interesting interplay between coordination and reactivity. Thus, different types of products are observed, depending on the substitution of the allene and of the terminal double bond of the diene.[43]

[Insert Chart 2]

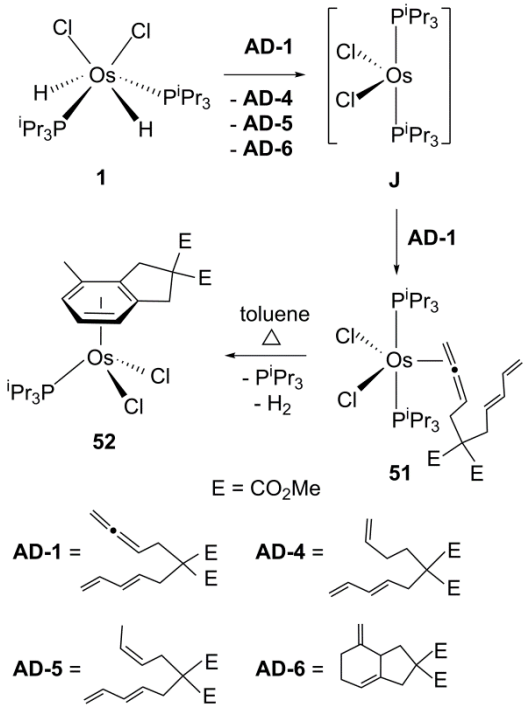
Chart 2 Studied allenedienes.



The reaction of **1** with 2 equiv of **AD-1** at room temperature leads to a 0.4:0.4:0.2 mixture of the organic products **AD-4**, **AD-5**, and **AD-6** and the π-allene complex **51** (Scheme 16). The trienes **AD-4** and **AD-5** are the result of the hydrides transfer from **1** to the internal and terminal double bonds, respectively, of the allene moiety of the allenediene, whereas the tetrahydroindene derivative **AD-6** results from an intramolecular (4+2) cycloaddition reaction of **AD-1** promoted by **J**, arising from hydride transfer processes. Complex **51** is generated from the coordination of the terminal double bond of the allene unit of the second equivalent of **AD-1** to the osmium atom of **J.** Complex **51** is moderately stable. In toluene solution evolves to the arene derivative **52** and free phosphine. The arene ligand results from the intramolecular (4+2) cycloaddition of the coordinated allenediene and the subsequent aromatization of the resulting tetrahydroindene, with the loss of a hydrogen molecule.

[Insert Scheme 16]

Scheme 16 Reaction of **1** with allenediene **AD-1**.

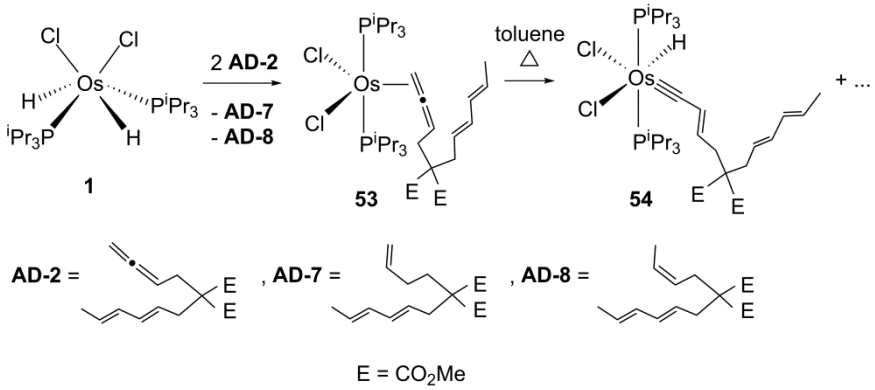


The reaction of **1** with 2 equiv of **AD-2** at room temperature gives a 0.5:0.5 mixture of the trienes **AD-7** and **AD-8** related to **AD-4** and **AD-5** and the π-allene derivative **53** (Scheme 17). Complex **53** is also moderately stable in solution, like **51**. However, in contrast to the latter, in toluene, it does not evolve into an arene species

similar to **52**. The presence of a methyl substituent at the terminal double bond of the diene moiety prevents the coordination of this double bond and therefore the (4+2) cycloaddition. It yields a complex mixture of compounds, being the main component (about 50%) the hydride-alkenylalkylidyne **54**. Its formation is consistent with Scheme 15.

[Insert Scheme 17]

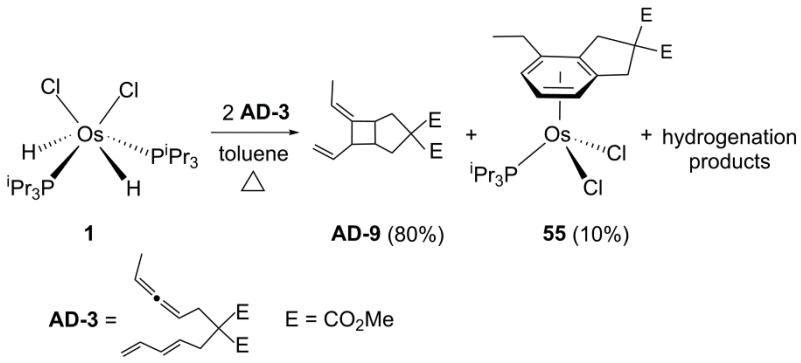
Scheme 17 Reaction of **1** with allenediene **AD-2**.



The replacement of a hydrogen atom of the allenic CH_2 group of **AD-1** by a methyl substituent to afford **AD-3** hinders the coordination of the corresponding double bond. Thus, the reaction of **1** with **AD-3** needs temperatures higher (80 ºC) than the reactions with **AD-1** and **AD-2**. Treatment of toluene solutions of **1** with 2 equiv of **AD-3** at this temperature leads to the bicycle **AD-9** together with the arene complex **55** and hydrogenated products, in the approximate proportion indicated in Scheme 18. Bicycle **AD-9** is a result of the intramolecular (2+2) cycloaddition of **AD-3**, whereas the arene ligand of **55** results from an intramolecular (4+2) cycloaddition of **AD-3** and subsequent aromatization of the resulting tetrahydroindene, in a process which resembles that shown in Scheme 16. The difference in behavior between **AD-3** and **AD-1** can be understood in terms of a competitive coordination of either allenic double bond to the osmium atom.

[Insert Scheme 18]

Scheme 18 Reaction of **1** with allenediene **AD-3**.



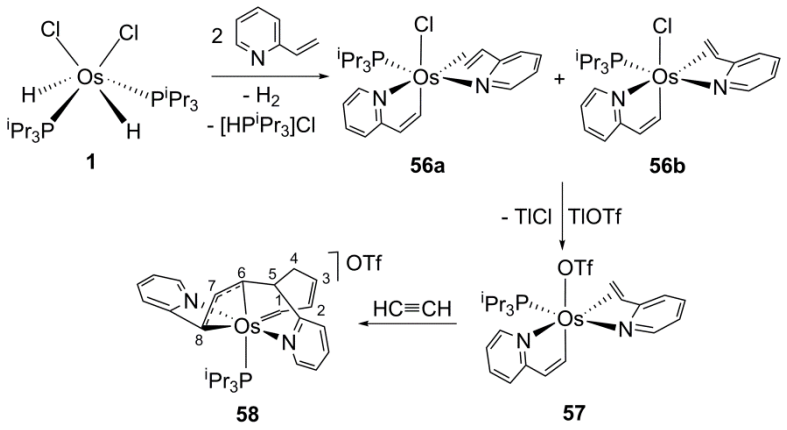
The (2+2) cycloaddition can be accomplished in a catalytic manner. Heating of benzene solutions of **AD-3** with 10% of **1** produces about 50% conversion to the bicycle **AD-9**. Unfortunately, the simultaneous formation of **55** sequesters the active catalyst and suppresses further turnovers.

4.4 C(sp^2)-H bond activation and subsequent C-C bond formation[44]

Complex **1** reacts with 2 equiv of 2-vinylpyridine to give molecular hydrogen, [HP^{i}Pr$_3$]Cl, and compound **56**. The latter is isolated as a 6:4 mixture of the isomers **56a** and **56b** shown in Scheme 19. Complex **56** bears two molecules of the starting heterocycle. One of them is metalated, as a result of the C(sp^2)-H bond activation of the CH_2 group of vinyl substituent, while the other one is coordinated to the metal center by the nitrogen atom and the vinylic C-C double bond. Complex **56** reacts with Tl(OTf) (OTf = trifluoromethanesulfonate). The reaction produces the replacement of chloride by trifluoromethanesulfonate to selectively afford **57**. Under atmospheric pressure of acetylene, complex **57** is converted into compound **58**. Its formation is a one-pot synthesis of multiple complex reactions. In addition to a 1,3-hydrogen shift, three selective C-C coupling processes are assembled to give this species: (i) coupling of the substituents of the pyridines to afford an Os{κ^3-N,N,C(5)-[py-C(8)H=C(7)H-C(6)H$_2$-C(5)H-py]}moiety, (ii) coupling on the osmium coordination sphere of two acetylene molecules to give an Os{=C(4)H-C(3)H=C(2)H-C(1)H=}-osmacyclopentatriene unit, and (iii) C(4)-C(5) bond formation by migratory insertion of the Os=C(4) double bond of the osmacyclopentatriene unit into the Os-C(5) single bond of the Os{κ^3-N,N,C(5)-[py-C(8)H=C(7)H-C(6)H$_2$-C(5)H-py]}moiety. The 1,3-hydrogen shift takes place between C(6) and C(4).

[Insert Scheme 19]

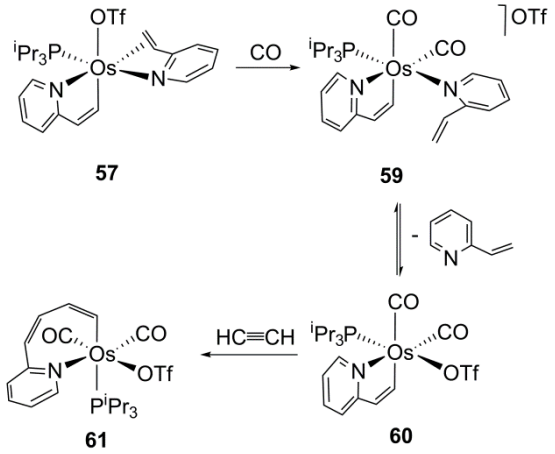
Scheme 19 2-Vinylpyridine-acetylene multiple coupling induced by **1**.



The transformation from **57** to **58** reveals that the insertion of the η^2-coordinated –CH=CH_2 group into the bond between the metal center and the metalated substituent is favored with regard to the insertion of acetylene. The latter occurs in absence of coordinated vinylpyridine (Scheme 20). Under an atmosphere of carbon monoxide the OTf^- anion and the η^2-coordinated vinyl group of **57** are displaced by CO to give the *cis*-dicarbonyl salt **59**. In dichloromethane, the cation of **59** slowly dissociates 2-vinylpyridine and coordinates the anion to afford **60**. Under atmospheric pressure of acetylene, complex **60** reacts with the alkyne to yield **61**, which contains a metalated 2-butadienylpyridine ligand. The butadienyl moiety is the result of the insertion of the C-C triple bond of acetylene into the osmium-vinyl bond.

[Insert Scheme 20]

Scheme 20 2-vinylpyridine-acetylene coupling induced by **57** and carbon monoxide.

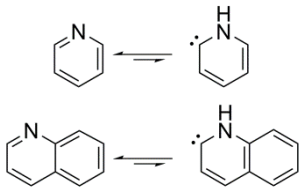


4.5 Formation of N-H wingtip NHC ligands by tautomerization of heterocycles

Pyridine and quinoline have NHC-tautomers, which lie about 40 and 44 kcal mol^{-1}, respectively, above the usual ones (Scheme 21).

[Insert Scheme 21]

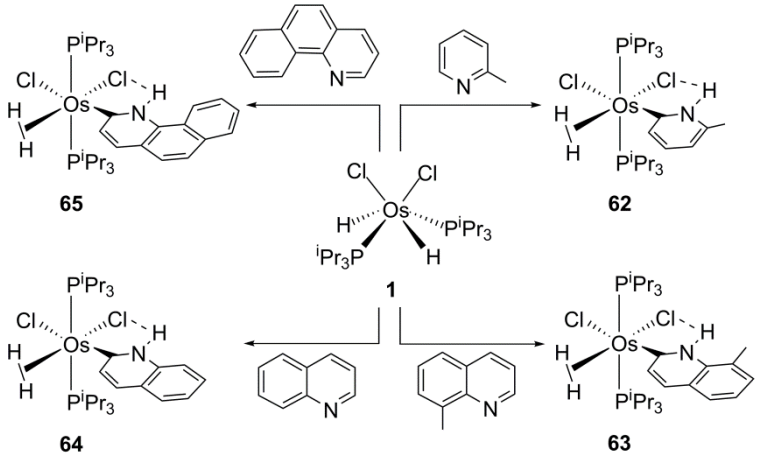
Scheme 21 NHC-tautomers of pyridine and quinoline.



Dichloride-dihydride complex **1** promotes the tautomeric transformation of this class of heterocycles and stabilizes the NHC-tautomer. Thus, its reactions with 2-methylpyridine,[45] 8-methylquinoline, quinoline,[46] and benzo[*h*]quinoline[47] lead to the respective NHC-derivatives **62-65** (Scheme 22), which undergo an additional stabilization as a consequence of an intramolecular Cl···H-N hydrogen bond. A dihydride-to-elongated dihydrogen transformation also takes place during the tautomerizations.

[Insert Scheme 22]

Scheme 22 Reactions of **1** with N-heterocycles: Stabilization of NHC-tautomers of pyridines and quinolines by metal coordination.

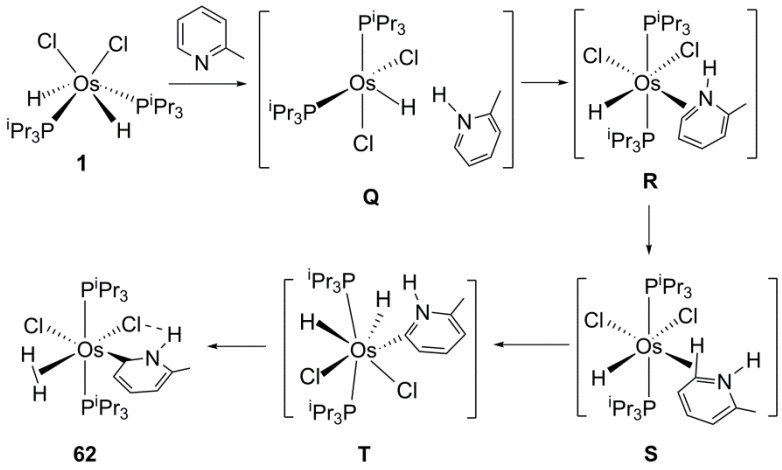


DFT calculations[45] on the tautomerization of 2-methylpyridine promoted by the model compound $OsH_2Cl_2(PMe_3)_2$ (B3PW91) suggest that the formation of **62-65** is a process of three stages: (i) intermolecular osmium to nitrogen hydrogen migration, (ii)

C_α-H_α bond activation of the resulting protonated heterocycle to afford a dihydride species, and (iii) dihydride-dihydrogen intramolecular reduction (Scheme 23).

[Insert Scheme 23]

Scheme 23 Mechanism of the tautomerization of 2-methylpyridine.

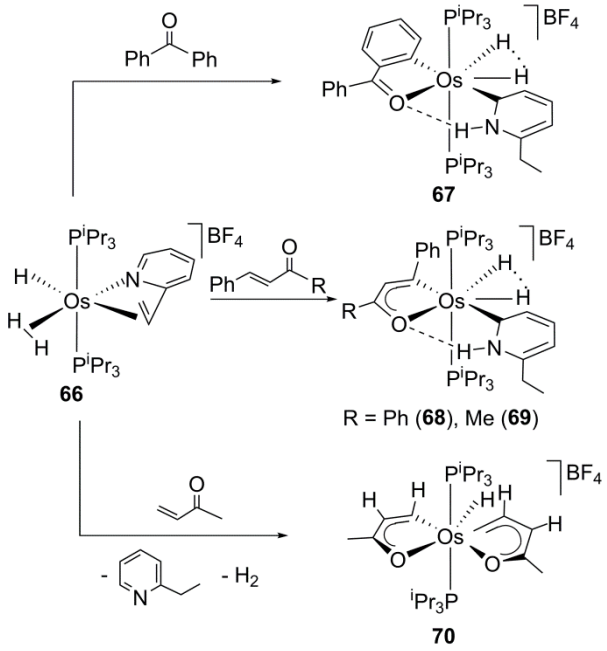


The intermolecular osmium to nitrogen hydrogen migration leads to $[HNheterocycle]^+[OsHCl_2(P^iPr_3)_2]^-$ (**Q**) cation-anion pairs. The C_α-H_α bond activation of the cation by the anion subsequently occurs. This process is initiated by the coordination of a C-N bond of the protonated heterocycles to the metal center, resulting η^2-C,N-intermediates **R**. Then, the slippage of the metal center from the C_α-N bond to the C_α-H_α one gives **S**, which undergo the activation of the coordinated C-H bond. Finally, the resulting dihydride **T** tautomerizes to give the elongated dihydrogen products.

The steric hindrance experienced between the heterocycle and the phosphines of **1** is determinant for the tautomerization. Thus, the presence of the methyl substituent in 2-methylpyridine is required for the transformation of the heterocycle. In its absence the 1,2-hydrogen shift does not take place. In contrast to 2-methylpyridine, pyridine reacts with **1** to give $OsCl_2(py)_3(P^iPr_3)$. In agreement with this, it has been observed that benzophenone,[48] benzylideneacetophenone, and benzylideneacetone[49] promote the reduction and subsequent tautomerization of the 2-vinylpyridine ligand of the hydride elongated dihydrogen **66** to afford **67**-**69**, while the smaller methyl vinyl ketone induces the reduction of the coordinated double bond and the release of 2-ethylpyridine to form **70** (Scheme 24).

[Insert Scheme 24]

Scheme 24 Reactions of **66** with ketones: Reduction and NHC-tautomers of 2-vinylpyridine.

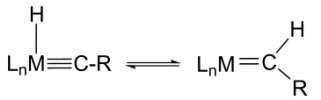


5. C-C bond activation

Hydride-alkylidyne and -alkenylalkylidyne type compounds shown in Schemes 13-15 are also formed by reaction of the dihydride-dichloride complex **1** with terminal alkynes and alkynols, respectively.[50] They are the osmium-counterpart of the well-known Grubbs's catalysts for olefin metathesis.[51] The ruthenium-alkylidene complexes and the osmium-hydride-alkylidyne derivatives are both parts of the same redox equilibrium (Scheme 25). Ruthenium, more oxidizing than osmium, favors the reduced form. However, osmium is more reducing than ruthenium and, preferring saturated species, stabilizes the saturated oxidized form.[42]

[Insert Scheme 25]

Scheme 25 Redox equilibrium M-alkylidene / M-hydride-alkylidyne.

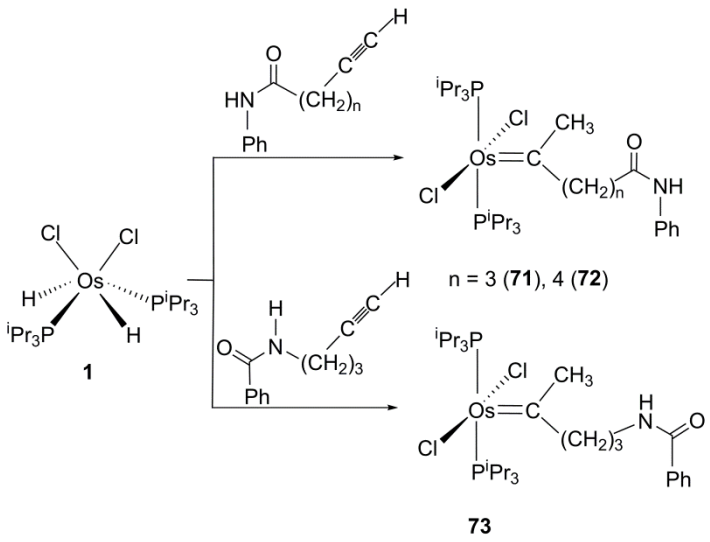


A distal amide function at an appropriate position of an alkylic chain of a terminal alkyne changes the reactivity of the latter with regard to **1**. In contrast to other terminal alkynes, *N*-phenylhex-5-ynamide and *N*-phenylhept-6-ynamide react with **1** to

give the alkylidene derivatives $OsCl_2\{=C(CH_3)(CH_2)_n(CO)NHPh\}(P^iPr_3)_2$ (n = 3 (**71**), 4 (**72**)), as a result of the addition of both hydride ligands of **1** to the terminal carbon atom of the alkynes (Scheme 26). The transformation also occurs in substrates in which the alkyne and the amide are connected through the nitrogen instead of the carbonyl group. In fact, the reaction of **1** with *N*-(pent-4-yn-1-yl)benzamide leads to $OsCl_2\{=C(CH_3)(CH_2)_3NH(CO)Ph\}(P^iPr_3)_2$ (**73**).[52]

[Insert Scheme 26]

Scheme 26 Reactions of **1** with *N*-phenylhex-5-ynamide and *N*-phenylhept-6-ynamide.



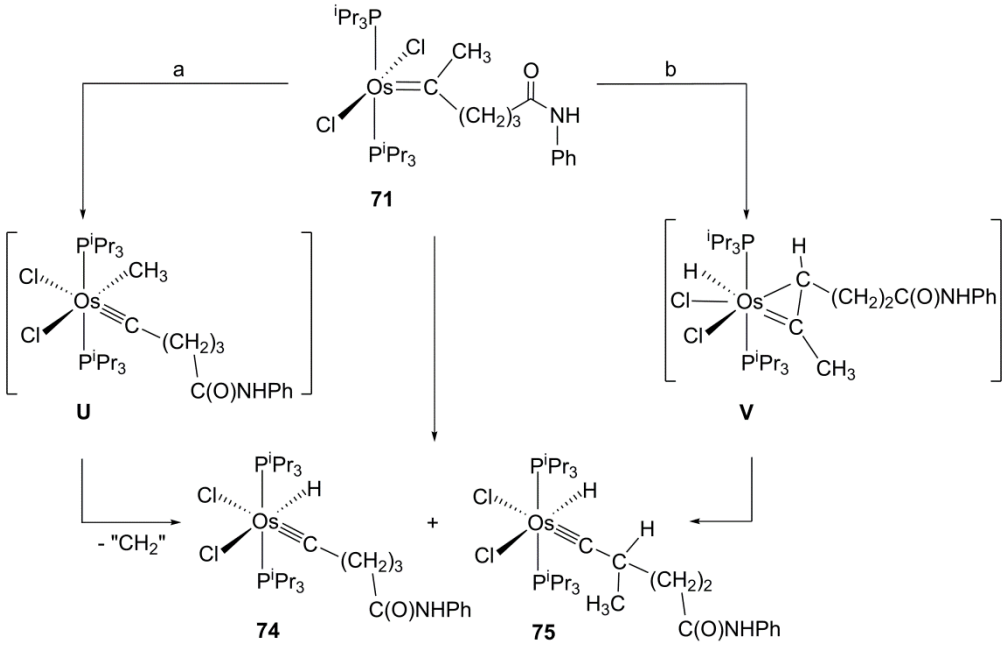
These alkylidene compounds are intermediate species in the osmium-mediated rupture of the C-C triple bond of the initial alkynes. Thus, they are unstable and undergo the rupture of the C_α-CH_3 bond of the alkylidene to evolve into six-coordinated hydride-alkylidyne derivatives, in agreement with the strongly reducing character of osmium and its marked preference to form saturated species.

Complex **71** experiences two different transformations, which are competitive in dichloromethane at 60 ºC (Scheme 27). The migration of the methyl group from the C_α atom of the alkylidene to the metal center, to afford intermediate **U**, and the subsequent methylidene extrusion yield the hydride-alkylidyne derivative $OsHCl_2\{\equiv C(CH_2)_3C(O)NHPh\}(P^iPr_3)_2$ (**74**), containing a linear spacer between the alkylidyne C_α atom and the amide (pathway **a**). On the other hand, the activation of one of the C-H bonds of the $C_\beta H_2$ group and a concerted 1,2-methyl shift in the resulting osmacyclopropene **V** give $OsHCl_2\{\equiv CCH(CH_3)(CH_2)_2C(O)NHPh\}(P^iPr_3)_2$ (**75**), with a

branched spacer between the alkylidyne C_α atom and the amide (pathway **b**). As a result of both processes, a 10:7 mixture of both hydride-alkylidynes is formed.

[Insert Scheme 27]

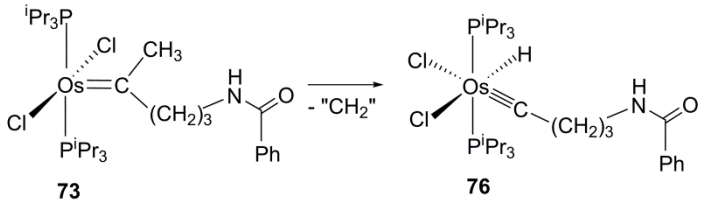
Scheme 27 Transformations of complex **71** into hydride-alkylidyne derivatives.



The relative position of the carbonyl and the NH groups in the amide influences the behavior of the alkylidene. In contrast to **71**, complex **73** selectively evolves into $OsHCl_2\{\equiv C(CH_2)_3NHC(O)Ph\}(P^iPr_3)_2$ (**76**), the benzamide counterpart of **74**, containing a linear spacer (Scheme 28).

[Insert Scheme 28]

Scheme 28 Transformations of complex **73** into a hydride-alkylidyne derivative.

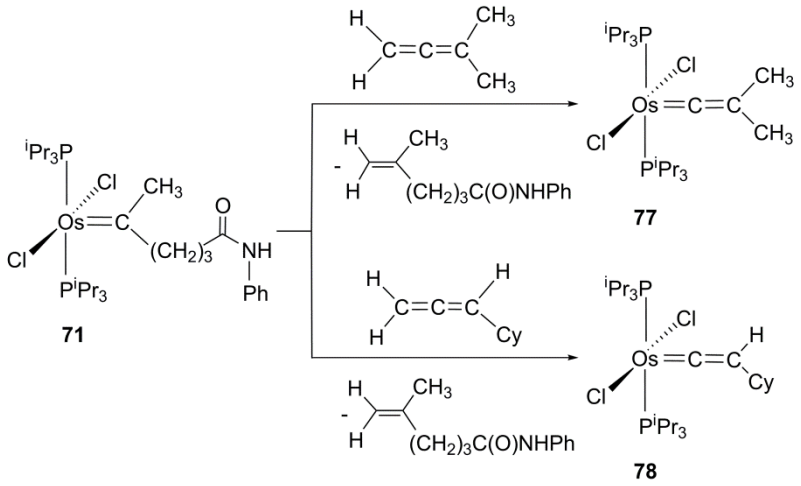


These elusive five-coordinate osmium-alkylidene compounds undergo metathesis with allenes, being in this way a useful entry to interesting dicarbon-disubstituted vinylidene derivatives (Scheme 29). Treatment of complex **71** with 3-

methyl-1,2-butadiene and cyclohexylallene yields $OsCl_2(=C=CR_2)(P^iPr_3)_2$ (CR_2 = CMe_2 (**77**), CHCy (**78**)).

[Insert Scheme 29]

Scheme 29 Reactions of **71** with allenes.

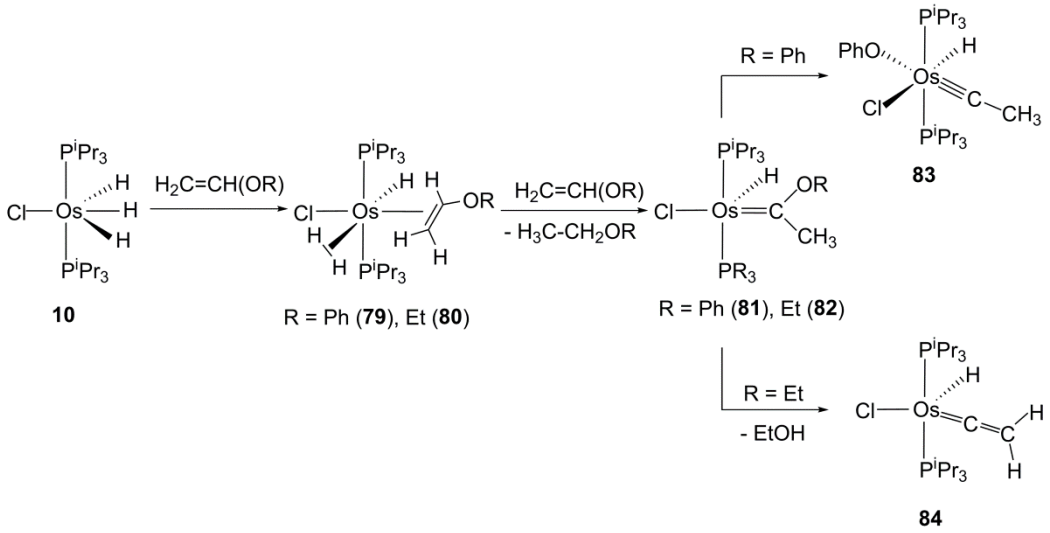


6. C-O bond activation

Trihydride complex **10** adds vinyl ethers to form η^2-olefin adducts, which evolve to carbene derivatives in the presence of additional vinyl ether. Subsequent R-dependent reactions involve C(sp^2)-OR bond cleavage, to make either alkylidyne or vinylidene complexes (Scheme 30).[53]

[Insert Scheme 30]

Scheme 30 Reactions of **10** with vinyl ethers.

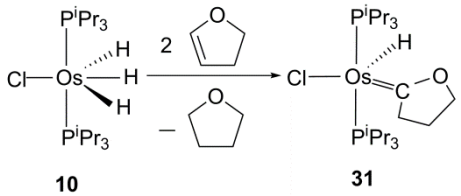


The addition of phenyl vinyl ether and ethyl vinyl ether, to toluene solutions of **10**, at -80 ºC leads to the elongated dihydrogen-π-olefin intermediates OsHCl(η^2-H_2){η^2-CH_2=C(OR)H}(P^{i}Pr$_3$)$_2$ (R = Ph (**79**), Et (**80**)). At about -10 ºC, in the presence of additional vinyl ether, these compounds generate ethyl phenyl ether, or diethyl ether, and form the unsaturated Fischer-type carbene derivatives OsHCl{=C(OR)Me}(P^{i}Pr$_3$)$_2$ (R = Ph (**81**), Et (**82**)), which are unstable at room temperature. Again, in agreement with the strongly reducing character of osmium and its marked preference to form saturated species, complex **81** undergoes a C_α-to-Os migration of the phenoxy group to give the alkylidyne complex OsHCl(OPh){≡CMe}(P^{i}Pr$_3$)$_2$ (**83**). In contrast to the latter, compound **82** eliminates ROH to afford OsHCl(=C=CH_2)(P^{i}Pr$_3$)$_2$ (**84**), which is one of the few five-coordinate hydride-vinylidenes known.[54,55]

There is a ring constraint against intramolecular migration to make an alkylidyne when the vinyl ether is cyclic. Thus, the reaction of **10** with 2,3-dihydrofuran gives tetrahydrofuran and the hydride-cyclic carbene derivative **31** (Scheme 31), which is stable in contrast to **81** and **82**.[53]

[Insert Scheme 31]

Scheme 31 Reaction of **10** with 2,3-dihydrofuran.

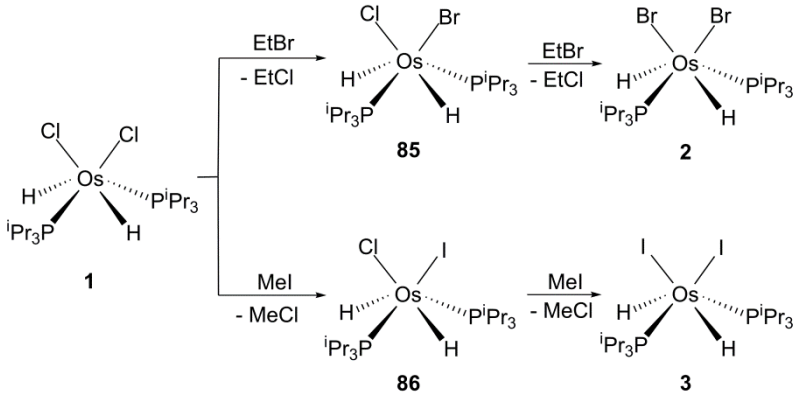


7. C-halogen bond activation

Dihydride-dichloride complex **1** undergoes halide exchange at room temperature, by simple dissolving in ethyl bromide or methyl iodide. The exchanges lead to the dibromide and diiodide derivatives **2** and **3**, respectively, via the heteroleptic dihalides **85** and **86** (Scheme 32). The reaction rate depends upon the solvent and is faster for methyl iodide than for ethyl bromide, in agreement with a C-halide bond dissociation energy (BDE) smaller for methyl iodide than for ethyl bromide. In both cases, the rate of the halide exchange is drastically increased by using trimethylsilyl halide reagents. Typically, BDE(C-Cl) is about 28 kcal mol^{-1} greater than BDE(C-I). The difference is even greater for the silicon-halide bonds: BDE(Si-Cl) - BDE(Si-I) ≈ 35 kcal mol^{-1}. This increased driving force appears to accelerate the reaction. Thus, halide exchange occurs very rapidly with only a slight excess of Me_3Si-halide in dichloromethane.[56]

[Insert Scheme 32]

Scheme 32 C-halogen bond activation reactions promoted by **1**.



The mechanism of the C-halide activation appears to involve halocarbon coordination to osmium as a pre-equilibrium step. By means of a four-centered transition state, the resulting species undergo combined Os-to-C chloride and C-to-Os halide migrations.

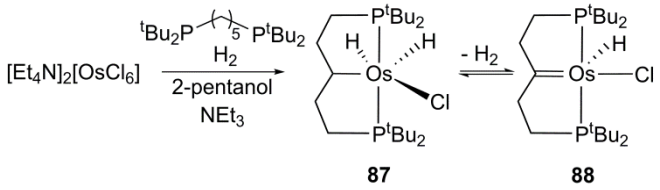
8. Si-H bond activation

Treatment of $[Et_4N]_2[OsCl_6]$ with 1,5-bis(di-*tert*-butylphosphino)pentane, in the presence of triethylamine, in pentan-2-ol, at 140 ºC, under hydrogen atmosphere leads

to the cyclometalated compound $OsH_2Cl\{\kappa^3$-P,C,P-$[CH(C_2H_4P^tBu_2)_2]\}$ (**87**), which undergoes thermal reductive dehydrogenation, to afford the osmium(II)-carbene derivative $OsHCl\{\kappa^3$-P,C,P-$[=C(C_2H_4P^tBu_2)_2]\}$ (**88**), according to Scheme 33.[57]

[Insert Scheme 33]

Scheme 33 Formation of **87** and **88**.

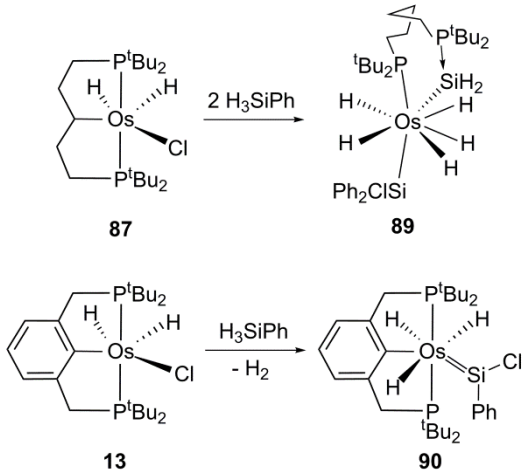


87 **88**

Complex **87** activates $PhSiH_3$ (Scheme 34).[58] Addition of 2 equiv of the silane to toluene solutions of the dihydride gives the base-stabilized silylene $OsH_5(SiPh_2Cl)\{\kappa^2$-Si,P-$[SiH_2P^tBu_2(CH_2)_5P^tBu_2]\}$ (**89**). During the process, complex **87** and two molecules of $PhSiH_3$ undergo a series of redistribution reactions culminating in the net hydrogenation of the Os-C(sp^3) bond and the generation of a silyl, one phosphine-stabilized silylene, and five hydride ligands. The donor atoms around the metal center define a dodecahedron consisting of two orthogonal trapezoidal planes. One of them contains the Si-silyl atom and the osmium-coordinated phosphorous atom at B sites and two hydride ligands, whereas the other plane contains three hydrides and the Si atom of the base-stabilized silylene. The unexpected behavior of **87** appears to be a consequence of the flexibility of the linker between the P^tBu_2 groups. In contrast to the latter, complex $OsH_2Cl\{\kappa^3$-P,C,P-$[C_6H_3$-2,6-$(C_2H_4P^tBu_2)_2]\}$ (**13**) bearing a pincer with a more rigid backbone reacts with $PhSiH_3$ to form the trihydride-free silylene derivative $OsH_3(=SiClPh)\{\kappa^3$-P,C,P-$[C_6H_3$-2,6-$(C_2H_4P^tBu_2)_2]\}$(**90**) and molecular hydrogen.

[Insert Scheme 34]

Scheme 34 Si-H bond activation reactions promoted by Os-PCP complexes.



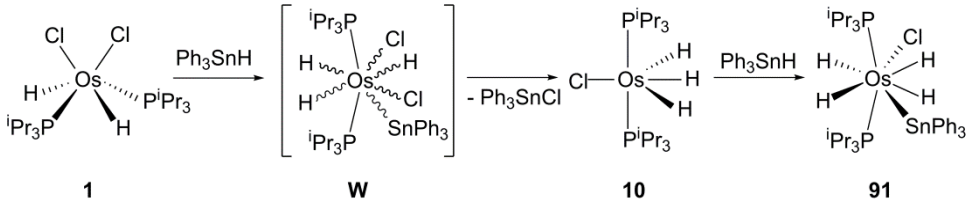
9. Sn-H bond activation

Dihydride-dichloride compound **1** also activates the Sn-H bond of Ph_3SnH. This activation has allowed to develop a rich chemistry of stannyl- and bis(stannyl)-polyhydride derivatives, including pentahydrides, tetrahydrides, trihydrides and compressed dihydride species.

Complex **1** reacts with 2 equiv of Ph_3SnH to afford the tetrahydride-stannyl compound $OsH_4Cl(SnPh_3)(P^iPr_3)_2$ (**91**) and Ph_3SnCl. It has been proposed that the reaction involves the initial oxidative addition of the Ph_3Sn-H bond to **1** to give the osmium(VI) intermediate $OsH_3Cl_2(SnPh_3)(P^iPr_3)_2$ (**W**), which evolves by reductive elimination of Ph_3SnCl into trihydride **10**. Thus, the subsequent oxidative addition of a second molecule of Ph_3SnH to the latter could yield **91** (Scheme 35). The structure of this compound is the expected dodecahedron with the bulky ligands at B sites of the orthogonal trapezoidal planes.[59]

[Insert Scheme 35]

Scheme 35 Reaction of **1** with Ph_3SnH.

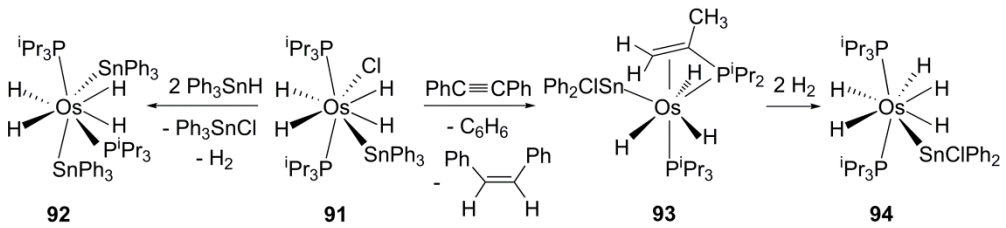


Complex **91** reacts with two new molecules of Ph_3SnH to give Ph_3SnCl, H_2, and the tetrahydride-bis(stannyl) derivative $OsH_4(SnPh_3)_2(P^iPr_3)_2$ (**92**). This species is a rare

example of bis(stannyl) compound with the transition metal in high oxidation state. A distinguishing feature of its structure is the P-Os-Sn angle in both orthogonal trapezoidal planes of 122.56(3)º, which is significantly smaller than the related angle in other eight-coordinate osmium-polyhydride complexes (145-156º). This seems to be the result of the steric hindrance experienced by the phosphine and stannyl ligands of different planes.[60] In the presence of diphenylacetylene, compound **91** affords the trihydride-stannyl derivative $OsH_3(SnClPh_2)\{\kappa^3\text{-}C,C,P\text{-}[CH_2{=}C(CH_3)P^iPr_2]\}(P^iPr_3)$ (**93**), *cis*-stilbene, and benzene. Its structure in the solid state can be rationalized as a highly distorted pentagonal bipyramid, with the phosphorous atom of triisopropylphosphine and the midpoint of the C-C double bond of the isopropenyl group of the dehydrogenated phosphine occupying axial positions. During the reaction, four different processes are assembled: (i) dehydrogenation of one isopropyl group of one triisopropylphosphine, (ii) reduction of diphenylacetylene to give *cis*-stilbene, (iii) hydrogenolysis of a phenyl group of the triphenylstannyl ligand, and (iv) chloride migration from the transition metal to the tin atom. The reaction appears to be radical-promoted, since the formation of **93** is inhibited in the presence of hydroquinone. Under hydrogen atmosphere, complex **93** yields the pentahydride-stannyl compound $OsH_5(SnClPh_2)(P^iPr_3)_2$ (**94**), as a result of the reduction of the coordinated olefin and a $d^4\text{-}d^2$ oxidative addition of H_2 (Scheme 36). The donor atoms around the metal center of **94** adopt the expected dodecahedral disposition with the bulky ligands at the B sites of the trapezoidal planes.[59]

[Insert Scheme 36]

Scheme 36 Reactions of **91** with Ph_3SnH and diphenylacetylene.

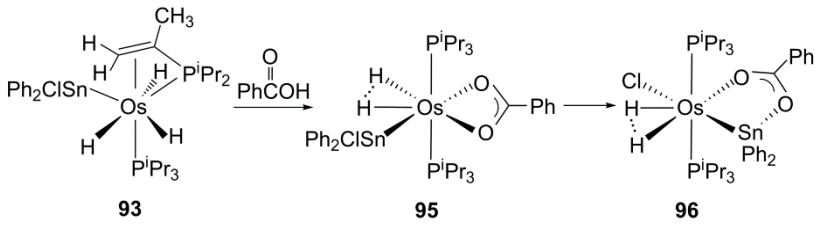


The coordinated olefin of **93** also undergoes reduction in the presence of benzoic acid (Scheme 37).[61] The addition of the latter to **93** initially leads to the compressed dihydride-stannyl derivative $OsH_2(SnClPh_2)(\kappa^2\text{-}O_2CPh)(P^iPr_3)_2$ (**95**). In toluene, the tin atom exchanges with the transition metal the chloride ligand by one of the oxygen

atoms of the carboxylate group, to afford $OsH_2Cl\{\kappa^2$-O,Sn-$[OC(Ph)OSnPh_2]\}(P^iPr_3)_2$ (**96**).

[Insert Scheme 37]

Scheme 37 Reaction of **93** with benzoic acid.



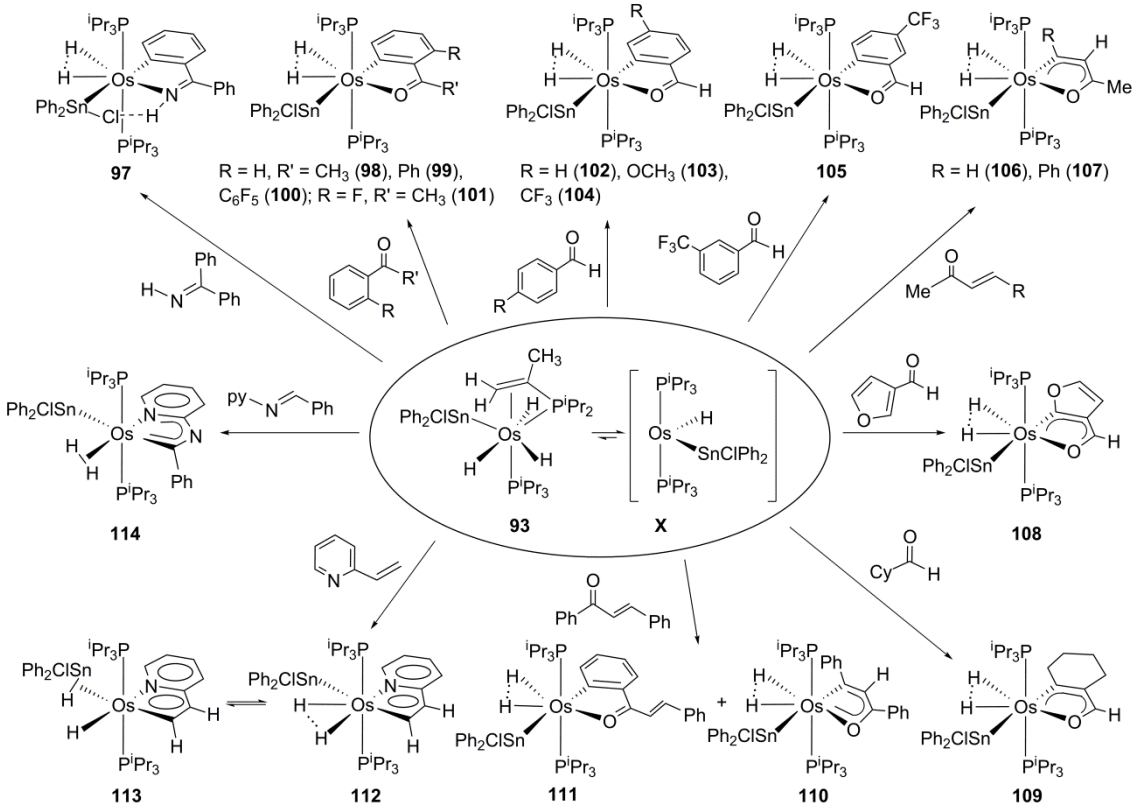
93 **95** **96**

The formation of **94** and **95** is consistent with the transformation of **93** into the 14-valence electrons monohydride $OsH(SnClPh_2)(P^iPr_3)_2$ (**X**), a stannyl-counterpart of **A**, which adds two hydrogen molecules or one molecule of benzoic acid. This functionally equivalent promotes the chelate-assisted $C(sp^2)$-H bond activation of aromatic-imines, -ketones, and –aldehydes; α,β-unsaturated-ketones, and –aldehydes; 2-vinylpyridine; and (*E*)-*N*-(phenylmethylene)-2-pyridinamine (Scheme 38). The reaction of **93** with benzophenone imine leads to $OsH_2(SnClPh_2)\{\kappa^2$-N,C-$[NHC(Ph)C_6H_4]\}(P^iPr_3)_2$ (**97**), whereas acetophenone and benzophenone afford $OsH_2(SnClPh_2)\{\kappa^2$-O,C-$[OC(R)C_6H_4]\}(P^iPr_3)_2$ (R = Me (**98**), Ph (**99**)). The *ortho*-CH bond activation is favored with regard to the *ortho*-CF bond activation. Thus, the reactions with 2,3,4,5,6-pentafluorobenzophenone and 2-fluoroacetophenone give $OsH_2(SnClPh_2)\{\kappa^2$-O,C-$[OC(C_6F_5)C_6H_4]\}(P^iPr_3)_2$ (**100**) and $OsH_2(SnClPh_2)\{\kappa^2$-O,C-$[OC(Me)C_6FH_3]\}(P^iPr_3)_2$ (**101**), respectively.[62] The *ortho*-CH bond activation is also favored over the OC-H bond activation in benzaldehydes. Treatment of **93** with these substrates yields the corresponding *ortho*-metalated compounds $OsH_2(SnClPh_2)\{\kappa^2$-O,C-$[OC(H)C_6R\,H_3]\}(P^iPr_3)_2$ (R = H (**102**), *p*-OCH_3 (**103**), *p*-CF_3 (**104**), *m*-CF_3 (**105**)).[63] α,β-Unsaturated-ketones and -aldehydes generate osmafuran derivatives; methyl vinyl ketone and benzylidenacetone afford $OsH_2(SnClPh_2)\{\kappa^2$-O,C-$[OC(CH_3)CHCR]\}(P^iPr_3)_2$ (R = H (**106**), Ph (**107**)),[64] whereas 3-furaldehyde and 1-cyclohexene-1-carboxaldehyde form $OsH_2(SnClPh_2)\{\kappa^2$-O,C-$[OCHC_4(O)H_2]\}(P^iPr_3)_2$ (**108**) and $OsH_2(SnClPh_2)\{\kappa^2$-O,C-$[OCHC_6H_8]\}(P^iPr_3)_2$ (**109**), respectively.[63] As expected, monohydride **X** activates both *β*-olefinic- and *ortho*-CH bonds of benzylidenacetophenone to give the osmafuran $OsH_2(SnClPh_2)\{\kappa^2$-O,C-

[OC(Ph)CHCPh]}(P^iPr_3)$_2$ (**110**) and the osmaisobenzofuran $OsH_2(SnClPh_2)\{\kappa^2$-O,C-[OC(CH=CHPh)$C_6H_4$]}($P^iPr_3$)$_2$ (**111**). The activation of the olefinic moiety is kinetically preferred. However, the osmaisobenzofuran complex **111** is the product of thermodynamic control. The activation of 2-vinylpyridine gives $OsH_2(SnClPh_2)\{\kappa^2$-N,C-(pyCHCH)}($P^iPr_3$)$_2$ (**112**) in equilibrium with $OsH\{\kappa^2$-N,C-(pyCHCH)}(η^2-H-$SnClPh_2$)(P^iPr_3)$_2$ (**113**), where the stannane is bonded to the transition metal by a Os-H-Sn three-centered bond. The activation of (*E*)-*N*-(phenylmethylene)-2-pyridinamine leads to $Os(SnClPh_2)\{\kappa^2$-N,C-(pyNCPh)}(η^2-H_2)(P^iPr_3)$_2$ (**114**). In this case, the OsH_2 unit appears form an elongated dihydrogen.[64]

[Insert Scheme 38]

Scheme 38 C-H bond activation reactions promoted by **93**.



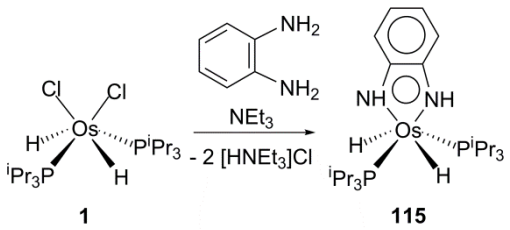
10. N-H bond activation

Dihydride-dichloride complex **1** activates one N-H bond of each NH_2 group of 1,2-phenylenediamine, in the presence of triethylamine, to give the six-coordinate d^4-dihydride derivative $OsH_2\{\kappa^2$-N,N-(*o*-NH-C_6H_4-NH)}(P^iPr_3)$_2$ (**115**), containing an osmabenzimidazolium core. The planarity and length equalization of the bicycle along

with negative nucleus-independent chemical shifts (NICS) values calculated for both rings and the aromatic MO delocalization indicate that, as the organic counterpart benzimidazolium cation, it is aromatic (Scheme 39).[65] A detailed analysis of the core interactions reveals that from the five frontier orbitals of the $[OsH_2(P^iPr_3)_2]^+$ fragment (LUMO+2, LUMO+1, LUMO, HOMO, and HOMO-1), LUMO+2 and LUMO are involved in σ-interactions, whereas LUMO+1 is engaged in the delocalization of the π-electron system of the metalabicycle; i. e., the metal center does not have an empty orbital to interact with Lewis bases and therefore, in contrast to other six-coordinate d^4-dihydride-osmium compounds,[25,66,67] complex **115** is inert in the presence of these ligands.[65]

[Insert Scheme 39]

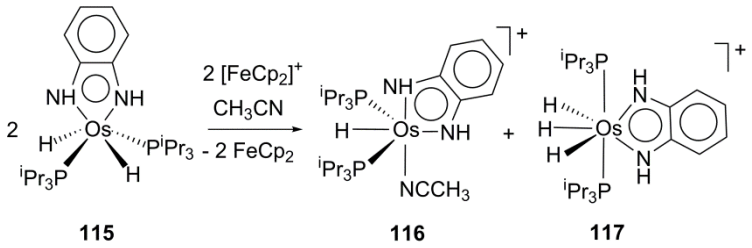
Scheme 39 N-H bond activation of 1,2-phenylenediamine promoted by **1**.



Complex **115** reduces the cation $[FeCp_2]^+$. The addition of 1 equiv of the PF_6-salt of this cation to acetonitrile solutions of **115** gives rise to a 1:1 mixture of the monohydride $[OsH\{\kappa^2\text{-N,N-}(o\text{-NH-}C_6H_4\text{-NH})\}(CH_3CN)(P^iPr_3)_2]PF_6$ (**116**) and the trihydride $[OsH_3\{\kappa^2\text{-N,N-}(o\text{-NH-}C_6H_4\text{-NH})\}(P^iPr_3)_2]PF_6$ (**117**), in addition to $Fe(\eta^5\text{-}C_5H_5)_2$ (Scheme 40). The first of them is the result of the substitution of one of the hydride ligands by an acetonitrile molecule, while the second one is a consequence of the protonation of the metal center. In this context, it should be mentioned that HOMO-1 of the $[OsH_2(P^iPr_3)_2]^+$ fragment remains nonbonding in **115**. Bicycles of **116** and **117** also appear to be aromatic.

[Insert Scheme 40]

Scheme 40 Reduction of $[FeCp_2]^+$ by **115**.

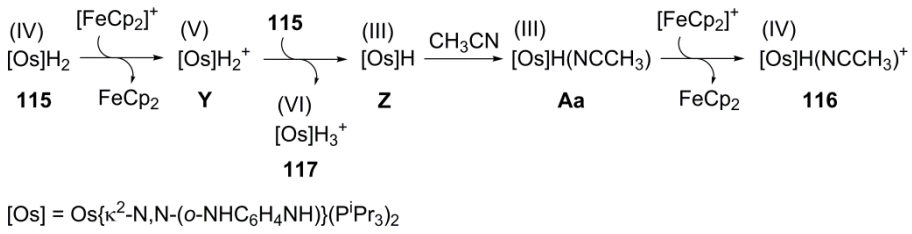


115 **116** **117**

The formation of the mixture has been rationalized according to Scheme 41. The one-electron oxidation of 0.5 equiv of **115** with 0.5 equiv of ferrocenium could initially afford the osmium(V)-dihydride intermediate **Y**, which should protonate the remaining 0.5 equiv of **115** to give **117** and the 15-valence electrons osmium(III)-hydride **Z**. Then, the coordination of the solvent to the metal center of the latter could afford **Aa**, which should reduce the remaining 0.5 equiv of ferrocenium to yield **116**.

[Insert Scheme 41]

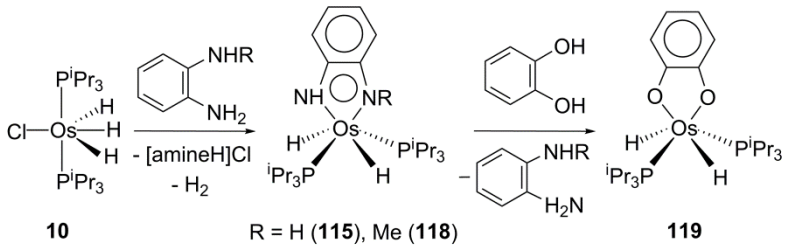
Scheme 41 Rationalization of the formation of **116** and **117**.



Trihydride **10** activates 1,2-phenylenediamine and *N*-methyl-1,2-phenylenediamine. The reaction with the first of them gives **115**, whereas the reaction with the second one affords $OsH_2\{\kappa^2$-N,N-(*o*-NH-C_6H_4-NMe)$\}(P^iPr_3)_2$ (**118**). Catechol replaces the chelated diamine from the osmium atom of these compounds. Thus, its addition in excess to toluene solutions of **115** and **118** leads to $OsH_2\{\kappa^2$-O,O-(*o*-O-C_6H_4-O)$\}(P^iPr_3)_2$ (**119**), according to Scheme 42.[68]

[Insert Scheme 42]

Scheme 42 N-H bond activation reactions of 1,2-phenylenediamine and *N*-methyl-1,2-phenylenediamine promoted by **10**.

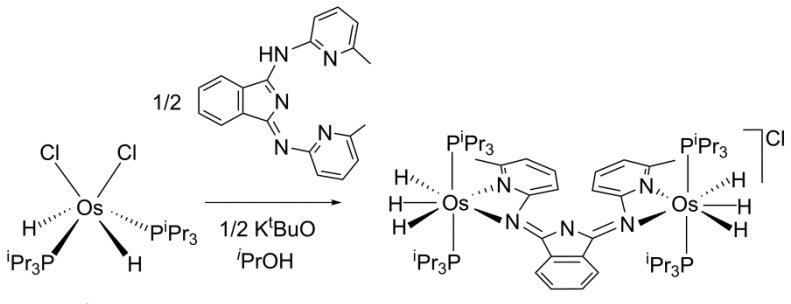


10 R = H (**115**), Me (**118**) **119**

Dihydride-dichloride **1** also activates the N-H bond of 1,3-bis(6'-methyl-2'-pyridylimino)isoindoline (HBMePI), which is a sterically demanding version of 1,3-bis(2-pyrilimino)isoindoline (HBPI).[69] The activation generates the isoindolinate anion BMePI and HCl. The latter is removed from the reaction medium with K^{t}BuO. In contrast to BPI, which generally acts as κ^3-(N_{py},N_{iso},N_{py})$_{mer}$,[70] anion BMePI coordinates κ^2-N_{py},N_{imine} to the osmium atom. The reason for this novel preference is thermodynamic, since it gives rise to the most stable structure from all the possible options.[69] Accordingly, treatment of 2-propanol solutions of **1** with 0.5 equiv of HBMePI, in the presence of 0.5 equiv of K^{t}BuO, at room temperature gives the salt [{OsH_3(P^{i}Pr$_3$)$_2$}$_2${μ-(κ^2-N_{py},N_{imine})$_2$-BMePI}]Cl (**120**), containing a cation that can be formally described as the result of the coordination of an [OsH_3(P^{i}Pr$_3$)$_2$]$^+$ fragment to the free chelate-N_{py},N_{imine} moiety of complex OsH_3(κ^2-N_{py},N_{imine}-BMePI)(P^{i}Pr$_3$)$_2$ (Scheme 43). The latter is an efficient catalyst precursor for the acceptorless and base-free dehydrogenation of secondary and primary alcohols and cyclic and lineal amines. The primary alcohols afford aldehydes. The amount of H_2 released per gram of heterocycle depends upon the presence of a methyl group adjacent to the nitrogen atom, the position of the nitrogen atom in the heterocycle, and the size of the heterocycle.

[Insert Scheme 43]

Scheme 43 N-H bond activation of 1,3-bis(6'-methyl-2'-pyridylimino)isoindoline promoted by **1**.

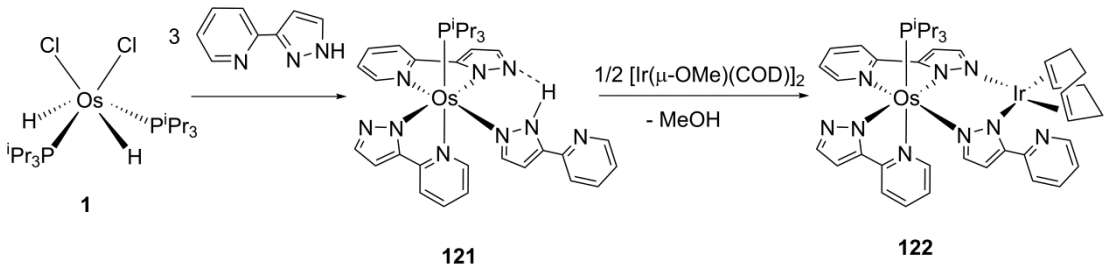


1 **120**

A more efficient catalyst for the base-free and acceptorless dehydrogenation of alcohols have been prepared by N-H bond activation of 3-(2-pyridyl)pyrazol (3-py-pzH) and subsequent coordination of the Ir(η^4-COD) fragment to the resulting N,N,N-osmaligand (Scheme 44).[71] Complex **1** reacts with 3-py-pzH in toluene under reflux, to give the osmium(II) derivative Os{κ^2-N,N-(3-py-pz)}$_2$(3-py-pzH)(P^{i}Pr$_3$) (**121**). This compound can be deprotonated by the bridging methoxy groups of the dimer [(μ-OMe)(η^4-COD)]$_2$. The deprotonation produces the coordination of two free nitrogen atoms of the metalloligand to iridium to afford the heterobimetallic derivative **122**.

[Insert Scheme 44]

Scheme 44 N-H activation of 3-(2-pyridyl)pyrazol promoted by **1**.



The iridium center of **122** catalyzes the dehydrogenation of secondary alcohols to ketones, primary alcohols to aldehydes or esters, and diols to lactones. Cyclooctatriene was detected during the catalysis, suggesting that the active species is a iridium(III)-dihydride compound with the anionic osmaligand κ^3-(N,N,N)$_{mer}$-coordinated. The presence of a phenyl group in the substrates favors the dehydrogenations. The products of the reactions of benzyl alcohols bearing a substituent at the phenyl group shows a marked dependence upon the Hammett σ_p value of the substituent, which is consistent with the transitory formation of hemiacetals in the dehydrogenative homocoupling to generate esters.

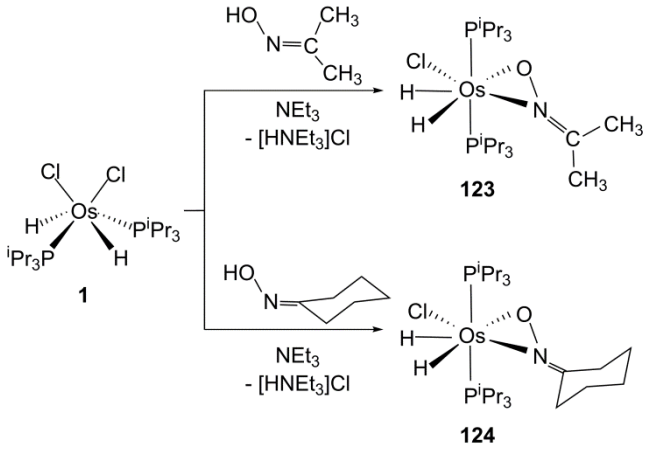
11. O-H bond activation

Complex **1** activates the O-H bond of acetone oxime and cyclohexanone oxime, at room temperature, in the presence of triethylamine (Scheme 45). The reactions give the oximate derivatives OsH$_2$Cl{κ^2-O,N-(ON=CR$_2$)}(P^{i}Pr$_3$)$_2$ (CR$_2$ = CMe$_2$ (**123**), CC$_5$H$_{10}$ (**124**)). The structure of these compounds, determined by X-ray diffraction analysis, has been rationalized as a distorted pentagonal bipyramid with the phosphines

occupying two relative *trans* positions. The perpendicular plane is formed by the hydrides, the chloride and the oximate group. The latter acts as bidentate ligand with a bite angle of 36.6(1)º, which strongly deviates of the ideal value of 72º.[72]

[Insert Scheme 45]

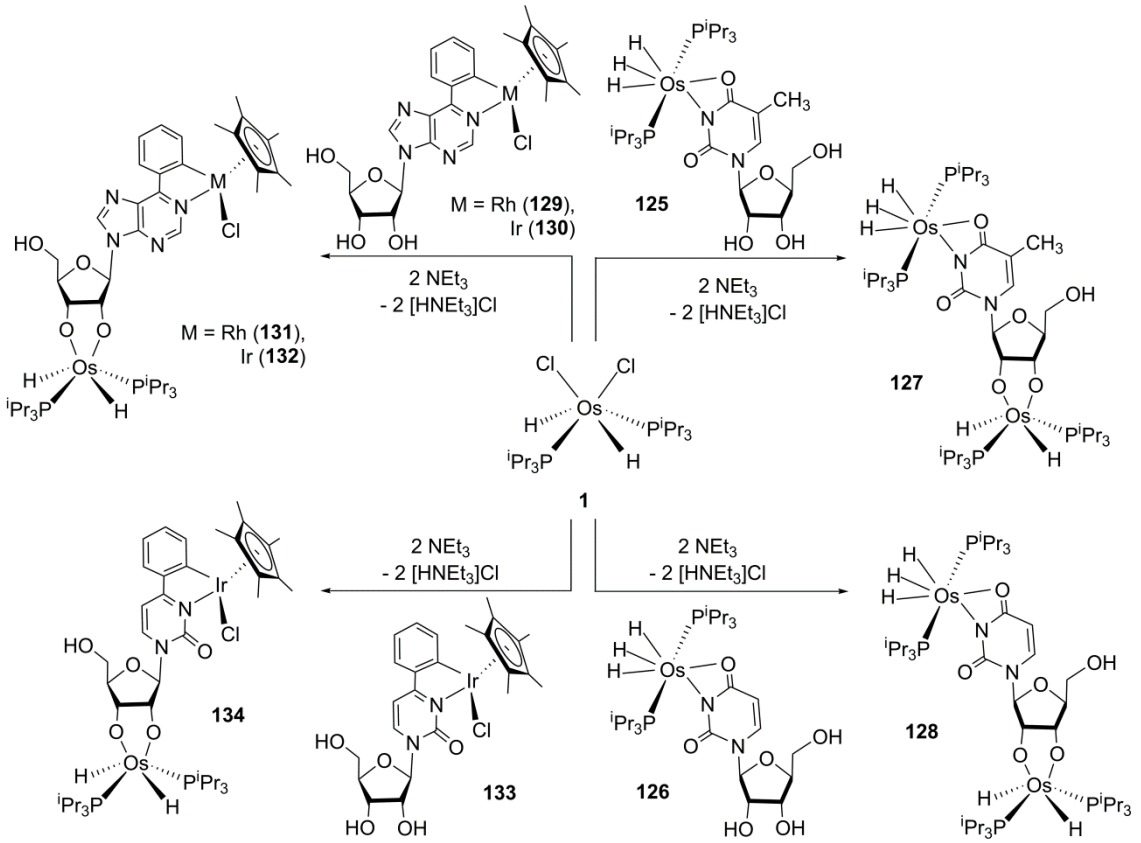
Scheme 45 O-H activation of oximes promoted by complex **1**.



Complex **1** also activates O-H bonds of metal-nucleosides, in the presence of triethylamine. The reactions lead to dinuclear species formed by two different metal fragments (Scheme 46). Treatment of **1** with complexes methylurinate **125** and urinate **126**, containing nucleosides derived from ribose, in the presence of the base leads to the dinuclear species $OsH_3(P^iPr_3)_2$(nucleobase)-(ribose)$OsH_2(P^iPr_3)_2$ **127** and **128**, as a result of the replacement of the proton of the OH functional groups of the ribose five-membered ring by the $[OsH_2(P^iPr_3)_2]^{2+}$ metal fragment.[73] Similarly, the reactions with the complexes rhodium- and iridium-purine **129** and **130** afford the heterobimetallic compounds **131** and **132**, respectively, whereas the iridium-pyrimidine **133** gives **134**.[74]

[Insert Scheme 46]

Scheme 46 O-H activation of metal-nucleosides promoted by complex **1**.

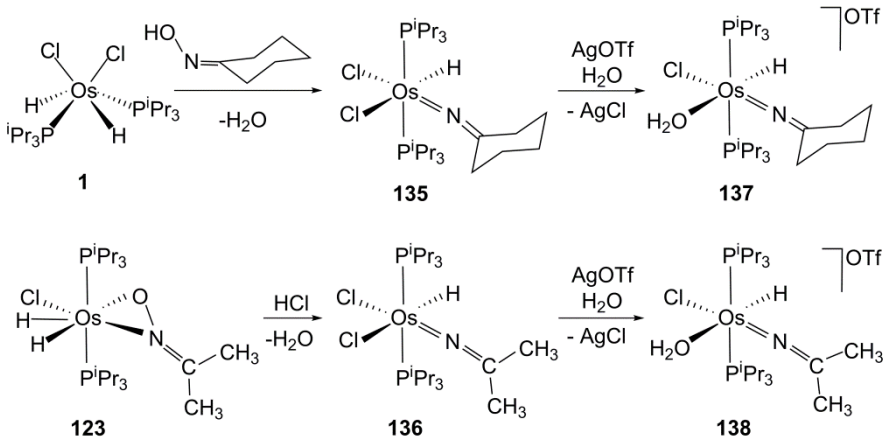


12. O-N bond activation: azavinylidene compounds

Treatment of toluene solutions of **1** with cyclohexanone oxime, in the absence of triethylamine, under reflux leads to the hydride azavinylidene derivative $OsHCl_2(=N=CC_5H_{10})\}(P^iPr_3)_2$ (**135**) and water (Scheme 47). The reaction takes place via the oximate complex **124**, which is initially formed along with HCl according to Scheme 45. In agreement with this, it has been also observed that the addition of HCl to **123** affords $OsHCl_2(=N=CMe_2)\}(P^iPr_3)_2$ (**136**).[75] The azavinylidene ligands of **135** and **136** are stable toward hydrolysis. Both compounds react with AgOTf in the presence of water to afford the salts $[OsHCl(=N=CR_2)(H_2O)(P^iPr_3)_2]OTf$ (CR_2 = CC_5H_{10} (**137**), CMe_2 (**138**)).[76]

[Insert Scheme 47]

Scheme 47 Formation of azavinylidene complexes.

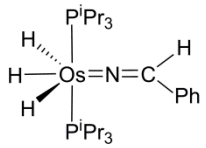


The structures of **135** and **138** have been determined by X-ray diffraction analysis. Although they are six-coordinate diamagnetic species of a formally d^4-ion, the geometries around the metal center are octahedral with the phosphines occupying *trans* positions. The hydride and azavinylidene ligands lie at the perpendicular plane disposed mutually *cis*. The chloride ligands appear to play a main role in this ligand distribution. In contrast to **135** and **138**, the trihydride derivative $OsH_3(=N=CHPh)\}(P^iPr_3)_2$ (**139**), which does not bear any chloride ligand, displays a structure of *Cs* symmetry which resembles those of **10-12** with the azavinylidene group at the position of the halide. To gain insight into the reason of this difference and the influence having in the reactivity, the osmium-azavinylidene bonding situations in **139** and a model hydride-dichloride-counterpart $OsHCl_2(=N=CHPh)\}(P^iPr_3)_2$ (**140**) were analyzed, by means of the energy decomposition analysis – Natural orbitals for chemical valence (EDA-NOCV) method, using two different bonding schemes: the donor-acceptor bonding in their electronic singlet state, with charged fragments ($[OsH_3(P^iPr_3)_2]^+$, $[[OsHCl_2(P^iPr_3)_2]^+$, and $[N=CHPh]^-$), and electron sharing mixed with donor-acceptor bonding where the fragments ($[OsH_3(P^iPr_3)_2]^{\cdot}$, $[OsHCl_2(P^iPr_3)_2]^{\cdot}$, and $[N=CHPh]^{\cdot}$) were calculated in their doublet state. According to the results of the analysis (Table 1) the donor-acceptor description of the Os-N bond dominates over mixed electron-sharing/dative bonding in **139**. However, this situation is markedly different in **140**; for it, the mixed electron-sharing/donor-acceptor bonding better describes the Os-N interaction.[77] In this context, it should be mentioned that quantum chemical calculations using DFT at the BP86-D3(BJ)/def2-TZVPP level of theory have revealed that electrophilic alkylidynes, like those of **43** and **44** (Scheme 13), also engage in a mixture of dative bonding (σ-donation and π-backdonation) and one electron-sharing π-bond. The EDA-NOCV calculations of nucleophilic alkylidynes using open-shell species in their quartet electronic state gave

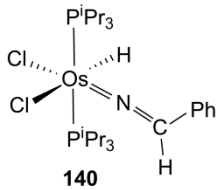
ΔE_{orb} values similar to those of neutral fragments in their electronic doublet state.[78] For **139** and **140**, a pure electron-sharing bonding with the fragments in the quartet state afforded the highest ΔE_{orb} and was therefore discarded.[77]

[Insert Table 1]

Table 1. Results of EDA-NOCV method computed at the ZORA-BP86-D3/TZ2P//BP86-D3/def2-SPV level.



139



140

	Donor-acceptor	**Electron-sharing/Donor-acceptor**	**Donor-acceptor**	**Electron-sharing/Donor-acceptor**
Fragments	$[Os]^+$ $[N{=}CHPh]^-$	$[Os]^\cdot$ (d) $[N{=}CHPh]^\cdot$ (d)	$[Os]^+$ $[N{=}CHPh]^-$	$[Os]^\cdot$ (d) $[N{=}CHPh]^\cdot$ (d)
ΔE_{int}	-202.2	-112.0	-258.5	-117.4
ΔE_{Pauli}	244.2	210.0	347.1	293.6
ΔE_{elstat}[a]	-277.4 (62.2)	-145.9 (45.3)	-313.0 (52.4)	-189.5 (46.1)
ΔE_{orb}[a]	-154.7 (34.6)	-161.9 (50.3)	-268.9 (45.0)	-205.8 (50.1)
ΔE_{disp}[a]	-14.3 (3.2)	-14.3 (4.4)	-15.7 (2.6)	-15.7 (3.8)
$\Delta E_{orb}(\rho_1)$[b]	-50.9 (32.9)	-81.9 (50.6)	-127.0 (47.2)	-92.5 (44.9)
$\Delta E_{orb}(\rho_2)$[b]	-27.7 (17.9)	-28.5 (17.6)	-35.0 (13.5)	-37.6 (18.3)
$\Delta E_{orb}(\rho_3)$[b]	-47.0 (30.4)	-36.9 (22.8)	-69.5 (7.9)	-57.3 (27.9)
$\Delta E_{orb}(rest)$[b]	-29.1 (18.8)	-14.6 (9.0)	-37.4 (13.9)	-18.4 (8.9)

[a] The values in parentheses indicate the percentage to the total attractive interaction energy: $\Delta E_{elstat} + \Delta E_{orb} + \Delta E_{disp}$. [b] The values in parentheses give the percentage contribution to the total orbital interactions ΔE_{orb}. The smallest ΔE_{orb} value indicates the most faithful description of the type of the binding.

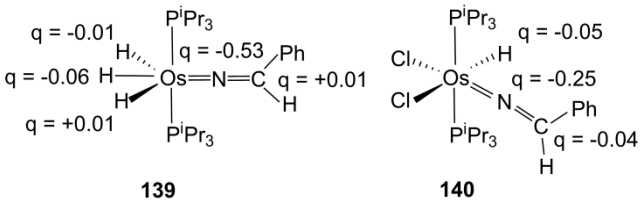
Azavinylidenes are usually viewed as *α*-nitrogen counterparts of vinylidenes. However, they compare better with alkylidynes according to that previously mentioned. Vinylidenes are two-electron donor ligands with a standardized reactivity, which is dominated by the addition of nucleophiles at the *α*-carbon, whereas the electrophiles attack at the *β*-carbon atom.[79] In contrast both azavinylidenes and alkylidynes are three-electron donors and display two different electronic situations, depending upon the metal fragment, which give rise to different chemical behaviors, although the difference between nitrogen and carbon generates significant changes in reactivity.

The differences in the osmium-azavinylidene bonding situation are also reflected in the charges on the atoms of the C=N bond and in the hydride ligands (Chart 3). The

N atom of the azavinylidene ligand of **139** supports a negative charge that is approximately twice that on the N atom of **140**. On the other hand, while the C atom of the azavinylidene of **139** is slightly positive, that of **140** is slightly negative. Furthermore, interestingly, one of the hydride ligands of the trihydride is slightly positive, whereas the other two and that of **140** are slightly negative.

[Insert Chart 3]

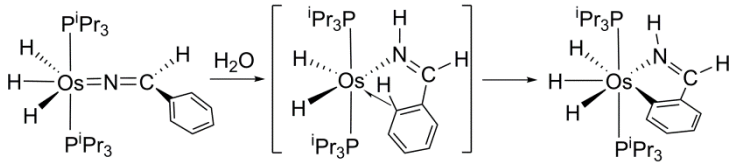
Chart 3 Computed (BP86-D3/def2-SVP level) natural bond orbital (NBO) partial charges for **139** and **140**.



The electronic differences between **139** and **140** translate into the chemical behaviors. In contrast to **135-138**, complex **139** is not stable in the presence of water. The addition of 1 equiv of water to the toluene or tetrahydrofuran solutions of the latter rapidly produces its isomerization to the orthometalated phenylmethanime derivative $OsH_3\{\kappa^2\text{-N,C-}(NH{=}CHC_6H_4)\}(P^iPr_3)_2$ (**141**). The participation of water in the reaction was confirmed by means of the addition of D_2O instead of H_2O, which afforded selectively and quantitatively $OsH_3\{\kappa^2\text{-N,C-}(ND{=}CHC_6H_4)\}(P^iPr_3)_2$ (**141-*d*$_1$**). The formation of **141** involves the migration of the electrophilic hydride from the metal center to the nucleophilic N atom of the azavinylidene group to afford an unsaturated dihydride-osmium-aldimine intermediate **Ab**, which evolves by oxidative addition of an *ortho*-CH bond of the phenyl substituent of the aldimine (Scheme 48). According to the generation of **141-*d*$_1$**, the hydride migration is promoted by water, which acts as a proton shuttle. This was confirmed by DFT calculations (B3LYP-D3/SDD/6-31G**). The direct migration of the hydride to the N atom takes place with activation energy of 31.4 kcal·mol^{-1}, whereas the proton shuttle formed by three water molecules, consecutively associated by means of hydrogen bonds, reduces the barrier for the hydride migration to 19.6 kcal·mol^{-1}.

[Insert Scheme 48]

Scheme 48 Isomerization of **139** to **141**.

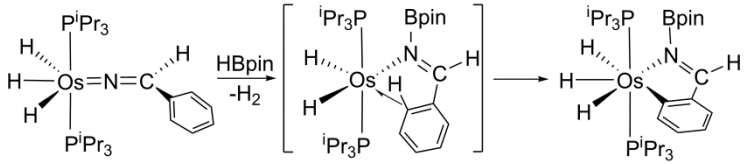


139 **Ab** **141**

The pair formed by the electrophilic hydride and the nitrogen atom of the azavinylidene of **139** promotes the heterolytic rupture of the B-H bond of HBpin (Scheme 49). In toluene, at 80 ºC, the reaction of the trihydride with the borane affords H_2 and a dihydride-osmium-boryl(aldimine) species **Ac**, which similarly to **Ab** undergoes the oxidative addition of an *ortho*-CH bond of the phenyl substituent of the aldimine to give $OsH_3\{\kappa^2\text{-N,C-[N(Bpin)=CHC}_6H_4]\}(P^iPr_3)_2$ (**142**). In agreement with the formation of **142**, complex **139** also isomerizes into **141** under 1 atm of H_2.[77]

[Insert Scheme 49]

Scheme 49 B-H bond activation of HBpin promoted by **139**.

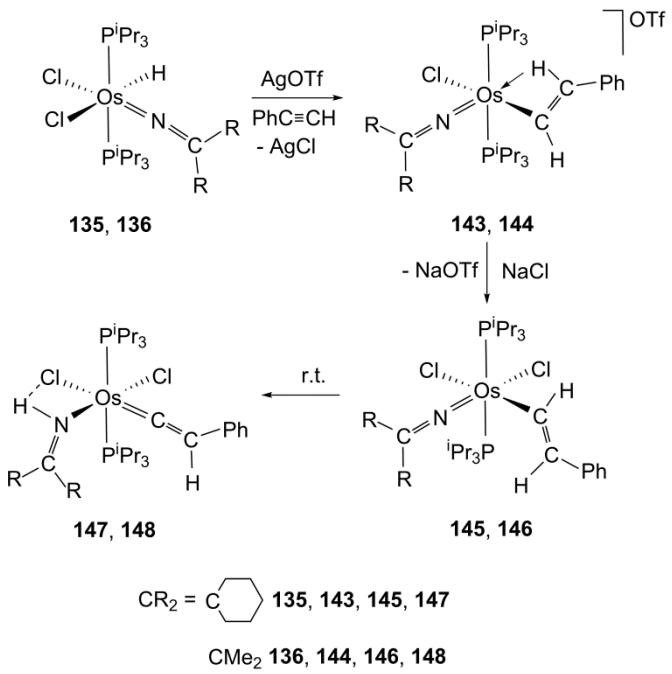


139 **Ac** **142**

Azavinylidene ligands of octahedral complexes **135** and **136** promote an interesting intramolecular C(sp^2)-H bond activation (Scheme 50). Treatment of their dichloromethane solutions with AgOTf, at room temperature, and the subsequent addition of phenylacetylene to the resulting solution at -25 ºC leads to the alkenyl-azavinylidene derivatives $[Os\{(E)\text{-CH=CHPh}\}Cl(=N=CR_2)(P^iPr_3)_2]OTf$ ($CR_2 = CC_5H_{10}$ (**143**), CMe_2 (**144**)), as a result of the insertion of the C-C triple bond of the alkyne into the Os-H bond of the starting azavinylidene complexes. The metal center of these species is saturated through an agostic bond with the alkenyl H_β atom. Addition of NaCl to the tetrahydrofuran solutions of **143** and **144**, at -30 ºC, produces the split of the agostic interaction and the formation of the neutral six-coordinate compounds $Os\{(E)\text{-CH=CHPh}\}Cl_2(=N=CR_2)(P^iPr_3)_2$ ($CR_2 = CC_5H_{10}$ (**145**), CMe_2 (**146**)), which evolve into the imine-vinylidene derivatives $OsCl_2(=C=CHPh)(NH=CR_2)(P^iPr_3)_2$ ($CR_2 = CC_5H_{10}$ (**147**), CMe_2 (**148**)) as a consequence of a C_α-to-N hydrogen migration.[80]

[Insert Scheme 50]

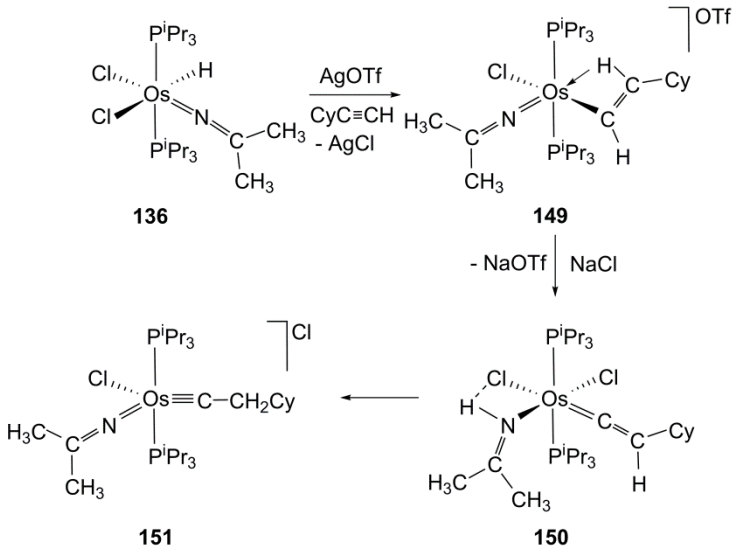
Scheme 50 Transformation of **135** and **136** in **147** and **148**: formation of imine-vinylidene derivatives.



The phenyl group stabilizes the vinylidene ligand of **147** and **148**. Thus, in contrast to phenyl, cyclohexyl promotes an additional N-to-C_β hydrogen migration in the imine-vinylidene derivative, which affords an azavinylidene-alkylidyne compound (Scheme 51). The addition of cyclohexylacetylene, at -25 ºC, to the dichloromethane solutions resulting from the treatment of **136** with AgOTf affords [Os{(*E*)-CH=CHCy}Cl(=N=CMe_2)(P^iPr_3)$_2$]OTf (**149**), related to **143** and **144**. Similarly to them, it evolves into the neutral imine-vinylidene $OsCl_2$(=C=CHCy)(NH=CMe_2)(P^iPr_3)$_2$ (**150**) in the presence of NaCl, at -30 ºC, in tetrahydrofuran. In contrast to **147** and **148**, complex **150** is not stable in dichloromethane at room temperature and isomerizes to the azavinylidene-alkylidyne salt [OsCl(=N=CMe_2)(≡CCH_2Cy)(P^iPr_3)$_2$]Cl (**151**).[81]

[Insert Scheme 51]

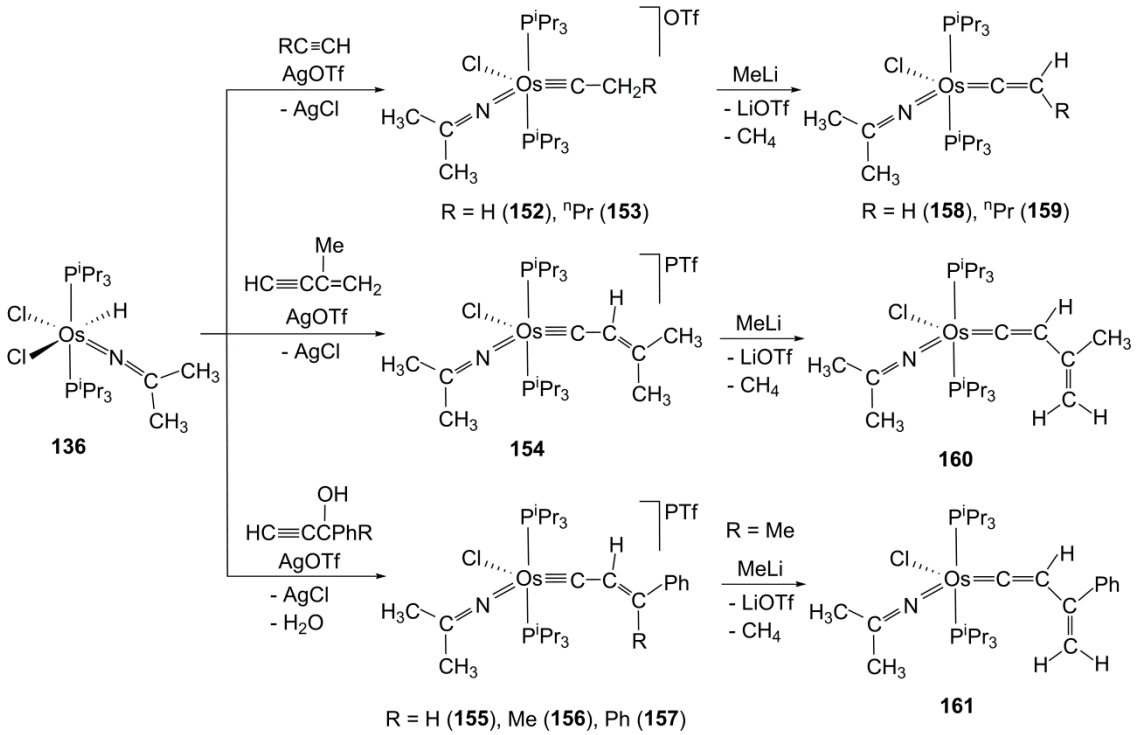
Scheme 51 Transformation of **136** in **151**: formation of azavinylidene-alkylidyne derivatives.



Addition of acetylene, 1-pentyne, 2-methyl-1-buten-3-yne,1-phenyl-2-propyn-1-ol, 2-phenyl-3-butyn-2-ol, and 1,1-diphenyl-2-propyn-1-ol, at room temperature, to dichloromethane solutions resulting from the treatment of **136** with AgOTf also afford azavinylidene-alkylidyne derivatives, which give azavinylidene-vinylidenes by deprotonation (Scheme 52). Acetylene and 1-pentyne generate the alkylalkylidyne complexes $[OsCl(=N=CMe_2)(\equiv CCH_2R)(P^iPr_3)_2]OTf$ (R = H (**152**), ^{n}Pr (**153**)), whereas the enyne and the alkynols give the respective alkenylalkylidyne compounds $[OsCl(=N=CMe_2)(\equiv CCH=CMe_2)(P^iPr_3)_2]OTf$ (**154**) and $[OsCl(=N=CMe_2)(\equiv CCH=CPhR)(P^iPr_3)_2]OTf$ (R = H (**155**), Me (**156**), Ph (**157**)). The deprotonation of alkylidyne ligands of **152** and **153** with MeLi leads to the vinylidene complexes $OsCl(=N=CMe_2)(=C=CHR)(P^iPr_3)_2$ (R = H (**158**), ^{n}Pr (**159**)), whereas the alkenylalkylidyne ligands of **154** and **156** give the alkenylvinylidenes of derivatives $OsCl(=N=CMe_2)\{=C=CHC(R)=CH_2\}(P^iPr_3)_2$ (R = Me (**160**), Ph (**161**)) under the same conditions. Treatment of the imine-vinylidene **147** and **148** with ^{n}BuLi yields the azavinylidene-vinylidene $OsCl(=N=CR_2)(=C=CHPh)(P^iPr_3)_2$ (CR_2 = CC_5H_{10} (**162**), CMe_2 (**163**)), related to **158** and **159**.[82]

[Insert Scheme 52]

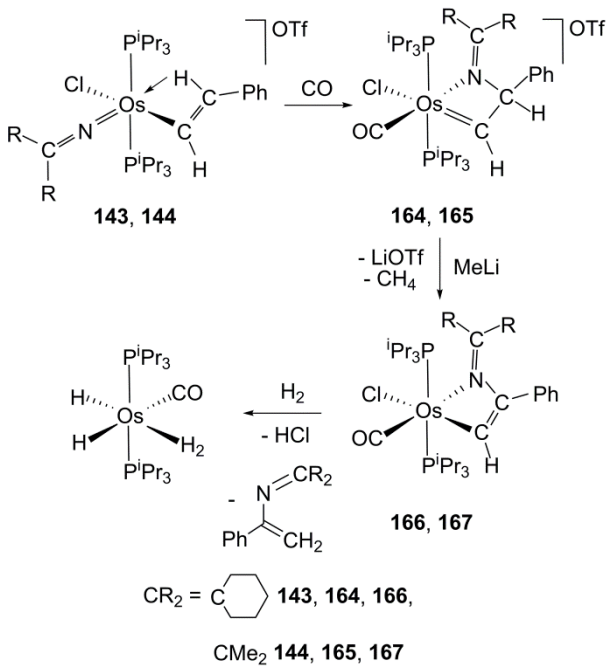
Scheme 52 Reactions of **136** with alkynes, enynes, and alkynoles.



The coordination of chloride to the metal center of **143** and **144** is certainly responsible of the C_α-to-N hydrogen migration, which leads to the imine-vinylidene derivatives **147** and **148**. Thus, in contrast to chloride, carbon monoxide promotes the coupling between the azavinylidene and styryl ligands (Scheme 53).[83] Under 1 atm of this gas, complex **143** and **144** evolve to the respective Δ^2-1,2 azaosmetine compounds **164** and **165**. Their formation has been rationalized as intramolecular [2+2] cycloaddition reactions between the Os-N and C-C double bonds. The π-acceptor character of the initially coordinated carbonyl ligand appears to excite the π-donor nature of the azavinylidene group, which increases the double character of the Os-N bond and therefore favors the cyclization. The deprotonation of the C(sp^3) atom of the four-membered heterometalaring with MeLi produces a Δ^2-to-Δ^3 transformation of the azaosmetine to give **166** and **167**, which react with molecular hydrogen to afford the well-known dihydride-dihydrogen derivative $OsH_2(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$[84] and the corresponding 2-aza-1,3-butadienes.[83]

[Insert Scheme 53]

Scheme 53 Carbon monoxide promoted azavinylide-styryl coupling.



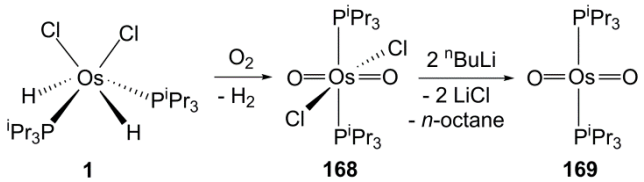
13. Rupture of the oxygen molecule

Oxo complexes are extremely important due to their applications for the *cis*-hydroxylation of alkenes to *cis*-diols. The reduction of the oxo compound by the organic substrate can directly occur. However, in general, the resultant reduced metallic species cannot be reoxidized by molecule oxygen but require strong oxidants.[85] Given the advantages of air or dioxygen as final oxidant, the metal-promoted activation of the O_2 molecule is a reaction of great interest.

Dihydride-dichloride complex **1** is capable of activating the O-O double bond of molecular oxygen from the air or pure oxygen, to give the osmium(VI)-dioxo derivative *trans*-$OsO_2Cl_2(P^iPr_3)_2$ (**168**), in toluene, at room temperature. Subsequent treatment of toluene solutions of **168** with ^{n}BuLi affords *trans*-$OsO_2(P^iPr_3)_2$ (**169**) and *n*-octane (Scheme 54).[86]

[Insert Scheme 54]

Scheme 54 Reaction of **1** with oxygen.



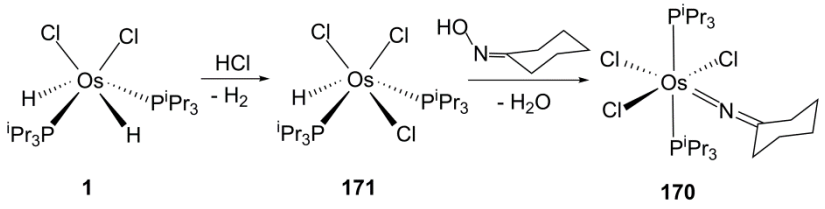
The geometry of **168** is octahedral with O-Os-O, P-Os-P, and Cl-Os-Cl angles of 180º, whereas the geometry of **169** is square-planar and can be viewed as derived from that of **168** by loss of the chloride ligands and shortening of the Os-O and Os-P bonds. Thus, the O-Os-O and P-Os-P angles are also 180º, while the Os-O (1.743(2) Å) and Os-P (2.4178(9) Å) bond lengths are about 0.03 and 0.1 Å, respectively, shorter than the Os-O (1.767(6) Å) and Os-P (2.519(2) Å) distances found in **168**. DFT Calculations on **169** revealed that the electron filling pattern is consistent with a formal d^4 electron count for the metal ion. The occupied HOMO and HOMO-1 have mainly d character of nonbonding nature. The three next empty orbital (LUMO, LUMO+1, and LUMO+2) are of metal-ligand antibonding character. The LUMO and LUMO+1 result from π-antibonding interactions between π-donor p orbitals of the oxygen atoms and d orbitals of the metal, whereas LUMO+2 is σ-phosphorous-osmium antibonding. The high energy of the empty orbitals leads to a sizable HOMO-LUMO gap, which is in agreement with the stability of this unusual four-coordinate molecule.

14. Cl-H bond activation

This bond activation has been invoked to rationalize the formation of the trichloride-azavinylidene complex $OsCl_3(=N=CC_5H_{10})\{(P^iPr_3)_2$ (**170**), as a side product of the reaction shown in Scheme 47, which yields **135** as main product. The HCl molecule generated in the formation of the initial oximate intermediate, complex **124**, is activated by the starting complex **1**, to give H_2 and the hydride-trichloride $OsHCl_3(P^iPr_3)_2$ (**171**). The subsequent reaction of the latter with cyclohexanone oxime should afford **170** and water, by a process similar to the formation of **135** (Scheme 55).[75] The hydride-trichloride complex **171** is usually prepared as a blue-green solid, by treatment of **1** with 1 equiv of *N*-chlorosuccinimide in chloroform at room temperature.[27]

[Insert Scheme 55]

Scheme 55 Formation of the trichloride-azavinylidene **170**.



1 **171** **170**

The osmium-azavinylidene bonding situation in **170** is similar to that of the hydride-dichloride derivatives **135** and **136**; i. e., the Os-N interaction is well described by means of a mixed electron-sharing/donor-acceptor bonding.[77]

15. Conclusions

The number of unsaturated osmium(IV)-hydride complexes is certainly limited. However, their chemistry is very rich. They display a notable ability to activate symmetrical and asymmetrical σ-bonds of a wide range of organic and inorganic molecules. A characteristic of the activation processes is that do not result in an increase of the formal oxidation state of the metal center. This is a consequence of that they are usually dihydride or trihydride derivatives, which undergo an intramolecular reduction to afford saturated Kubas-type or elongated dihydrogen species, when coordinate the σ-bond. Before the activation, these intermediates dissociate the Kubas-type dihydrogen or eliminate a HX molecule as consequence of the heterolytic cleavage of the elongated dihydrogen. In this way, even the homolytic cleavage of the coordinated σ-bond does not increase the formal metal oxidation state over that of the starting compound.

Dihydride-dichloride complex **1** is the compound of this family showing the widest variety of reactions. Thus, it has become one of the cornerstones in the development of the modern osmium organometallic chemistry. Its ability to activate $C(sp^2)$-H and $C(sp^2)$-C bonds of unsaturated organic substrates and to generate Os-C multiple bonds is noticeable. The variety of stannyl-polyhydrides that its reactions with Ph_3SnH have provided and the ability of some of them to activate $C(sp^2)$-H bonds should be also pointed out. The formation of azavinylidenes with an interesting reactivity, which promotes C-to-N and N-to-C hydrogen migrations to convert single Os-C bonds into double and subsequently into triple bonds, should be also mentioned, as well as its rupture capacity of molecular oxygen.

Unsaturated osmium(IV)-hydride complexes have been usually stabilized with bulky phosphines. This has been certainly one of the reasons that have limited the number of available compounds of this class. New ligands are necessary to reach further development in the chemistry of these type of complexes. In this context, the use of pincers is promising, according to the results obtained with pincer-diphosphines in Si-H bond activation reactions.[58] N-heterocyclic carbenes (NHCs) are other ligands of interest, which could stabilize these species improving their properties. Some mixed

phosphine-osmium-NHC complexes have been prepared in recent years and their chemical behavior is currently in study.[87]

The revised reactions suggest two lines of future application. On one hand, the possibility of stabilizing compounds with both electrophilic and nucleophilic centers, as the trihydride azavinylidene **139**, opens new reactivity pathways out the metal coordination sphere, which can result of interest to design novel types of catalysis. On the other, the incorporation of two different metal fragments by means of the O-H bond activation of metal-nucleosides could be used as a way for the orthogonal functionalization of oligonucleotides, taking advantage of the particular reactivity and properties of each metal fragment to promote specific metal transformations.

In conclusion, unsaturated osmium(IV)-hydride complexes are a class of compounds now stabilized by bulky phosphines, which promote a wide range of σ-bond activation reactions and could have interesting new future applications if the number and variety of ligands for their stabilization is increased.

Acknowledgments

Financial support from the MINECO of Spain (Projects CTQ2017-82935-P and RED2018-102387-T (AEI/FEDER, UE)), Gobierno de Aragón (Group E06_17R and project LMP148_18), FEDER, and the European Social Fund is acknowledged.

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