Osmium Complexes With POP Pincer Ligands

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16.1. INTRODUCTION

We are interested in complexes of platinum group metals with POP ligands such as 9,9-dimethyl-4,5-bis(diisopropylphosphino)xanthene ($\text{xant}(\text{P}^i\text{Pr}_2)_2$) and 4,6-bis(diisopropylphosphino)dibenzofuran ($\text{dbf}(\text{P}^i\text{Pr}_2)_2$) and in the study of the similarities and differences between the 4d and 5d counterparts of each group, with the aim of finding new and more efficient catalysts for the conversion and storage of regenerative energy and in metal-promoted organic synthesis.

POP-ether diphosphines are flexible, which allows them to change their coordination fashion for adapting to the requirement of the participating intermediates in multistep processes [1–3]. Thus for instance, Weller and coworkers have demonstrated that 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene ($\text{xant}(\text{PPh}_2)_2$) has the ability of changing its coordination mode in several relevant rhodium- and iridium-mediated processes, such as the hydroacylation [4] and carbothiolation [5] of alkenes and alkynes and the dehydrocoupling of amine-boranes [6].

Platinum group metals certainly occupy a prominent place in pincer-metal chemistry [7–9]. Osmium is nevertheless a notable exception. The scarce development of the pincer-osmium chemistry is probably due to the rooted belief that osmium is not useful in catalysis because it is a reductant and prefers to be coordinatively saturated and forms redox isomers with greater metal–carbon multiplicity [10–13]. However, recent findings have proved that osmium can be a promising alternative to the metals classically used in catalysis [14–23].

The chemistry of the pincer-osmium complexes has been mainly focused on a few PCP derivatives reported by the groups of Gusev [24–28], Jia [29–31], and Milstein [32,33] and PNP complexes described by the groups of Caulton [34–37], Gusev [38–41], and Jia [42], along with some CCC [43–46], CCN [47], CNC [48,49], CNN [50–52], CNO [53], and NNN [54–59] species.

We synthesized the diphosphines $\text{xant}(\text{P}^i\text{Pr}_2)_2$ and $\text{dbf}(\text{P}^i\text{Pr}_2)_2$ in 2010 [60], and subsequently started our research program on POP complexes of platinum group metals [3,60–65], including osmium [60,66–71]. In this chapter, we summarize the results obtained for this element until now.

16.2. LEVELLING EFFECT OF THE METAL CENTER

Ligands $\text{dbf}(\text{P}^i\text{Pr}_2)_2$, $\text{xant}(\text{P}^i\text{Pr}_2)_2$, and $\text{xant}(\text{PPh}_2)_2$ react with $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$ in 2-propanol under reflux to provide the osmium(III) derivatives $\text{OsCl}_3\{\kappa^3\text{-P,O,P-[dbf}(\text{P}^i\text{Pr}_2)_2]\}$ (1), $\text{OsCl}_3\{\kappa^3\text{-P,O,P-[xant}(\text{P}^i\text{Pr}_2)_2]\}$ (2), and $\text{OsCl}_3\{\kappa^3\text{-P,O,P-[xant}(\text{PPh}_2)_2]\}$ (3), which were isolated in high yields, according to Scheme 16.1, and characterized by X-ray diffraction analysis [60].

The structures reveal that the rigid polycyclic backbones do not have any significant influence in the coordination of the diphosphines because OsCl_3 produces a levelling effect on the relevant coordinating parameters of the ligands, such as the separation between the phosphorous atoms or the P–M–P bite angle. Thus although the separation between the phosphorous atoms in the free ligands is very sensitive to the rigidity imposed by the central ring of the polycycle, the

SCHEME 16.1

sum of the Os–P bond lengths in the three compounds is similar ($\approx 4.81 \text{ \AA}$ (**1**), $\approx 4.70 \text{ \AA}$ (**2**), and $\approx 4.65 \text{ \AA}$ (**3**)). The differences between the P–Os–P angles are also not significant. The P–Os–P angle in **1** ($159.95(3)^\circ$) is about 6° smaller than those of **2** ($166.20(5)^\circ$) and **3** ($165.38(5)^\circ$).

16.3. POLYHYDRIDE DERIVATIVES

Two different entries to the chemistry of $(\text{POP})\text{OsH}_n$ compounds have been developed, starting from the commercially available $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$. One route uses the adduct $\text{cis-OsCl}_2\{\kappa^1\text{-S}(\text{DMSO})\}_4$ (**4**) as intermediate species and allows to prepare a wide range of complexes including $n=1, 3, 4, 5$, and 6 . The other one has been designed to specifically prepare the compounds $\text{OsH}_3\text{Cl}\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ and $\text{OsH}_4\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$, employs the dihydride $\text{OsH}_2\text{Cl}_2(\text{P}^i\text{Pr}_3)_2$ (**5**) as key intermediate, affords similar or better yields, and is more direct [67].

Treatment of 2-propanol solutions of **4** with 1.0 equivalent of $\text{dbf}(\text{P}^i\text{Pr}_2)_2$ or 1.0 equivalent of $\text{xant}(\text{P}^i\text{Pr}_2)_2$, under reflux leads to $\text{OsCl}_2\{\kappa^3\text{-P,O,P-[dbf(P}^i\text{Pr}_2)_2]\}(\kappa^1\text{-S-DMSO})$ (**6**) or $\text{OsCl}_2\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}(\kappa^1\text{-S-DMSO})$ (**7**), as a result of the displacement of three DMSO molecules by the pincer ligand. These complexes were isolated in 86% (**6**) and 68% (**7**) yield, according to Scheme 16.2.

Complex **6** reacts with molecular hydrogen under 3 atm, in the presence of a Brønsted base [66]. The products of the reactions depend upon the base and the experimental conditions. Triethylamine produces the abstraction of a chloride ligand. Thus the trihydride $\text{OsH}_3\text{Cl}\{\kappa^3\text{-P,O,P-[dbf(P}^i\text{Pr}_2)_2]\}$ (**8**) is formed in toluene, at 90°C , and in the presence of the amine. On the other hand, NaH removes both chloride ligands. As a result, the tetrahydride $\text{OsH}_4\{\kappa^3\text{-P,O,P-[dbf(P}^i\text{Pr}_2)_2]\}$ (**9**) is obtained in tetrahydrofuran, at 50°C , and in the presence of the salt (Scheme 16.3). These compounds are isolated in 50% (**8**) and 65% (**9**) yields.

Complex **7** also reacts with molecular hydrogen in the presence of a Brønsted base. The stirring of its toluene solutions in the presence of Et_3N , under 3 atm of H_2 , at 90°C , for 60 h leads to the trihydride $\text{OsH}_3\text{Cl}\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ (**8**).

SCHEME 16.2

SCHEME 16.3

$[\text{xant}(\text{P}^i\text{Pr}_2)_2]\}$ (**10**), which is isolated in 57% yield; i.e., 20% yield to regard to $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$. An alternative method involving the use of the unsaturated six-coordinate d^4 -dihydride derivative **5** and $\text{OsH}_3\text{Cl}(\text{P}^i\text{Pr}_3)_2$ (**11**) and affords **10** in 55% yield with regard to $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$. Although it is also a three-step procedure (Scheme 16.4), the substitution of P^iPr_3 by $\text{xant}(\text{P}^i\text{Pr}_2)_2$ is a relatively rapid process of about 4 h, in toluene, under reflux.

The position of the chloride ligand determines the nature of **10**. Density functional theory (DFT) calculations reveal the existence of a *trans*-chloride-oxygen isomer **10a**, 20.1 kcal/mol (ΔG , 1 atm, 298.15 K) less stable than **10**, which is a hydride-dihydrogen species.

Complex **10** reductively eliminates H_2 , in toluene, at 90°C . In the presence of DMSO, the resulting unsaturated d^6 -monohydride is trapped by the S-donor solvent to afford $\text{OsHCl}\{\kappa^3\text{-P,O,P-[xant}(\text{P}^i\text{Pr}_2)_2]\}(\kappa^1\text{-S-DMSO})$ (**12**), according to Scheme 16.5.

The reaction of **7** with molecular hydrogen is sensible to the Brønsted base used and to the experimental conditions as that of **6**. In contrast to Et_3N in toluene, NaH in tetrahydrofuran removes both chloride ligands and, furthermore, a hydrogen molecule displaces the oxygen atom of the diphosphine, which becomes $\kappa^2\text{-P,P-binding}$. The stirring of tetrahydrofuran solutions of **7** in the presence of 10 equivalents of the superbase, under 3 atm of hydrogen at 50°C for 48 h, leads to the hexahydride $\text{OsH}_6\{\kappa^2\text{-P,P-[xant}(\text{P}^i\text{Pr}_2)_2]\}$ (**13**), which was isolated in 50% yield according to Scheme 16.6. A briefer method implies the treatment of tetrahydrofuran solutions of **7** with 20 equivalents of LiAlH_4 , at 80°C , for

SCHEME 16.4

SCHEME 16.5

SCHEME 16.6

3 h. By this procedure, complex **7** was obtained in 37% yield. In agreement with other OsH_6 species and related eight-coordinate osmium-polyhydrides [9], the coordination geometry around the metal center can be rationalized as being derived from a distorted dodecahedron, which is defined by two intersecting BAAB orthogonal trapezoidal planes. In this case, the phosphorous atoms occupy a B-site at each trapezoidal plane forming a P-Os-P angle of 105.4° .

Complex **13** is stable under hydrogen atmosphere at temperatures below 293K. In methanol, under argon, it slowly loses H_2 and the diphosphine coordinates the oxygen atom to the metal center. Thus the stirring of methanol solutions of **13**, at room temperature, for 6 days gives rise to the quantitative precipitation of the tetrahydride $\text{OsH}_4\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ (**14**), which was isolated as a white solid in 30% yield with regard to $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$. Complex **14** can be prepared through a briefer method by using **5**. The latter is initially transformed into the hexahydride $\text{OsH}_6(\text{P}^i\text{Pr}_3)_2$ (**15**). Subsequent treatment of a toluene solution of the latter with 1.1 equivalent of the diphosphine affords **14** in a 20% yield with regard to $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$, after 13 h, under reflux (Scheme 16.7).

Tetrahydride **14** is a strong reductor, which is able to promote the reduction of H^+ (Scheme 16.8) in spite of the high oxidation state of the metal center. Thus the addition of 4 equivalents of triflic acid (HOTf) to its dichloromethane solutions gives H_2 and the dihydride-elongated dihydrogen cation $[\text{OsH}_2(\text{OTf})(\eta^2\text{-H}_2)\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}]^+$ (**16**). In agreement with the ^1H NMR spectrum, the DFT-optimized structure of this species shows two groups of two equivalent hydrogen atoms, one of them in the P,H,H,P-trapezoidal plane and the other one in the O,H,H,O-trapezoidal plane. In the first plane the hydrogen atoms are separated by $1.545 \text{ \AA}$, whereas in the second one the H-H distance is $1.250 \text{ \AA}$.

The redox reaction occurs in two stages. Initially complex **14** adds a proton to afford $[\text{OsH}_5\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}]^+$ (**17**), which reacts with HOTf to give H_2 and **16**. Because both **14** and **16** are osmium(IV) species, the reaction of **17** with HOTf should initially lead to the osmium(VI) $[\text{OsH}_4(\text{OTf})\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}]^+$, which undergoes reductive tautomerization of an OsH_2 unit to afford **16**. DFT calculations reveal that **17** (Chart 16.1) has two tautomers very close in energy ($< 3 \text{ kcal/mol}$): a hydride-compressed dihydride-dihydrogen (**17a**) and a trihydride-compressed dihydride (**17b**). In **17a** the dihydrogen ligand is disposed almost parallel to the P-Os-P direction with a H-H bond length of $0.87 \text{ \AA}$, whereas the compressed dihydride ($1.40 \text{ \AA}$) lies in the perpendicular plane along with the oxygen atom of the

SCHEME 16.7

SCHEME 16.8

CHART 16.1

diphosphine. In **17b** the disposition of the hydrogen atoms is the same as in **17a** with the hydrogen atoms in the P,H,H,P plane separated by 1.762 Å.

Acetonitrile displaces the coordinated trifluoromethane sulfonate anion of **16** to afford the dicationic complex dihydride-dihydrogen $[\text{OsH}_2(\eta^2\text{-H}_2)(\text{CH}_3\text{CN})\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}]^{2+}$ (**18**). The dihydrogen ligand of this compound is situated in the perpendicular plane to the P-Os-P direction, with the hydrogen atoms separated by 0.898 Å, while the compressed dihydride lies in the trapezoidal plane containing the phosphorous atoms with the hydrogens separated by 1.475 Å. The treatment of **18** with Et_3N causes its deprotonation and the formation of the trihydride $[\text{OsH}_3(\text{CH}_3\text{CN})\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}]^+$ (**19**). The reaction is reversible and the addition of HOTf to **19** regenerates **18** (Scheme 16.9).

The position of the acetonitrile molecule also determines the nature of the OsH_3 unit of **19**. Similar to **10**, complex **19** has a hydride-dihydrogen tautomer, with the acetonitrile ligand *trans* to the oxygen atom of the diphosphine. This species is 10.7 kcal/mol (ΔG , 1 atm, 298.15K) less stable than **19**.

16.4. RUTHENIUM VERSUS OSMIUM

The ruthenium metal fragment $\text{Ru}\{\text{xant(P}^i\text{Pr}_2)_2\}$ avoids the oxidation state four. As a result, the osmium d^4 -polyhydrides are d^6 -dihydrogens in the ruthenium chemistry, which require different synthetic procedures from those of osmium for their preparation [68].

The ruthenium counterpart of **4**, *cis*- $\text{RuCl}_2\{\kappa^1\text{-S-(DMSO)}\}_4$ (**20**), has also proved to be a useful starting point to develop the $\{\text{xant(P}^i\text{Pr}_2)_2\}\text{Ru}$ chemistry. Treatment of toluene solutions of **20** with 1 equivalent of $\text{xant(P}^i\text{Pr}_2)_2$, under reflux, affords $\text{RuCl}_2\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}(\kappa^1\text{-S-DMSO})$ (**21**), which was isolated in 75% yield (Scheme 16.10).

Complex **21** also reacts with H_2 in the presence of a Brønsted base. Like in the osmium case, the reactions are very sensitive to the base used and the experimental conditions (Scheme 16.11). Treatment of toluene solutions of **21** with Et_3N , under 3 atm of H_2 , produces the replacement of a chloride ligand by hydride to give $\text{RuHCl}\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}(\kappa^1\text{-S-DMSO})$ (**22**). In contrast to Et_3N in toluene, NaH in tetrahydrofuran causes the substitution of both chloride ligands to afford the *cis*-dihydride $\text{RuH}_2\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}(\kappa^1\text{-S-DMSO})$ (**23**). Stirring of **22** in 2-propanol under 3 atm of H_2 for 4 weeks gives rise to the elimination of DMSO and the coordination of H_2 to yield $\text{RuHCl}(\eta^2\text{-H}_2)\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ (**24**), the ruthenium counterpart of **10**, which is however a hydride-dihydrogen derivative,

SCHEME 16.9

SCHEME 16.10

SCHEME 16.11

agreement with the tendency of ruthenium to avoid the oxidation state four. In opposition to **22**, the dihydride **24** does not undergo DMSO elimination to give $\text{RuH}_2(\eta^2\text{-H}_2)\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ (**25**) under H_2 atmosphere.

DFT calculations have revealed that there are three isomers of **24** with the chloride ligand *cis*-disposed to the oxygen atom of the diphosphine and the hydrogen atoms bonded to the metal center lying in the perpendicular plane to the P-Ru-P direction, which differ by 1.6 kcal/mol (ΔG , 1 atm, 298.15 K): the *trans*-Cl-Ru-H₂ derivatives **24a** and **24b** and the *trans*-O-Ru-H₂ species **24c** (Chart 16.2). The main difference between **24a** and **24b** is the separation between the atoms of the dihydrogen: 1.248 Å for the first of them and 0.907 Å for the second one. The separation in **24c** of 0.933 Å is similar to that of **24b**. The average of these distances, 1.03 Å, is consistent with the $J_{\text{H-D}}$ value found, suggesting a fast equilibrium between the three isomers in solution. The *trans*-disposition of the π -donor oxygen and chlorine atoms causes the destabilization of **24**. Thus there are also three *trans*-hydride-dihydrogen structures ($d_{\text{H}_2} = 0.812 - 0.820$ Å), which lie between 8.6 and 11.0 kcal/mol above **24** [68].

An efficient procedure to obtain **25** involves the sequential hydrogenation of the allenylidene derivative $\text{RuCl}_2(\text{C}=\text{C}=\text{CPh}_2)\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ (**26**) with ammonia-borane. Complex **26** is formed from the reaction of **21** with 1,1-diphenyl-2-propyn-1-ol. The hydrogenation initially gives $\text{RuCl}_2(\text{C}=\text{CHCHPh}_2)\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ (**27**), which undergoes the subsequent reduction of the Ru-C double bond to yield the hydride-tetrahydridoborate complex $\text{RuH}(\eta^2\text{-H}_2\text{BH}_2)\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ (**28**) and 3,3-diphenyl-1-propene. The formation of **28** takes place via the unsaturated dihydride $\text{RuH}_2\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ (**A**) resulting from the substitution of the chloride ligands by hydrides. Complex **28** is stable in a solution of hydrocarbons and in the solid state at room temperature, under argon. However, its stirring in 2-propanol, under 1 atm of H_2 , at 80°C, for 24 h gives rise to the formation of **25** in quantitative yield (Scheme 16.12).

The osmium complex **7** reacts with 1,1-diphenyl-2-propyn-1-ol in a similar manner to its ruthenium counterpart **21**, to afford the allenylidene derivative $\text{OsCl}_2(\text{C}=\text{C}=\text{CPh}_2)\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ (**29**). Ammonia-borane also reduces the $\text{C}_\beta\text{-C}_\gamma$ double bond of the allenylidene of **29**. However, the resulting vinylidene complex $\text{OsCl}_2(\text{C}=\text{CHCHPh}_2)\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ (**30**) is inert (Scheme 16.13). As a consequence, it is not possible to apply a methodology related to that summarized in Scheme 16.12 for preparing the osmium tetrahydride **14**. In this context, it should be noted

CHART 16.2

SCHEME 16.12

SCHEME 16.13

that osmium not only reduces more than ruthenium but also prefers complexes with greater metal–carbon bond multiplicity [10–13].

16.5. HETEROLYTIC FORMATION OF H₂

Some osmium polyhydrides stabilized by $\text{xant}(\text{P}^i\text{Pr}_2)_2$ sequentially add H^+ and H^- , or H^- and H^+ to generate H_2 in a cyclic manner (Scheme 16.14). During the process, the diphosphine changes its coordination mode from $\kappa^3\text{-mer}$ to $\kappa^3\text{-fac}$ and $\kappa^2\text{-P,P-bidentate}$, depending upon the electronic and steric requirements of the involved intermediates, to form both polyhydrides with nonclassical interactions and classical polyhydrides. The nonclassical interactions are favored by the tridentate coordination, in particular by the *mer* dispositions [70].

Complex **10** adds a proton, in agreement with the Lewis base character of the saturated polyhydrides. Under a hydrogen atmosphere, the addition of 1 equivalent of $\text{HBF}_4 \cdot \text{OEt}_2$ to **10** in dichloromethane leads to the cation $[\text{OsCl}(\text{H} \cdots \text{H})(\eta^2\text{-H}_2)\{\kappa^3\text{-P,O,P-}[\text{xant}(\text{P}^i\text{Pr}_2)_2]\}]\text{BF}_4$ (**31**). DFT calculations reveal that there are two compressed dihydride–dihydrogen structures differing by 3.0 kcal/mol (ΔG , 1 atm, 298.15 K): **31a** and **31b** (Chart 16.3). In both cases the diphosphine is *mer*-coordinate. The most stable structure **31a** shows the dihydrogen ligand (1.029 Å) at the plane perpendicular to the P–Os–P direction, disposed *trans* to the chloride, whereas the compressed dihydride (1.427 Å) lies

SCHEME 16.14

CHART 16.3

trans to the oxygen atom of the diphosphine, almost parallel to the P-Os-P direction. In **31b** the dihydrogen (1.091 Å) and the compressed dihydride (1.358 Å) ligands exchange their positions.

Complex **31** can be kept in dichloromethane, under a hydrogen atmosphere at room temperature, for a few hours. However, under argon it loses the dihydrogen ligand to afford the dimer $[(\text{Os}(\text{H}\cdots\text{H})\{\kappa^3\text{-P,O,P-}[\text{xant}(\text{P}^i\text{Pr}_2)_2]\})_2(\mu\text{-Cl})_2]^{2+}$ (**32**). The X-ray diffraction structure of the latter shows a change in the coordination mode of the diphosphine, which now coordinates in a $\kappa^3\text{-fac}$ fashion. The *fac* coordination of the diphosphine in **32** is a determining factor for the stabilization of the dimeric structure with regard to **31**, which appears to be related to the flexibility of the xanthene group. In fact, the most rigid dibenzofuran stabilizes the OsH_4 -species and prevents the formation of a counterpart dimer of **32**. Thus under argon, the addition of 1 equivalent of $\text{HBF}_4\cdot\text{OEt}_2$ to **8** in dichloromethane leads to the compressed dihydride-dihydrogen complex $[\text{OsCl}(\text{H}\cdots\text{H})(\eta^2\text{-H}_2)\{\kappa^3\text{-P,O,P-}[\text{dbf}(\text{P}^i\text{Pr}_2)_2]\}]\text{BF}_4$ (**33**). In contrast to **31**, this $\text{dbf}(\text{P}^i\text{Pr}_2)_2$ is moderately stable under argon and does not release H_2 to dimerize. Its X-ray diffraction structure is in full agreement with the optimized structure of the most stable isomer of **31** (Scheme 16.15).

The coordination change from $\kappa^3\text{-mer}$ to $\kappa^3\text{-fac}$ of the diphosphine is a requirement for the coordinative saturation of the metal center of the $[\text{OsClH}_2\{\kappa^3\text{-P,O,P-}[\text{xant}(\text{P}^i\text{Pr}_2)_2]\}]^+$ fragment resulting from the dissociation of molecular hydrogen from **31**, since the steric hindrance experienced by the isopropyl substituents of the *mer*-coordinated diphosphine of two unsaturated fragments appears to prevent the dimerization. However, the coordination $\kappa^3\text{-mer}$ is clearly favored over $\kappa^3\text{-fac}$, when the metal center of a mononuclear complex is saturated. As a proof of concept, it should be mentioned that the chloride bridges of **32** are broken in acetonitrile to form the saturated dihydrogen complex $[\text{OsCl}(\eta^2\text{-H}_2)(\text{CH}_3\text{CN})\{\kappa^3\text{-P,O,P-}[\text{xant}(\text{P}^i\text{Pr}_2)_2]\}]\text{BF}_4$ (**34**), which contains a $\kappa^3\text{-mer}$ -coordinated diphosphine (Scheme 16.16).

The hydride ion also breaks the chloride bridges of **32**. The addition of KH to tetrahydrofuran solutions of the dimer regenerates **10**, closing a cycle for the formation of H_2 by reaction of H^+ and H^- on the osmium center of **10** (route a in Scheme 16.14). A second hydride ion displaces the chloride ligand of the latter to afford the tetrahydride **14**. Similar to chloride, the oxygen atom of the *mer*-coordinated diphosphine of **14** has a tendency to be displaced by the hydride ion. Thus the addition of KH to the latter in tetrahydrofuran leads to the anionic pentahydride $[\text{OsH}_5\{\kappa^2\text{-P,P-}[\text{xant}(\text{P}^i\text{Pr}_2)_2]\}]^-$ (**35**), containing a $\kappa^2\text{-P,P-bidentate}$ diphosphine. Complex **35** is strong Brønsted base which is even protonated by traces of water. The protonation leads to the hexahydride **13**, which releases molecular hydrogen and coordinates the oxygen atom to regenerate the tetrahydride **14**, closing a second cycle for the formation of H_2 by reaction of H^- and H^+ on the metal center of the tetrahydride **14** (route b in Scheme 16.14). In this context, it should be mentioned that the kinetically controlled formation of molecular hydrogen by the exothermic neutralization of the hydride ion is a process of great interest in connection with the storage of H_2 in solid materials, which would become a safe and efficient way to store energy for both stationary and mobile applications [72–75].

SCHEME 16.15

SCHEME 16.16

16.6. ELONGATED Σ -BORANE VERSUS Σ -BORANE COMMENT: WHEN WE DOWNLOAD THE PROOF AS A PDF FILE, THE TITLES OF THE DIFFERENT SECTIONS ARE IN CAPITAL LETTERS. IN THIS PARTICULAR TITLE, THE GREEK LETTER Σ IS THEN CHANGED TO Σ , WHICH IS NOT CORRECT. THE GREEK LETTER Σ HAS TO BE USED

The square pyramidal metal fragments $\text{OsHX}\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ ($\text{X}=\text{Cl, H}$) stabilize the coordination of the B–H bond of boranes *trans* to the X ligand. The strength of the interaction between the metal center and the borane is sensitive to the nature of X. As a consequence, elongated σ -borane and σ -borane complexes have been isolated and the interaction between the metal fragment and the coordinated B–H bond has been analyzed as a function of X [71].

The BF_4 -salt of the dinuclear cation **32** reacts with catecholborane (HBcat) and pinacolborane (HBpin) to give the elongated σ -borane derivatives $\text{OsHCl}(\eta^2\text{-H-BR}_2)\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ ($\text{BR}_2=\text{Bcat}$ (**36**), Bpin (**37**)), H_2 , FBR_2 , and BF_3 (Scheme 16.17). The elongated σ -borane characteristic of these compounds has been supported by the X-ray diffraction analysis and DFT-optimized structures of both compounds, which show distances between the coordinated B and H atoms of the borane in the range 1.6–1.7 Å. In contrast to **32**, the reaction of the tetrahydride **14** with HBcat leads to the σ -borane derivative $\text{OsH}_2(\eta^2\text{-H-Bcat})\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ (**38**), which shows a distance between the atoms of the coordinated B–H bond in the range 1.4–1.5 Å.

The interaction between the metal center and the borane involves σ -donation from the double occupied $\sigma(\text{B-H})$ orbital to a vacant d atomic orbital of the metal and $\text{d}(\text{Os}) \rightarrow \sigma^*(\text{B-H})$ back donation. The electron withdrawing ability of the chloride ligand in **36** and **37** increases the donation from the $\sigma(\text{B-H})$ orbital to the osmium atom, whereas its π -donor power favors the $\text{d}(\text{Os}) \rightarrow \sigma^*(\text{B-H})$ back-donation. As a result, the osmium-borane interaction is stronger for $\text{X}=\text{Cl}$ than for $\text{X}=\text{H}$. This can explain why the coordinated B–H bond is longer in **36** and **37** than in **38**. In this context, it should be mentioned that Energy Decomposition Analysis-Natural Orbital for Chemical Valence (EDA-NOCV) methods suggest that the much lower interaction strength between the metal fragment $\text{OsH}_2\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ and the borane is due to less stabilizing electrostatic and orbital interactions.

A notable difference between elongated σ -borane complexes and σ -borane compounds is revealed by the Natural Bond Orbital-Atom in Molecules (NBO-AIM) analysis of **36** and **38**. The analysis of **36** displays a triangular topology for the OsHB unit involving Os–B, Os–H, and B–H bond critical points and a ring critical point. In contrast, the analysis of the OsHB unit of **38** only shows Os–B and B–H critical points, therefore lacking a similar triangular topology [71].

SCHEME 16.17

16.7. C–H BOND ACTIVATION

The tetrahydride osmium complex **14** and its ruthenium counterpart **25** promote the *ortho*-C–H bond activation of aromatic and fluorinated aromatic ketones, the C_β-H bond activation of α,β-unsaturated ketones, and the OC–H bond activation of aldehydes [69].

Treatment of toluene solutions of **14** with 1 equivalent of acetophenone and benzophenone under reflux lead to the osmaisobenzofuran derivatives $\text{OsH}\{\kappa^2\text{-O,C-[OC(R)C}_6\text{H}_4]\}\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ (R=Me (**39**), Ph (**40**)). Isotopic labeling experiments, using perdeuterated benzophenone as a substrate, demonstrate that the selectivity of the *ortho*-C–H bond activation is thermodynamic in origin, while the activations of the C–H bonds at *meta* and *para* positions are kinetically preferred. Complex **14** favors the C–H bond activation over the C–F bond cleavage in fluorinated aromatic ketones. Thus the fluorinated osmaisobenzofurans $\text{OsH}\{\kappa^2\text{-O,C-[OC(Me)C}_6\text{H}_3\text{F}]\}\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ (**41**) and $\text{OsH}\{\kappa^2\text{-O,C-[OC(C}_6\text{H}_3\text{F}_2)\text{C}_6\text{H}_4]\}\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ (**42**) are obtained from the reactions with 2-fluoroacetophenone and 2,6-difluorobenzophenone, respectively. Complex **14** also activates benzylideneacetone and methyl vinyl ketone to afford the osmafurans $\text{OsH}\{\kappa^2\text{-O,C-[OC(Me)CHC(R)]}\}\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ (R=Ph (**43**), H (**44**)). The reaction with benzylideneacetophenone yields a mixture of $\text{OsH}\{\kappa^2\text{-O,C-[OC(CH=CHPh)C}_6\text{H}_4]\}\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ (**45**) and $\text{OsH}\{\kappa^2\text{-O,C-[OC(Ph)CHCPh]}\}\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ (**46**) in a 2:1 molar ratio (Scheme 16.18).

The dihydride-dihydrogen-ruthenium(II) complex **25** also activates acetophenone and benzophenone. The reactions afford the ruthenaisobenzofurans $\text{RuH}\{\kappa^2\text{-O,C-[OC(R)C}_6\text{H}_4]\}\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ (R=Me (**47**), Ph (**48**)). Because the dihydride **A** reduces ketones, 2 equivalents of substrate are necessary to prepare **47** and **48**. It has been proposed that this reduction occurs via the intermediate **B** shown in Scheme 16.19. Thus the elimination of alcohol should lead to the 14-valence electrons ruthenium(0) derivative **C**, which could undergo the oxidative addition of the second molecule of ketone. An alternative pathway would involve the direct heterolytic C–H bond activation of the second ketone molecule promoted by **B**, using the alkoxide ligand as a base. The participation of both mechanisms is consistent with the presence of about 0.5 deuterium atoms at the hydride positions of the product resulting from the reaction of **25** with perdeuterated benzophenone. Furthermore, the distribution of deuterium and hydrogen atoms in the orthometalated product indicates

SCHEME 16.18

SCHEME 16.19

that the activation of the *meta*-C–H bonds of the ketone is kinetically favored over the *ortho*-C–H bonds and proves that the *ortho*-C–H bond cleavage is not chelated-directed, also for ruthenium [69].

The ruthenium complex **25** also favors the C–H bond activation over the C–F bond cleavage. Thus its reaction with 2-fluoroacetophenone affords the C–H bond activation product $\text{RuH}\{\kappa^2\text{-O,C-[OC(Me)C}_6\text{H}_3\text{F]}\}\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ (**49**). It further promotes the $\text{C}_\beta\text{-H}$ bond activation of benzylideneacetone and methyl vinyl ketone to give the ruthenafurans $\text{RuH}\{\kappa^2\text{-O,C-[OC(Me)CHC(R)]}\}\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ (R = Ph (**50**), H (**51**)). The reaction with benzylideneacetophenone yields a 1:1 mixture of the corresponding products resulting from the *ortho*-C–H bond, $\text{RuH}\{\kappa^2\text{-O,C-[OC(CH=CHPh)C}_6\text{H}_4]\}\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ (**52**), and $\text{C}_\beta\text{-H}$ bond, $\text{RuH}\{\kappa^2\text{-O,C-[OC(Ph)CHCPh]}\}\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ (**53**), activations (Scheme 16.20).

The OC–H bond is only about 23 kcal/mol weaker than the C–H bond of a phenyl group. As a consequence, the OC–H cleavage and the *ortho*-C–H bond activation in aromatic aldehydes are competitive processes. Thus depending upon the metal precursor, products of both types of reactions can be isolated [76–78]. However, treatment of toluene solutions of **14** with 1 equivalent of benzaldehyde under reflux leads to the aryl-hydride-carbonyl derivative $\text{OsH(Ph)(CO)}\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ (**54**). This complex is the result of the selective activation of the OC–H bond of the

SCHEME 16.20

aldehyde, which affords the unsaturated hydride-acyl intermediate **D**, to subsequently evolve by deinsertion of the phenyl group (Scheme 16.21). Under the same conditions, the $\text{Ru}\{\text{xant}(\text{P}^i\text{Pr}_2)_2\}$ skeleton also favors the OC–H bond activation over the cleavage of an *ortho*-C–H bond of the phenyl group. Thus the treatment of toluene solutions of **25** with 2 equivalents of benzaldehyde affords the complex $\text{RuH}(\text{Ph})(\text{CO})\{\kappa^3\text{-P,O,P-[xant}(\text{P}^i\text{Pr}_2)_2]\}$ (**55**), via the unsaturated hydride-acyl intermediate **E** [69].

The OC–H bond activation is also preferred over the vinylic C–H bond activation in α,β -unsaturated aldehydes. Similar to benzaldehyde, tetrahydride **14** reacts with 1-cyclohexene-1-carboxaldehyde to give $\text{OsH}(\text{C}_6\text{H}_9)(\text{CO})\{\kappa^3\text{-P,O,P-[xant}(\text{P}^i\text{Pr}_2)_2]\}$ (**56**), the cyclohexenyl counterpart of **54**, although in this case the OC–H activation-deinsertion product is contaminated with the dihydride-carbonyl derivative $\text{OsH}_2(\text{CO})\{\kappa^3\text{-P,O,P-[xant}(\text{P}^i\text{Pr}_2)_2]\}$ (**57**), which is generated as a consequence of the release of 1,3-cyclohexadiene from **56** (Scheme 16.22). The dehydrogenation of the substituent of the aldehyde is favored for alkyl with regard to alkenyl. The dihydride complex **57** is obtained as a pure organometallic species, along with cyclohexene, from the reaction of **14** with cyclohexane carboxaldehyde (Scheme 16.22) [69].

16.8. CATALYTIC PROCESSES

The $\text{dbf}(\text{P}^i\text{Pr}_2)_2$ tetrahydride complex **9** shows a marked tendency to activate the O–H bond of primary alcohols. It reacts with benzyl alcohol to afford the hydride-aryl-carbonyl derivative $\text{OsH}(\text{Ph})(\text{CO})\{\kappa^3\text{-P,O,P-[dbf}(\text{P}^i\text{Pr}_2)_2]\}$ (**58**). Its formation has been rationalized through the intermediates **E–H** shown in Scheme 16.23. The O–H bond activation of the alcohol by **9** could initially give **E**, which should lead to the unsaturated species **F** by dissociation of H_2 . Then, a β -elimination reaction in the alkoxide group could afford the dihydride-aldehyde **G**, which should generate the acyl intermediate **H**. Finally, the deinsertion of the phenyl group should yield **58**.

SCHEME 16.21

SCHEME 16.22

SCHEME 16.23

Intermediate **G** dissociates the aldehyde to afford an equilibrium mixture with the unsaturated dihydride **I**, an osmium counterpart of **A**. Thus when the reaction is carried out in the presence of a primary amine, the corresponding imine is formed. Because the addition of the O–H bond of the alcohol to **I** regenerates **E**, complex **9** catalyzes the selective formation of a variety of imines from alcohols and amines with liberation of H_2 , under an argon atmosphere (Scheme 16.24). The reactions include the formation of aliphatic imines, which are inherently more challenging due to their instability [66].

The $\text{xant}(\text{P}^i\text{Pr}_2)_2$ counterpart of **9**, the tetrahydride **14**, is an efficient catalyst precursor for the regio- and stereoselective head-to-head (*Z*)-dimerization of phenylacetylene and *tert*-butylacetylene. In toluene- d_8 at 110°C , the enynes (*Z*)- $\text{PhC}\equiv\text{CCH}=\text{CHPh}$ and (*Z*)- $\text{tBuC}\equiv\text{CCH}=\text{CHtBu}$ are formed in 94% and 90% yield with turnover

SCHEME 16.24

frequencies at 50% conversion ($\text{TOF}_{50\%}$) of 100 and 30 h^{-1} , respectively (Eq. 16.1).

Complex **14** is transformed into the bis(alkynyl) vinylidene derivatives $\text{Os}(\text{C}\equiv\text{CR})_2(\text{=C=CHR})\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ (R=Ph (**59**), ^tBu (**60**)) along with 2 equivalents of the corresponding olefin and 1 hydrogen molecule, under catalytic conditions before the first turnover. Once these species are generated, the migratory insertion of the vinylidene ligand into one of the osmium–alkynyl bonds could afford the butenynyl intermediates **J**. The displacement of the coordinated carbon–carbon triple bond of the butenynyl ligand by an alkyne molecule should lead to **K**, which could release the (*Z*)-enynone to give **L**. The coordination of a new alkyne to **L** should regenerate **59** and **60** (Scheme 16.25).

The dihydride-dihydrogen-ruthenium(II) complex **25** is a more efficient catalyst precursor than its osmium counterpart **14** for the regio- and stereoselective head-to-head (*Z*)-dimerization of phenylacetylene and *tert*-butylacetylene. At 80°C instead of 110°C, yields higher than 90% are obtained for the formation of the corresponding (*Z*)-enynes with $\text{TOF}_{50\%}$ values significantly higher of 215 and 92 h^{-1} . Complex **25** is also an efficient catalyst precursor for the reduction of ketones by hydrogen transfer from 2-propanol and for the α -alkylation of nitriles and ketones.

The hydrogen transfer reactions (Eq. 16.2) were performed under argon, in 2-propanol, at 80°C, and in the absence of any base. Under these conditions, acetophenone, propiophenone, and cyclohexanone were reduced to the corresponding

SCHEME 16.25

alcohols in 87–97% yield with $\text{TOF}_{50\%}$ values between 1011 and 1960 h^{-1} .

The alkylations of phenylacetonitrile with benzyl alcohol and 1-octanol (Eq. 16.3) and of acetophenone with benzyl alcohol (Eq. 16.4) were performed in toluene at 110°C and in the presence of KOH. Under these conditions, the alkylation products were obtained in 70–80% yield with $\text{TOF}_{50\%}$ values between 1.4 and 18 h^{-1} .

16.9. CONCLUSION

The development of the chemistry of transition metals, in particular for those of the platinum groups, is in many cases caused by the existence of efficient routes of entry to their complexes. In the previous sections, we have shown two pathways to POP-osmium complexes—mainly polyhydride derivatives—which are allowing us to discover interesting properties of some of them as their ability to participate in processes of hydrogen generation, to activate C–H bonds, to stabilize the coordination of σ -bonds, or to promote organic synthetic reactions, including hydrogen borrowing processes, and the formation of C–C bonds.

The influence of coordinating parameters of the P,O,P-ligands, such as the separation between the phosphorous atoms or the natural bite angle, on the selectivity and activity of precursors containing this class of groups in some catalytic processes has been previously discussed [79,80]. In this context, it should be mentioned that the polycyclic backbones of the diphosphines have not any significant influence on the structural parameters of the complexes because the metal produces a levelling effect on the relevant coordination features of the ligand. However, the linker between the PR_2 groups determines the flexibility of the diphosphines, which allows them to adapt their coordination mode to the requirement of the sequential processes, changing from $\kappa^3\text{-mer}$ to $\kappa^3\text{-fac}$ and $\kappa^2\text{-P,P-bidentate}$ according to the electronic and steric requirements of the involved intermediates. Thus for instance, we have mentioned that in polyhydrides, the nonclassical interactions are favored by the tridentate coordination, mainly the *mer* disposition, whereas classical polyhydrides are usually found when the diphosphine is bidentate.

The differences between osmium and ruthenium have become also evident in the previous sections. The $\text{Ru}\{\text{xant}(\text{P}^i\text{Pr}_2)_2\}$ metal fragment avoids the oxidation state four. As a result, the osmium d^4 -polyhydrides are d^6 -dihydrogens in the ruthenium chemistry, which require different synthetic procedures from those of osmium for their preparation.

REFERENCES

- [1] A.J. Pontiggia, A.B. Chaplin, A.S. Weller, *J. Organomet. Chem.* 696 (2011) 2870–2876.
- [2] E. Dallanegra, A.B. Chaplin, A.S. Weller, *Organometallics* 31 (2012) 2720–2728.
- [3] M.A. Esteruelas, P. Nolis, M. Oliván, E. Oñate, A. Vallribera, A. Vélez, *Inorg. Chem.* 55 (2016) 7176–7181.
- [4] R.J. Pawley, G.L. Moxham, R. Dallanegra, A.B. Chaplin, S.K. Brayshaw, A.S. Weller, et al., *Organometallics* 29 (2010) 1717–1728.
- [5] P. Ren, S.D. Pike, I. Pernik, A.S. Weller, M.C. Willis, *Organometallics* 34 (2015) 711–723.
- [6] H.C. Johnson, E.M. Leita, G.R. Whittell, I. Manners, G.C. Lloyd-Jones, A.S. Weller, *J. Am. Chem. Soc.* 136 (2014) 9078–9093.
- [7] J. Choi, A.H.R. MacArthur, M. Brookhart, A.S. Goldman, *Chem. Rev.* 111 (2011) 1761–1779.
- [8] C. Gunanathan, D. Milstein, *Chem. Rev.* 114 (2014) 12024–12087.
- [9] M.A. Esteruelas, A.M. López, M. Oliván, *Chem. Rev.* 116 (2016) 8770–8847.
- [10] M.A. Esteruelas, L.A. Oro, *Adv. Organomet. Chem.* 47 (2001) 1–59.
- [11] M.A. Esteruelas, A.M. López, *Organometallics* 24 (2005) 3584–3613.
- [12] M.A. Esteruelas, A.M. López, M. Oliván, *Coord. Chem. Rev.* 251 (2007) 795–840.
- [13] T. Bolaño, M.A. Esteruelas, E. Oñate, *J. Organomet. Chem.* 696 (2011) 3911–3923.
- [14] A. Varela-Fernández, C. García-Yebra, J.A. Varela, M.A. Esteruelas, C. Saá, *Angew. Chem. Int. Ed.* 49 (2010) 4278–4281.
- [15] M.L. Buil, V. Cadierno, M.A. Esteruelas, J. Gimeno, J. Herrero, S. Izquierdo, et al., *Organometallics* 31 (2012) 6861–6867.
- [16] M.L. Buil, M.A. Esteruelas, J. Herrero, S. Izquierdo, I.M. Pastor, M. Yus, *ACS Catal.* 3 (2013) 2072–2075.
- [17] M.A. Esteruelas, I. Fernández, A.M. López, M. Mora, E. Oñate, *Organometallics* 33 (2014) 1104–1107.
- [18] M.A. Esteruelas, A.M. López, M. Mora, E. Oñate, *ACS Catal.* 5 (2015) 187–191.
- [19] T. Bolaño, M.A. Esteruelas, M.P. Gay, E. Oñate, I.M. Pastor, M. Yus, *Organometallics* 34 (2015) 3902–3908.
- [20] A. Álvarez-Pérez, C. González-Rodríguez, C. García-Yebra, J.A. Varela, E. Oñate, M.A. Esteruelas, et al., *Angew. Chem. Int. Ed.* 54 (2015) 13357–13361.
- [21] D. Spasyuk, C. Vicent, D.G. Gusev, *J. Am. Chem. Soc.* 137 (2015) 3743–3746.
- [22] M. Batuecas, R. Castro-Rodrigo, M.A. Esteruelas, C. García-Yebra, A.M. López, E. Oñate, *Angew. Chem. Int. Ed.* 55 (2016) 13749–13753.
- [23] S.A. Morris, D.G. Gusev, *Angew. Chem. Int. Ed.* 56 (2017) 6228–6231.
- [24] D.G. Gusev, F.M. Dolgushin, M.Y. Antipin, *Organometallics* 20 (2001) 1001–1007.
- [25] D.G. Gusev, A.J. Lough, *Organometallics* 21 (2002) 2601–2603.
- [26] D.G. Gusev, T. Maxwell, F.M. Dolgushin, M. Lyssenko, A.J. Lough, *Organometallics* 21 (2002) 1095–1100.
- [27] D.G. Gusev, F.-G. Fontaine, A.J. Lough, D. Zargarian, *Angew. Chem. Int. Ed.* 42 (2003) 216–219.
- [28] V.F. Kuznetsov, D.G. Gusev, *Organometallics* 26 (2007) 5661–5666.
- [29] T.B. Wen, Y.K. Cheung, J. Yao, W.-T. Wong, Z.Y. Zhou, G. Jia, *Organometallics* 19 (2000) 3803–3809.
- [30] T.B. Wen, Z.Y. Zhou, G. Jia, *Organometallics* 22 (2003) 4947–4951.
- [31] T.B. Wen, Z.Y. Zhou, G. Jia, *Angew. Chem. Int. Ed.* 45 (2006) 5842–5846.
- [32] R.M. Gauvin, H. Rozenberg, L.J.W. Shimon, D. Milstein, *Organometallics* 20 (2001) 1719–1724.
- [33] R.M. Gauvin, H. Rozenberg, L.J.W. Shimon, Y. Ben-David, D. Milstein, *Chem. Eur. J.* 13 (2007) 1382–1393.
- [34] J.-H. Lee, M. Pink, K.G. Caulton, *Organometallics* 25 (2006) 802–804.
- [35] J.-H. Lee, M. Pink, J. Tomaszewski, H. Fan, K.G. Caulton, *J. Am. Chem. Soc.* 129 (2007) 8706–8707.
- [36] N. Tsvetkov, M. Pink, H. Fan, J.-H. Lee, K.G. Caulton, *Eur. J. Inorg. Chem.* (2010) 4790–4800.
- [37] N. Tsvetkov, H. Fan, K.G. Caulton, *Dalton Trans.* 40 (2011) 1105–1110.
- [38] M. Bertoli, A. Choualeb, A.J. Lough, B. Moore, D. Spasyuk, D.G. Gusev, *Organometallics* 30 (2011) 3479–3482.
- [39] D. Spasyuk, S. Smith, D.G. Gusev, *Angew. Chem. Int. Ed.* 51 (2012) 2772–2775.
- [40] A. Acosta-Ramirez, M. Bertoli, D.G. Gusev, M. Schlaf, *Green Chem.* 14 (2012) 1178–1188.
- [41] D. Spasyuk, D.G. Gusev, *Organometallics* 31 (2012) 5239–5242.
- [42] S.H. Liu, S.T. Lo, T.B. Wen, Z.Y. Zhou, C.P. Lau, G. Jia, *Organometallics* 20 (2001) 667–672.
- [43] L.-H. Chung, S.-C. Chan, W.-C. Lee, C.-Y. Wong, *Inorg. Chem.* 51 (2012) 8693–8703.
- [44] R.G. Alabau, B. Eguillor, J. Esler, M.A. Esteruelas, M. Oliván, E. Oñate, et al., *Organometallics* 33 (2014) 5582–5596.
- [45] B. Eguillor, M.A. Esteruelas, V. Lezáun, M. Oliván, E. Oñate, J.-Y. Tsai, et al., *Chem. Eur. J.* 22 (2016) 9106–9110.
- [46] R.G. Alabau, M.A. Esteruelas, M. Oliván, E. Oñate, A.U. Palacios, J.-Y. Tsai, et al., *Organometallics* 35 (2016) 3981–3995.
- [47] L. Casarrubios, M.A. Esteruelas, C. Larramona, J.G. Muntaner, E. Oñate, M.A. Sierra, *Inorg. Chem.* 54 (2015) 10998–11006.
- [48] C.-Y. Wong, L.-M. Lai, P.-K. Pat, L.-H. Chung, *Organometallics* 29 (2010) 2533–2539.
- [49] B. Eguillor, M.A. Esteruelas, V. Lezáun, M. Oliván, E. Oñate, *Chem. Eur. J.* 23 (2017) 1526–1530.
- [50] W. Baratta, L. Fanfoni, S. Magnolia, K. Siega, P. Rigo, *Eur. J. Inorg. Chem.* (2010) 1419–1423.
- [51] G. Bossi, E. Putignano, P. Rigo, W. Baratta, *Dalton Trans.* 40 (2011) 8986–8995.
- [52] R.G. Alabau, M.A. Esteruelas, M. Oliván, E. Oñate, *Organometallics* 36 (2017) 1848–1859.
- [53] R. Castarlenas, M.A. Esteruelas, E. Oñate, *Organometallics* 26 (2007) 3082–3084.
- [54] J.-P. Sauvage, J.P. Collin, J.C. Chambron, S. Guillerez, C. Coudret, V. Balzani, et al., *Chem. Rev.* 94 (1994) 993–1019.
- [55] J.-L. Chen, Y. Chi, K. Chen, Y.-M. Cheng, M.-W. Chung, Y.-C. Yu, et al., *Inorg. Chem.* 49 (2010) 823–832.

- [56] A.L. Müller, H. Wadepohl, L.H. Gade, *Organometallics* 34 (2015) 2810–2818.
- [57] E. Vega, E. Lastra, M.P. Gamasa, *Inorg. Chem.* 52 (2013) 6193–6198.
- [58] C. Bhaumik, D. Saha, S. Das, S. Baitalik, *Inorg. Chem.* 50 (2011) 12586–12600.
- [59] J.-Y. Shao, Y.-W. Zhong, *Inorg. Chem.* 52 (2013) 6464–6472.
- [60] G. Asensio, A.B. Cuenca, M.A. Esteruelas, M. Medio-Simón, M. Oliván, M. Valencia, *Inorg. Chem.* 49 (2010) 8665–8667.
- [61] M.A. Esteruelas, M. Oliván, A. Vélez, *Inorg. Chem.* 52 (2013) 5339–5349.
- [62] M.A. Esteruelas, M. Oliván, A. Vélez, *Inorg. Chem.* 52 (2013) 12108–12119.
- [63] M.A. Esteruelas, M. Oliván, A. Vélez, *Organometallics* 34 (2015) 1911–1924.
- [64] M.A. Esteruelas, M. Oliván, A. Vélez, *J. Am. Chem. Soc.* 137 (2015) 12321–12329.
- [65] S.G. Curto, M.A. Esteruelas, M. Oliván, E. Oñate, A. Vélez, *Organometallics* 36 (2017) 114–128.
- [66] M.A. Esteruelas, N. Honczek, M. Oliván, E. Oñate, M. Valencia, *Organometallics* 30 (2011) 2468–2471.
- [67] J. Alós, T. Bolaño, M.A. Esteruelas, M. Oliván, E. Oñate, M. Valencia, *Inorg. Chem.* 52 (2013) 6199–6213.
- [68] J. Alós, T. Bolaño, M.A. Esteruelas, M. Oliván, E. Oñate, M. Valencia, *Inorg. Chem.* 53 (2014) 1195–1209.
- [69] J. Alós, M.A. Esteruelas, M. Oliván, E. Oñate, P. Puylaert, *Organometallics* 34 (2015) 4908–4921.
- [70] M.A. Esteruelas, C. García-Yebra, J. Martín, E. Oñate, *Inorg. Chem.* 56 (2017) 676–683.
- [71] M.A. Esteruelas, I. Fernández, C. García-Yebra, J. Martín, E. Oñate, *Organometallics* 36 (2017) 2298–2307.
- [72] V.C.Y. Kong, F.R. Foulkes, D.W. Kirk, J.T. Hinatsu, *Int. J. Hydrogen Energy* 24 (1999) 665–675.
- [73] V.C.Y. Kong, D.W. Kirk, F.R. Foulkes, J.T. Hinatsu, *Int. J. Hydrogen Energy* 28 (2003) 205–214.
- [74] I. Dincer, *Int. J. Hydrogen Energy* 37 (2012) 1954–1971.
- [75] I. Dincer, C. Acar, *Int. J. Hydrogen Energy* 40 (2015) 11094–11111.
- [76] B. Eguillor, M.A. Esteruelas, M. Oliván, E. Oñate, *Organometallics* 24 (2005) 1428–1438.
- [77] M.L. Buil, M.A. Esteruelas, K. Garcés, M. Oliván, E. Oñate, *Organometallics* 27 (2008) 4680–4690.
- [78] P. Barrio, M.A. Esteruelas, E. Oñate, *Organometallics* 23 (2004) 1340–1348.
- [79] M. Kranenburg, Y.E.M. van der Burgt, P.C.J. Kamer, P.W.N.M. van Leeuwen, K. Goubitz, J. Fraanje, *Organometallics* 14 (1995) 3081–3089.
- [80] R.P.J. Bronger, P.C.J. Kamer, P.W.N.M. van Leeuwen, *Organometallics* 22 (2003) 5358–5369.