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Influence of the Diphosphine Coordinated to Molybdenum and Tungsten Triangular M_3S_4 Cluster Hydrides in the Catalytic Hydrodefluorination of Pentafluoropyridine

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Abstract. Hydrido molybdenum and tungsten (IV) cluster cations of formula $[M_3S_4H_3(dppe)_3]^+$ (dppe = 1,2-(bis)dimethylphosphinoethane), [**Mo-1**]$^+$ (M=Mo) and [**W-1**]$^+$ (M=W), have been isolated by reacting their halide precursors with borohydride. Synthetic procedures have been optimized by appropriate choice of the solvent. Furthermore, $[M_3S_4F_3(dppe)_3]^+$ fluorido cluster complexes, [**Mo-2**]$^+$ (M=Mo) and [**W-2**]$^+$ (M=W) have been prepared through halogen substitution reactions using an excess of cesium fluoride. The structures of [**Mo-1**]$^+$ and [**Mo-2**]$^+$ have been determined by single crystal X-ray diffraction experiments. These [**M-1**]$^+$ hydrido and [**M-2**]$^+$ fluorido clusters have been used as catalysts and precatalysts, respectively, in the catalytic hydrodefluorination (HDF) of pentafluoropyridine using $HSiMe_2Ph$ as hydrogen source. The reaction proceeds under microwave and reflux conditions to selectively afford 2,3,5,6-tetrafluoropyridine. The [**W-1**]$^+$ hydrido cluster is the most efficient catalyst with turnover numbers of 124, while the [**Mo-1**]$^+$ hydrido cluster reacts faster. Fluorido [**Mo-2**]$^+$ and [**W-2**]$^+$ complexes provide lower yields and turnover numbers. In general, the molybdenum and tungsten [**M-1**]$^+$ and [**M-2**]$^+$ diphosphino complexes are more efficient than their dmpe (1,2-(bis)dimethylphosphinoethano) analogues and activate pentafluoropyridine under softer conditions.

Introduction

The increasing demand of fluorine-containing pharmaceutical drugs and agrochemicals has inspired the development of several synthetic strategies for derivatization of readily available fluorinated compounds [1-3]. Selective removal of fluorine atoms provides high value building blocks for the preparation of organofluorine fine chemicals [4]. In this sense, the simplest and more promising transformation consists in the replacement of C-F bonds by C-H bonds, commonly known as hydrodefluorination (HDF), which has been extensively studied in presence of transition metal complexes and a hydrogen source [5]. One of the most common reaction types described for intermolecular HDF involves the hydrogen/fluorine exchange between a metal-hydrido complex and the fluorinated organic substrate, as represented in equation 1, to form the hydrogen substituted organic product and the metal-fluorine complex.

$$[M]\text{-}H + R\text{-}F \longrightarrow [M]\text{-}F + R\text{-}H \qquad (1)$$

The high affinity of early transition metals towards fluorine provides a thermodynamically feasible route to the HDF of organic R-F substrates. In this context, lanthanides and group 4 hydrido complexes have been extensively studied for stoichiometric and catalytic HDF of aromatic, vinylic and aliphatic fluorinated substrates, although the number of catalytic *versus* stoichiometric transformations is still small [6-13]. Development of a catalytic process implies the challenging conversion of a stable fluorido complex into the corresponding hydrido derivative. For this purpose, silanes and aluminium hydrides have been successfully used as regenerating hydrogen sources. Rosenthal and coworkers reported that zirconocene dihydrides catalyse pentafluoropyridine HDF at room temperature in the presence of diisobuthylaluminum hydride [10]. The reaction occurs with high efficiency (turnover numbers of 67) and high selectivity at the four-position in which the ligands play a pivotal role in the reaction yield. Kühnel and Lentz reported on the catalytic hydrodefluorination of hexafluoropropene using titanocene dihalides as precatalysts and a silane as the hydrogen source [14]. These reactions are assumed to proceed by nucleophilic attack of the hydrido ligand to the electrophilic

organic substrate via alkene insertion/β-fluoride elimination or σ-bond metathesis mechanism through a four centered M-H/C-F transition state [15].

Several more electron-rich transition metal centers also catalyse HDF of fluorinated organic substrates in the presence of silanes in agreement with their lower metal-fluorine bond energies. Holland and coworkers have shown that β-dikeminato iron (II) fluoride complexes catalyse HDF of perfluoroaromatics and perflluoroalkenes in the presence of silanes [16]. In particular, HDF of pentafluoropyridine selectively affords the *para*-substituted product as the only HDF product, although high catalyst loadings are needed. Whittlesey and coworkers employed a ruthenium (II) N-heterocyclic carbene hydrido complex and a source of silanes for the catalytic HDF of pentafluorobenzene that shows a unique *orto*-regioselectivity and high efficiency [17]. This selectivity is attributed to a stepwise reaction mechanism that starts by decoordination of a phosphine followed by η^2-coordination of a non-perfluorinated arene double bond [18,19]. Replacement of the triphenylphosphine ligand by bidentated phosphines results in inactive catalysts [20]. Very likely, the chelating effect of the diphosphine prevents phosphine decoordination required for π-arene coordination. More recently, rhodium (I) hydrido binuclear complexes have been used for HDF of fluorinated organic substrates in the presence of triethylsilane as hydrogen source [21]. Catalytic reaction with pentafluoropyridine occurs at 50 ºC and affords a mixture of HDF products with predominant H/F substitution at the *para* position. Experimental and theorerical studies give evidence of two different C-F activation pathways that involve mono- and bimetallic hydrido complexes as active species.

In 2011 our group reported the first example of HDF of fluorinated substrates catalyzed by molybdenum and tungsten hydrido clusters. Regioselective HDF of pentafluoropyridine at the *para* position was achieved in moderate to high yields under microwave radiation using trinuclear $[M_3S_4H_3(dmpe)_3]^+$ (M = Mo or W, dmpe= 1,2-(bis)dimethylphosphinoethane complexes as catalysts, in the presence of silanes as regenerating hydrogen source [22]. When catalytic hydrodefluorination was started with the $[M_3S_4F_3(dmpe)_3]^+$ fluoride complexes, the reaction yields decrease for both molybdenum and tungsten, probably due to the inefficient production of hydrides by reaction of the

fluoride clusters with silanes. A higher activity was observed for the tungsten hydride cluster complexes with turnover numbers close to 100, while reactions catalysed by molybdenum cluster analogues are faster. DFT studies give support to a three steps reaction mechanism starting by partial decoordination of the diphosphine ligand to generate an empty position in the metal coordination sphere. In a second step, the unsaturated intermediate reacts with one equivalent of pentafluoropyridine and the C-F bond is activated-through a M-H/C-F four center σ-bond metathesis transition state. Next, the dangling diphosphine coordinates the metal center to afford the substituted product and the corresponding fluorido trimetallic cluster. Regeneration of the $[M_3S_4H_3(dmpe)_3]^+$ hydrido catalyst by silanes also occurs through an analogous three step mechanism via a four centered M-F/Si-H intermediate. As previously stated, phosphine decoordination in the ruthenium N-heterocyclic carbene complexes promotes HDF of fluoroarenes, and the nature of the diphosphine plays a crucial role in the catalytic activity of these systems [17,18]. Motivated by these findings we decided to investigate the role of the diphosphine basicity on the catalytic hydrodefluorination of pentafluoropyridine mediated by trimetallic molybdenum and tungsten $[M_3S_4X_3(diphosphine)_3]^+$ hydrides (X=H) or fluorides (X=F) replacing the dmpe ligand by the less basic dppe (1,2-(bis)diphenylphosphinoethane)diphosphine). Assuming that a similar HDF reaction mechanism operates, one would expect that diphosphine basicity influences the energetics related to the partial decoordination and further coordination of the diphosphine.

In this work we present the synthesis and crystal structure of a new molybdenum $[Mo_3S_4H_3(dppe)_3]^+$ hydrido cluster as well as an improved procedure for the isolation of the analogous hydrido tungsten cluster. The choice of the solvent on the reaction outcome is discussed in detail. These hydrido clusters have been employed as catalysts in the HDF of pentafluoropyridine under microwave and thermal activation. We also report on the preparation and structure of two new $[M_3S_4F_3(dppe)_3]^+$ (M = Mo or W) fluorido clusters and their activity as precatalysts in HDF of pentafluoropyridine in the presence of silanes, in order to validate the catalytic cycle proposed for the analogous dmpe trimetallic complexes and to compare their catalytic activity.

Experimental Section

General Remarks. Electrospray mass spectra were recorded with a Quattro LC (quadrupole-hexapole-quadrupole) mass spectrometer with an orthogonal Z-spray electrospray interface (Micromass, Manchester, UK). The cone voltage was set at 20 V unless otherwise stated using CH_3CN as the mobile phase solvent. Nitrogen was employed as drying and nebulising gas[23]. ^1H, ^{19}F and ^{31}P NMR spectra were recorded on a Varian Innova 300 MHz using CD_3CN as solvent. MW promoted reactions were carried out in a Discover Labmate (CEM Corp.) equipment. Solvents were dried and degassed by standard methods before use. Compounds $[Mo_3S_4(dppe)_3Cl_3]PF_6$ and $[W_3S_4Br_3(dppe)_3]PF_6$ were prepared by following literature procedures [23].

Preparation of $[Mo_3S_4H_3(dppe)_3]BPh_4$, [Mo-1]$BPh_4$. To a green solution of $[Mo_3S_4Cl_3(dppe)_3]PF_6$ (90.4 mg, 0.0485 mmol) in methanol (15 mL) was added an excess of $NaBH_4$ (91.78 mg, 2.4261 mmol) under nitrogen. The solution colour turned brown. After the mixture was stirred 2 hours, an excess of $NaBPh_4$ was added to the brown solution, resulting in precipitation of a brown solid. This solid was filtered and washed with methanol and ether, to afford [**Mo-1**]BPh_4 (70.40 mg, yield 75%).

$^{31}P\{^1H\}$ NMR (CD_3CN, 121 MHz) δ= 33.10 (d, 3P, $^2J(^{31}P,^{31}P)$=8.5 Hz , 59.29 (d,3P,$^2J(^{31}P,^{31}P)$=7.3 Hz). ^1H NMR (CD_3CN, 282 MHz) δ= -1.05 (dd,3H,$^2J(^1H,^{31}P)$=37.0 Hz, $^2J(^1H,^{31}P)$=75.0 Hz). ESI-MS (CH_3CN, 20 V) m/z: 1614 [M+].

Preparation of $[Mo_3S_4F_3(dppe)_3]X$, [Mo-2]X, (X = PF_6^-, BPh_4^-). This compound was prepared from $[Mo_3S_4Cl_3(dppe)_3]PF_6$ (97.4 mg, 0.0523 mmol) in dry acetonitrile, following the same procedure described for the synthesis of [**W-2**]PF_6, but using a higher excess of CsF (6.5 eq), and heating at 60 ºC during 24 h. The product was purified following the procedure described for [**W-2**]PF_6 and a green solid (61.6 mg, yield 65 %) was obtained, identified as [**Mo-2**]PF_6. Anion exchange, PF_6^- to BPh_4^-, was carried out as described for [**W-2**]PF_6, to afford a green solid characterized as [**Mo-2**]BPh_4.

$^{31}P\{^1H\}$ NMR (CD_3CN, 121 MHz) δ= -143.3 (septet, 1P, $^1J(^{31}P,^{19}F)$=706.4 Hz), 22.2 (d, 3P, $^2J(^{31}P,^{19}F)$=103.3 Hz , 30.4 (d,3P,$^2J(^{31}P,^{19}F)$=40.1 Hz). ^{19}F NMR (CD_3CN, 282 MHz) δ= -177.5 (dd,3F,$^2J(^{19}F,^{31}P)$=40.9 Hz ,$^2J(^{19}F,^{31}P)$=103.1 Hz), -72.9 (d,6F,$^1J(^{19}F,^{31}P)$= 700.3 Hz). ESI-MS (CH_3CN, 20 V) m/z: 1668 [M+].

Preparation of $[W_3S_4H_3(dppe)_3]BPh_4$, [W-1]BPh_4. Compound [**W-1**]BPh_4 was prepared improving literature procedures [23].To a blue solution of $[W_3S_4Br_3(dppe)_3]BPh_4$ (99.1 mg, 0.0407 mmol) in dry THF (20 mL) was added a 9-fold excess of $NaBH_4$ under nitrogen. After 2 hours, the mixture was taken to dryness, extracted with CH_2Cl_2 (30 mL) and washed with water (3 x 15 mL). The resulting organic phase was dried over anhydrous $MgSO_4$, filtered and dried under vacuum to afford a dark pink solid identified as $[W_3S_4H_3(dppe)_3]BPh_4$ (yield: 86.8 mg, 97%).

Preparation of $[W_3S_4F_3(dppe)_3]X$, [W-2]X, (X = PF_6^-, BPh_4^-). To a blue solution of $[W_3S_4Br_3(dppe)_3]PF_6$ (95.7 mg, 0.0423 mmol) in dry CH_3CN (20 mL) was added a 4-fold excess of CsF (28.94 mg, 0.191 mmol) under a nitrogen atmosphere. The mixture was stirred under reflux conditions. After 24 hours of reaction, a colour change from blue to violet is observed. The mixture was filtered, and the filtrated was taken to dryness under vacuum and the solid was dissolved in dichloromethane. Then, the solution was filtered in order to eliminate the inorganic salts and the solvent was removed under vacuum. The resulting violet solid was washed with 100 mL of a toluene/acetone mixture (98:2) to afford 52.7 mg of [**W-2**]PF_6 (yield 60 %). Anion exchange, PF_6^- to BPh_4^-, was achieved by the addition of an excess of $NaBPh_4$ to a methanol solution of $[W_3S_4F_3(dppe)_3]PF_6$, resulting in precipitation of [**W-2**]BPh_4.

$^{31}P\{^1H\}$ NMR (CD3CN, 121 MHz) δ= -143.1 (septet, 1P, $^1J(^{31}P,^{19}F)$=706.5 Hz), 7.7 (d, 3P, $^2J(^{31}P,^{19}F)$=114.2 Hz), 6.7 (d,3P,$^2J(^{31}P,^{19}F)$=51.0 Hz. ^{19}F NMR (CD_3CN, 282 MHz) δ= -182.4 (dd,3F,$^2J(^{19}F,^{31}P)$=50.8 Hz ,$^2J(^{19}F,^{31}P)$=112.9 Hz), -75.5 (d,6F,$^1J(^{19}F,^{31}P)$= 711.6 Hz). ESI-MS (CH_3CN, 20 V) m/z: 1931 [M+].

X-ray data collection and structure refinement. Diffraction data for $[Mo_3S_4F_3(dppe)_3]PF_6$ and $[Mo_3S_4H_3(dppe)_3]PF_6{\cdot}H_2O$ were collected on a Agilent Supernova diffractometer equipped with an Atlas CCD detector using Mo Kα radiation (λ = 0.71073 Å). Absorption corrections based on the multiscan method were applied [24,25]. Structures were solved using direct methods in SHELX-2013 and refined by the full matrix method based on F^2 using the OLEX software package [26,27]. Suitable crystals for X-Ray studies of $[Mo_3S_4F_3(dppe)_3]PF_6{\cdot}H_2O$ were grown by slow diffusion of toluene into

a sample solution in CH_2Cl_2. Crystal data for $[Mo_3S_4F_3(dppe)_3]PF_6 \cdot H_2O$: $Mo_3S_4F_9C_{78}H_{74}P_7O$, M = 1831.22, monoclinic, space group $P2_1/c$, a = 13.6191 (4) Å, b = 21.2898 (6) Å, c = 26.7358 (6) Å, α = 90.00 º, β = 93.352 (3) º, γ = 90.00 º, V = 7738.7 (4) $Å^3$, T = 149.9 (1) K, Z = 4, μ = 0.798 mm^{-1}. Reflections (collected/unique) = 39617/11417 (R_{int} = 0.0310). Final refinement converged with R_1 = 0.0629 and wR_2 = 0.1162 for all reflections, GOF = 1.062, max/min residual electron density 3.04/-1.32 e· $Å^{-3}$. The three top peak in the last Fourier map had intensities of 3.04, 3.00 and 2.43 e· $Å^{-3}$, and they were too close to the heavy atom (*ca.* 0.92 Å) to be included in the model. Anisotropic displacement parameters were refined for all non-H atoms.

Suitable crystals of $[Mo_3S_4H_3(dppe)_3]PF_6$ were grown by slow diffusion of hexane into a sample solution in CH_2Cl_2. Crystal data for $[Mo_3S_4H_3(dppe)_3]PF_6$: $Mo_3S_4P_7C_{78}H_{72}F_6$, M = 1756.20, monoclinic, non-centrosymmetric space group Cc, a = 29.4364 (12) Å, b = 13.9514 (3) Å, c = 22.7696 (9) Å, α = 90.00 º, β = 127.208 (6) º, γ = 90.00 º, V = 7447.5 (5) $Å^3$, T = 150.0 (1) K, Z = 4, μ = 0.819 mm^{-1}. Reflections (collected/unique) = 43623/17371 (R_{int} = 0.0353). Final refinement converged with R_1 = 0.0449 and R_2 = 0.0771 for all reflections, GOF = 1.073, max/min residual electron density 0.65/-0.45 e· $Å^{-3}$. Flack parameter: -0.055(12). Anisotropic displacement parameters were refined for all non-H atoms.

Catalytic HDF of pentafluoropyridine. Catalytic studies were carried out under reflux conditions using a round bottom flask, and under microwave radiation using a capped high-pressure reactor. The reaction vessels were charged with pentafluoropyridine (0.38 mmol, 40 μL), fluorobenzene as internal reference (0.38 mmol, 36 μL), catalyst (0.7 % mol), dimethylphenylsilane (1.9 mmol, 296 μL) and 1 mL of acetonitrile. The microwave power was dynamically adjusted to achieve the defined temperature profile. The solution was heated to 115 ºC under MW radiation for the appropriate time. The maximum power was fixed at 70 W in order to avoid cluster decomposition. During the reaction monitoring, yields and conversions were determined by ^{19}F-NMR. The confirmation of the nature of 2,3,5,6-tetrafluoropyridine and $FSiMe_2Ph$ was performed by comparison with literature data.

Results and Discussion

Synthesis and Structure of hydrido and fluorido M_3S_4 complexes. The synthesis and isolation of hydrido clusters of formula $[M_3S_4H_3(dppe)_3]^+$ with M = Mo ([**Mo-1**]$^+$) and W ([**W-1**]$^+$) has been achieved by adapting the procedures published in the literature for other analogous diphosphino complexes, that is by reacting the corresponding halide precursor with borohydride in methanol or THF. The first synthesis of a $[W_3S_4H_3(diphosphino)_3]^+$ compound was reported in 1989 by Cotton *et al.* [28] and, twenty years later, our group was able to isolate an equivalent hydrido molybdenum cluster of formula $[Mo_3S_4H_3(dmpe)_3](BPh_4)$ using dry THF as solvent [29]. In general, molybdenum hydrides are more unstable than their tungsten congeners [30], and for the synthesis and isolation of this last molybdenum complex, the use of THF seemed to be crucial. Incidentally, the use of THF as solvent for the synthesis of $[Mo_3S_4H_3(dppe)_3]^+$ hampered the isolation of the [**Mo-1**]$^+$ salt as a pure product. Finally, reaction of $[Mo_3S_4Cl_3(dppe)_3]PF_6$ with a 50-fold excess of $NaBH_4$ in methanol, followed by addition of $NaBPh_4$, results in the precipitation of the desired [**Mo-1**]BPh_4 salt in 75% yield. In the case of tungsten, the procedure previously reported for the preparation of [**W-1**]$^+$ also uses methanol as reaction solvent [23]. In this work, we prove that substitution of methanol by THF increases the reaction yield from 46 % to 97 %.

The molybdenum and tungsten hydrido complexes have been used as catalysts for the HDF of pentafluoropyridine. Our previous studies on HDF using $[M_3S_4H_3(dmpe)_3]^+$ (M = Mo, W) as catalysts, demonstrate that catalytically active hydrido species can be generated by treating the corresponding molybdenum and tungsten fluorido complexes with silanes [22]. In order to corroborate that silanes were also appropriated hydride sources able to convert the $[M_3S_4F_3(dppe)_3]^+$, [**Mo-2**]$^+$ and [**W-2**]$^+$ fluorides, into the corresponding [**Mo-1**]$^+$ and [**W-1**]$^+$ hydrides, synthetic procedures towards the isolation of these fluorides have been developed.

Fluoride clusters are uncommon compared with their chloride or bromide analogues, although compounds of formula $[M_3S_4F_3(dmpe)_3]^+$ can be prepared by reacting their hydride precursors with fluoride-containing anions in the presence of acids. Quantitative transformation of $[M_3S_4H_3(dmpe)_3]^+$ to the fluoride-substituted product is achieved by reaction with aqueous solutions of HPF_6 in

acetonitrile/water mixtures [22]. However, in the case of dppe compounds, this transformation is not feasible, due to the decomposition of the cluster hydrides in the presence of such acid. Finally, complexes of formula $[M_3S_4F_3(dppe)_3]^+$ were prepared by reacting $[M_3S_4X_3(dppe)_3]^+$ (X = Cl, Br) precursors with an excess of a fluorinated salt such as CsF, according to equation 2. These fluoride clusters were obtained after heating the reaction mixture due to the lack of reactivity at room temperature.

$$\underset{\textbf{[Mo-1]}^+}{[M_3S_4X_3(dppe)_3]^+} \xrightarrow[CH_3CN,\ \Delta]{CsF\ (excess)} \underset{\textbf{[Mo-2]}^+}{[M_3S_4F_3(dppe)_3]^+} \qquad (2)$$

The structures of [**Mo-1**]PF_6 and [**Mo-2**]$PF_6 \cdot H_2O$ have been determined by single crystal X-ray diffraction. ORTEP drawings of the cationic species are presented in figure 1. In both complexes, the diphosphine is coordinated in a specific position, with one phosphorus atom *trans* to the capping sulphur and the other *trans* to the bridging sulphur. This situation results in cubane-type sulphido clusters with backbone chirality, although in this case, both compounds are synthesized as racemic mixtures. The third outer position is occupied by a hydrogen atom in [**Mo-1**]PF_6, seen as an empty site by x-ray diffraction, or by a fluorine atom in [**Mo-2**]$PF_6 \cdot H_2O$. The existence of three hydride ligands in [**Mo-1**]PF_6 is supported by ^{1}H-NMR spectroscopy, where we observe a double of doublets centered at -1.05 ppm, due to the coupling with two different phosphorus atoms bonded to the same metal. The fluorido cluster [**Mo-2**]$PF_6 \cdot H_2O$ crystallizes in a centrosymmetric $P2_1/c$ space group. Incidentally, the hydrido cluster $[Mo_3S_4H_3(dppe)_3]PF_6$ does it in a noncentrosymmetric Cc space group from a racemic mixture in dichloromethane. The preferential crystallization of one of the enantiomers from racemic mixtures has been previously described for the closely related heterobimetallic cubane-type $Mo_3NiS_4(dmpe)_3Cl_4$ neutral compound [31]. A list of relevant bond distances and angles is given in Table 1.

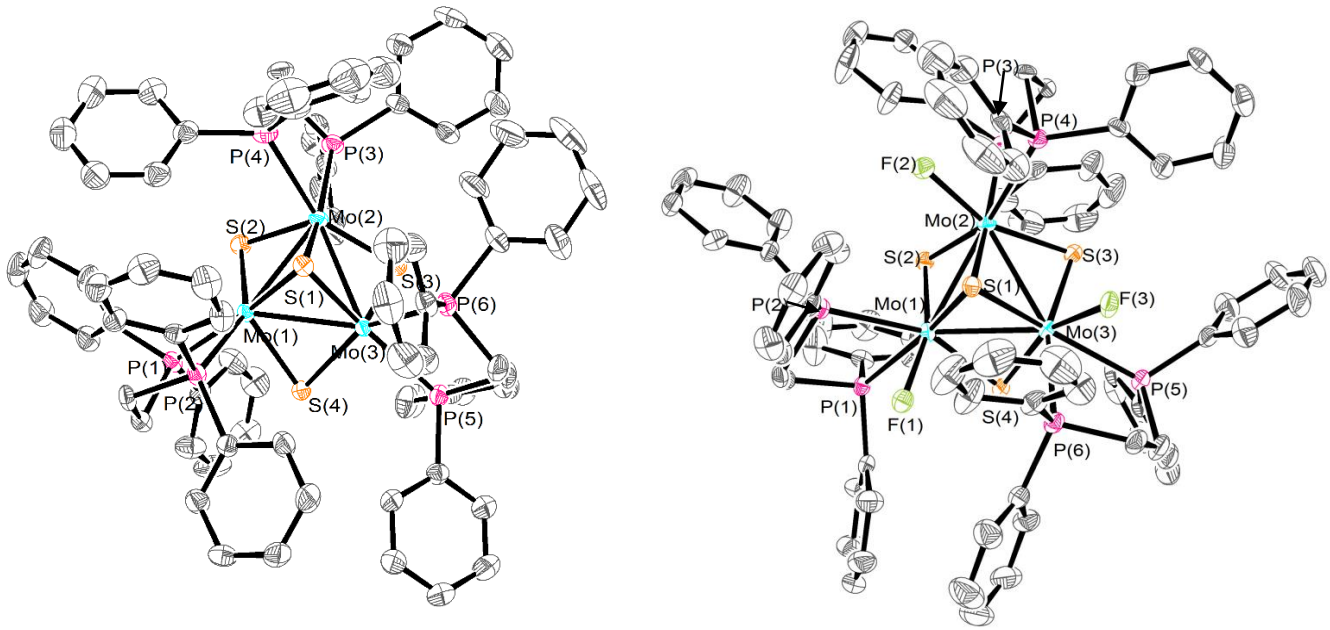


Figure 1. ORTEP representations of [**Mo-1**]$^+$ (left) and [**Mo-2**]$^+$ (right) cations.

Table 1. Selected Averaged Bond Distances for compounds $[Mo_3S_4H_3(dppe)_3]PF_6$ ([Mo-1]PF_6) and $[Mo_3S_4F_3(dppe)_3]PF_6 \cdot H_2O$ ([Mo-2]$PF_6 \cdot H_2O$).

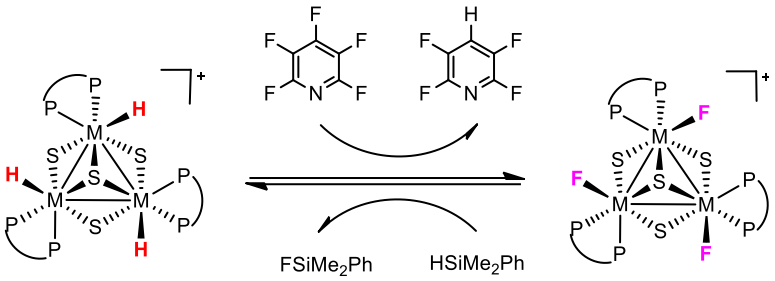
Distance (Å)[a]	[Mo-1]PF_6	[Mo-2]$PF_6 \cdot H_2O$	$[Mo_3S_4H_3(dmpe)_3]BPh_4$[b]
Mo-Mo	2.7663[5]	2.7584[6]	2.744[5]
Mo-(μ_3-S)	2.3642[13]	2.3550[14]	2.346[4]
Mo-(μ-S)[c]	2.3242[13]	2.3173[14]	2.329[4]
Mo-(μ-S)[d]	2.3315[13]	2.2824[14]	2.324[2]
Mo-P(1)[e]	2.5133[13]	2.5555[15]	2.467[12]
Mo-P(2)[f]	2.5557[13]	2.6232[15]	2.524[9]

[a]Standard deviations for averaged values are given in brackets. [b]Data taken from ref 30. [c]Distance *trans* to the Mo-P bond. [d]Distance *trans* to the Mo-X bond (X = H or F). [e]Distance *trans* to the Mo-(μ_3-S) bond. [f]Distance *trans* to the Mo-(μ-S) bond.

The [**Mo-1**]$^+$ and [**Mo-2**]$^+$ cations contain the incomplete cuboidal Mo_3S_4 cluster unit present in their precursors and their average Mo-Mo and Mo-S distances fall within the range observed for other M_3Q_4 (M=Mo, W and Q=S, Se) clusters [32]. The differences observed in the Mo-(μ-S) bond lengths in the [**Mo-2**]$^+$ cluster are due to the lower *trans* influence of the fluoride in comparison with the phosphorous atom of the diphosphine ligand. The Mo-P distances in the fluorido [**Mo-2**]$^+$ complex are *ca.* 0,05 Å longer than the corresponding bond lengths in the hydrido [**Mo-1**]$^+$ cluster. The Mo-F

distances in [**Mo-2**]$^+$ of 2.038[3] Å are similar to Mo-F(terminal) bond lengths found in the bifluoride cluster $[Mo_3S_4F_7(FHF)_2]K_5$, and *ca.* 0.1 Å shorter than the Mo-(F···H-F) distances reported for this complex [33].

Catalytic HDF of pentafluoropyridine with $[M_3S_4X_3(dppe)_3]^+$ (M = Mo or W; X = H or F). Catalytic HDF of pentafluoropyridine has been investigated using the hydrido [**Mo-1**]BPh_4 and [**W-1**]BPh_4 complexes as catalyst and $HSiMe_2Ph$ as hydrogen source, according to eq. 3. Reaction monitoring by ^{19}F NMR has confirmed the high selectivity of the reaction with the identification of 2,3,5,6-tetrafluoropyridine and the fluorinated silane reaction products.



(3)

Reaction conditions (catalyst loading, reaction time and temperature) under microwave and reflux activation have been optimized until full conversion. The best performance has been achieved with a catalyst loading of 0.7 mol % under microwave radiation at 115ºC with a maximum power of 70 W (see Table 2). Increase of temperature and power of radiation cause cluster decomposition. These conditions are less energetically demanding than those required for HDF of pentafluoropyridine analogous dmpe hydrido clusters, for which the best yields were observed with 1 mol % catalyst at 180ºC [22].

Table 2. Catalytic Hydrodefluorination of Pentafluoropyridine.

Entry	Catalyst	Reaction time (h)	Reaction conditions[a]	Yield[b] (%)	Turnover number[c]
1	[Mo-1]BPh_4	1	Microwave	21	30
2	[Mo-2]BPh_4	2	Microwave	19	27
3	[W-1]BPh_4	30	Reflux	55	79
4	[W-1]BPh_4	2.5	Microwave	87	124
5	[W-2]BPh_4	0.75	Microwave	65	94

[a]Amounts: 0.7 mol % cat., 0.38 mmol of pentafluoropyridine, 1.9 mmol of $HSiMe_2Ph$, 1 mL of CH_3CN. [b]Yield based on ^{19}F-NMR using fluorobenzene as internal standard. [c]Turnover number: mol of HDF product/mol of cat.

The hydrido tungsten cluster [**W-1**]$^+$ is the most efficient catalyst, giving 87 % yield and a turnover number of 124 (entry 4), while the hydrido molybdenum cluster [**Mo-1**]$^+$ reacts more rapidly (entry 1) to afford the *para*-substituted tetrafluoropyridine product in only 21 % yield and achieving a maximum turnover number of 30. While the $[M_3S_4H_3(dmpe)_3]^+$ (M = Mo or W) complexes show no HDF under reflux conditions, the [**W-1**]$^+$ cluster hydride catalyzes HDF of pentafluoropyridine in acetonitrile under these conditions (entry 3).

Regeneration of the cluster hydrides has been studied taking the fluoride [**Mo-2**]$^+$ and [**W-2**]$^+$ cluster cations as precatalysts and the silane, according to eq. 3. Reaction proceeds catalytically to afford selectively the *para*-substituted product, although yields and turnover numbers (entries 2 and 5) are lower than those obtained starting from the corresponding hydrido cluster complexes. A similar situation has been found when $[M_3S_4H_3(dmpe)_3]^+$ and $[M_3S_4F_3(dmpe)_3]^+$ complexes have been used as catalyst and precatalyst, respectively. We have attributed this low activity to the inefficient production of hydrides by treatment of the fluoride [**Mo-2**]$^+$ and [**W-2**]$^+$ cluster complexes with $HSiMe_2Ph$.

Conclusions

In conclusion, synthetic methods developed for the synthesis and isolation of trimetallic $[M_3S_4H_3(dmpe)_3]^+$ cluster hydrides and $[M_3S_4F_3(dmpe)_3]^+$ fluorides, can be easily adapted for the preparation of their corresponding dppe derivatives. The $[M_3S_4H_3(diphosphine)_3]^+$ (diphosphine= dmpe or dppe) cluster hydrides are the active species in the catalytic HDF of pentafluoropyrydine and they can be regenerated from their resulting $[M_3S_4F_3(diphosphine)_3]^+$ cluster fluorides using silanes. HDF of pentafluoropyridine occurs regioselectively at the 4-position and the mechanism involves partial decoordination of the diphosphine. Substitution of the dmpe diphosphine for the less basic dppe results in a higher catalytic activity. While catalytic HDF of pentafluoropyridine mediated by $[M_3S_4H_3(dmpe)_3]^+$ complexes requires microwave activation, the reaction occurs under reflux conditions when the trimetallic $[W_3S_4H_3(dppe)_3]^+$ cluster complex is used as catalyst.

Supporting Information

CCDC 995388 (compound $[Mo_3S_4F_3(dppe)_3]PF_6$) and 995389 (compound $[Mo_3S_4H_3(dppe)_3]PF_6$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or e-mail:deposit@ccdc.cam.ac.uk).

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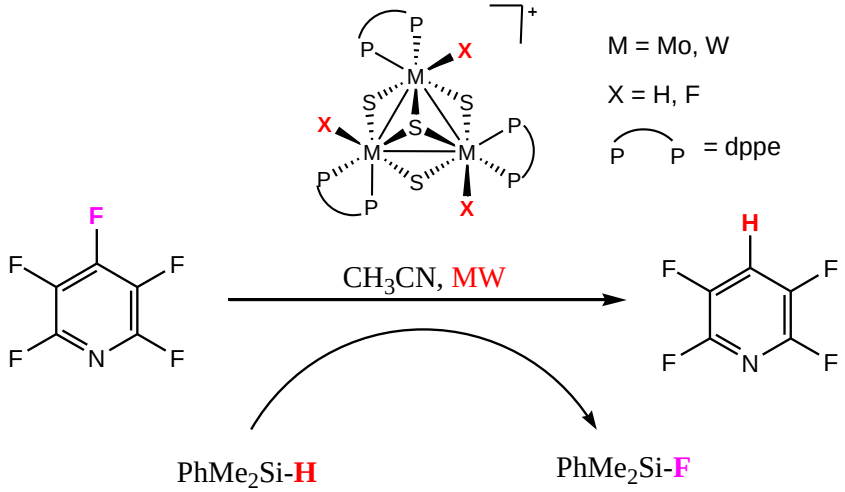
Graphical abstract



References

1. H. Amii, K. Uneyama, Chem. Rev. 109, 2119 (2009).
2. A. Nova, R. Mas-Ballesté, A. Lledós, Organometallics 31, 1245 (2011).
3. E. Clot, O. Eisenstein, N. Jasim, S. A. Macgregor, J. E. McGrady, R. N. Perutz, Acc. Chem. Res. 44, 333 (2011).
4. X. Ribas, C-H and C-X Bond Functionalization: Transition Metal Mediation (RSC, Cambridge, UK, 2013), pp. 471.
5. M. F. Kuehnel, D. Lentz, T. Braun, Angew. Chem. 52, 3328 (2013).
6. B. M. Kraft, R. J. Lachicotte, W. D. Jones, J. Am. Chem. Soc. 122, 8559 (2000).
7. E. Clot, C. Mégret, B. M. Kraft, O. Eisenstein, W. D. Jones, J. Am. Chem. Soc. 126, 5647 (2004).
8. B. M. Kraft, W. D. Jones, J. Am. Chem. Soc. 124, 8681 (2002).
9. B. M. Kraft, R. J. Lachicotte, W. D. Jones, J. Am. Chem. Soc. 123, 10973 (2001).
10. U. Jäger-Fiedler, M. Klahn, P. Arndt, W. Baumann, A. Spannenberg, V. V. Burlakov, U. Rosenthal, J. Mol. Cat. A: Chemical 261, 184 (2007).
11. R. D. Rieth, W. W. Brennessel, W. D. Jones, Eur. J. Inorg. Chem. 2007, 2839 (2007).
12. S. Yow, S. J. Gates, A. J. P. White, M. R. Crimmin, Angew. Chem. Int. Ed. 51, 12559 (2012).
13. M. Klahn, U. Rosenthal, Organometallics 31, 1235 (2012).
14. M. F. Kuhnel, D. Lentz, Angew. Chem. Int. Ed. 49, 2933 (2010).
15. M. F. Kuehnel, P. Holstein, M. Kliche, J. Kruger, S. Matthies, D. Nitsch, J. Schutt, M. Sparenberg, D. Lentz, Chem. Eur. J. 18, 10701 (2012).
16. J. Vela, J. M. Smith, Y. Yu, N. A. Ketterer, C. J. Flaschenriem, R. J. Lachicotte, P. L. Holland, J. Am. Chem. Soc. 127, 7857 (2005).
17. S. P. Reade, M. F. Mahon, M. K. Whittlesey, J. Am. Chem. Soc. 131, 1847 (2009).
18. J. A. Panetier, S. A. Macgregor, M. K. Whittlesey, Angew. Chem. Int. Ed. 50, 2783 (2011).
19. S. A. Macgregor, D. McKay, J. A. Panetier, M. K. Whittlesey, Dalton Trans. 42, 7386 (2013).
20. L. M. Guard, A. E. W. Ledger, S. P. Reade, C. E. Ellul, M. F. Mahon, M. K. Whittlesey, J. Organomet. Chem. 696, 780 (2011).
21. L. Zámostná, M. Ahrens, T. Braun, J. Fluorine Chem. 155, 132 (2013).
22. T. F. Beltran, M. Feliz, R. Llusar, J. A. Mata, V. S. Safont, Organometallics 30, 290 (2011).
23. F. Estevan, M. Feliz, R. Llusar, J. A. Mata, S. Uriel, Polyhedron 20, 527 (2001).
24. CrysAlis^{Pro} (Agilent Technologies, Santa Clara, CA, 2012).
25. R. C. Clark, J. S. Reid, Acta Crystallogr. Sect. A 51, 887 (1995).
26. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, J. Appl. Cryst. 42, 339 (2009).

27. G. M. Sheldrick, Acta Crystallogr. Sect. A 64, 112 (2008).
28. F. A. Cotton, R. Llusar, C. T. Eagle, J. Am. Chem. Soc. 111, 4332 (1989).
29. A. G. Algarra, M. G. Basallote, M. J. Fernandez-Trujillo, M. Feliz, E. Guillamon, R. Llusar, I. Sorribes, C. Vicent, Inorg. Chem. 49, 5935 (2010).
30. M. Minato, T. Ito, Coord. Chem. Rev. 252, 1613 (2008).
31. J. Andrés, M. Feliz, J. Fraxedas, V. Hernández, J. T. López-Navarrete, R. Llusar, G. Sauthier, F. R. Sensato, B. Silvi, C. Bo, J. M. Campanera, Inorg. Chem. 46, 2159 (2007).
32. R. Llusar, S. Uriel, Eur. J. Inorg. Chem. 2003, 1271 (2003).
33. Y. V. Mironov, S. S. Yarovoi, S. F. Solodovnikov, V. E. Fedorov, J. Mol. Struct. 656, 195 (2003).