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Bifunctional W/NH cuboidal aminophosphino W$_3$S$_4$ cluster hydrides: the puzzling behaviour behind the hydridic-protonic interplay

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This work is dedicated to Professor Rinaldo Poli on the occasion of his 65th birthday

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Abstract: The novel [W$_3$S$_4$H$_3$(edpp)$_3$]$^+$ (edpp = (2-aminoethyl)diphenylphosphine) (**1$^+$**) cluster hydride with an acidic –NH$_2$ functionality has been synthetized and studied. Its crystal structure shows the characteristic incomplete W$_3$S$_4$ cubane core with the outer positions occupied by the P and N atoms of the edpp ligands. Although no signal due to the hydride ligands is observed in the ^{1}H NMR spectrum, hydride assignment is supported by ^{1}H-^{15}N HSQC techniques, the changes in the ^{31}P{^{1}H} NMR chemical shift, and FT-IR spectra in the W-H region of the deuterated [W$_3$S$_4$D$_2$H(edpp)$_3$]$^+$ (**1$^+$-d$_2$**) samples. Moreover, all NMR evidences suggest that one of the hydrogen atoms of the NH$_2$ group in **1$^+$** is rapidly exchanging with the hydride. The reaction of **1$^+$** with acids (HCl, HBr and DCl) features complex polyphasic kinetics with zero-order dependence with respect to the acid concentration, being also independent of the solvent nature. This behavior differs from that of their diphosphino analogues, suggesting a different mechanism.

Introduction

Metal ligand multifunctional catalysis is implicated in many enzymatic transformations as well as in other chemical relevant processes aimed to the transformation of chemicals. In the case of the [FeFe] hydrogenase the amino group located in the second coordination sphere of the metal acts as a proton relay promoting hydrogen evolution.[1] On the other hand, molecular metal/N-H bifunctional complexes are among the most efficient artificial homogenous catalysts for the hydrogenation and dehydrogenation of organic substrates.[2] The discovery in the mid-1990s of Noyori-type catalysts led to the recognition that metal hydrides containing protic N-H ligand fragments in their proximities are important in catalysis.[3] The conventional Noyori mechanism postulates a direct participation of the N-H ligand moiety in the bond cleavage/formation events; however, more recent studies suggest that in most cases the N-H bond is not cleaved but serves to stabilize the turnover determining transition state via strong N-H···O hydrogen bonding interactions.[4] Therefore, the acidity of the N-H group is an important factor influencing the catalyst activity.

Motivated by the increasing interest in bifunctional metal/N-H catalysis and the latest results in our group on the catalytic activity of cuboidal Mo$_3$S$_4$ group six metal cluster hydrides decorated with diphosphine ligands in the transfer hydrogenation of nitrocompounds using formic acid, we became interested in the chemistry of analogous clusters functionalized with N-H containing ligands, their structural characterization and the study of the reactivity *versus* acids.[5] In addition, along the years we have achieved a full knowledge of the kinetics of diphosphine molybdenum and tungsten M$_3$Q$_4$ (Q=S, Se) hydrides *versus* acids.[6-8] An understanding of the consequences that result from replacing outer diphosphine by aminophosphine ligands may provide key information on the mechanistic details behind bifunctional metal/N-H catalysis.

Herein, we present the synthesis and crystal structure of the [W$_3$S$_4$H$_3$(edpp)$_3$]$^+$ (**1$^+$**) (edpp=(2-aminoethyl)diphenylphosphine) cluster shown in Figure 1. The puzzling behavior of the protonic-hydridic bifunctionality is analyzed by combining NMR spectroscopic techniques. The proton transfer kinetics and reaction mechanism are also discussed and compared with those of the analogous diphosphino complexes.
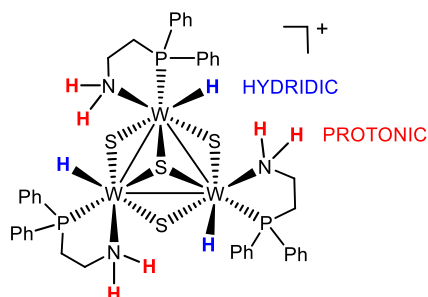
Figure 1. Structure of $[W_3S_4H_3(edpp)_3]^+$ emphasizing the protonic-hydridic bifunctionality.

Results and Discussion

As pointed out above, transition metal hydrides containing N-H functionalities are attractive targets in catalysis and an understanding of the kinetics and reaction mechanism is of fundamental interest in chemistry. Isolation of the first diphosphino W_3S_4 hydride was reported by substitution of the halide (X) atoms in $[W_3S_4X_3(diphosphine)_3]^+$ by hydride ligands using borohydride.[9] This chemistry was further extended by some of us to other diphosphines and later on to molybdenum.[10–11] In this work, we have succeeded to apply this procedure to the corresponding aminophosphino species (Eq. (1)).

$[W_3S_4Br_3(edpp)_3](BPh_4) + BH_4^-$ (excess) $\rightarrow [W_3S_4H_3(edpp)_3](BPh_4)$ (1)
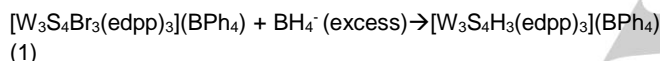
The reaction was carried out in THF at room temperature and it occurs with a color change from blue to pink-red. From the reaction mixture a solid was isolated in high yield (>90 %) whose elemental analysis, ESI-MS (Figure S1) and $^{31}P\{^1H\}$ NMR (Figure S2 (top)) spectra are consistent with it being the $(BPh_4)^-$ salt of the $[W_3S_4H_3(edpp)_3]^+$ (1^+) cation. Remarkably, no hydride signal is observed in the ^1H NMR spectra recorded using different solvents and temperatures in clear contrast with the hydride signals, δ_H= -0,80 − 0,97 ppm with $^2J_{P,H}$ = 45-58 and 23-30 Hz, reported for the analogous diphosphino clusters.[9,10] In 2009, Berke and coworkers reported a series of mononuclear aminophosphine hydrido complexes of formula $WH(NO)(CO)(P(OMe)_3)(edmp)$ and $WH(NO)L_2(edmp)$ with L= PMe_3 and $P(OMe)_3$ and edmp =2-aminoethyl-dimethyl phosphine. In contrast to 1^+, these mononuclear compounds are very unstable and the complexity of the reaction mixture made the assignment of the ^1H NMR signals of the edmp NH_2 and CH_2 protons difficult.[12] In spite of this, they were able to assign the hydrido resonances, which fall within the 2.4 and 4.3 ppm range. In the case of the most stable $WH(NO)[P(OMe)_3]_2(edmp)$ complex, NMR spectroscopic experiments and deuterium labelling suggest that this species coexists in equilibrium with the corresponding dihydrogen amide $W(H_2)(NO)[P(OMe)_3]_2(edmp-H)$ complex. Unfortunately, exchanging resonances of the hydride and all the N-H protons in Berke's complexes are hidden under the very intense signals of the CH protons. In addition, no single crystals could be grown for neither of these mononuclear species due to their instability. The higher stability of the 1^+ cluster has allowed us to obtain single crystals and also to gain information on the N-H/hydride exchange (*vide infra*).

Crystal structure of (1-d₂)(BPh₄)

Single crystals of the tetraphenylborate salt of 1^+-d_2 were grown from a reaction mixture obtained using deuterated borohydride. High-resolution mass spectrometry of the deuterated crystals agree with the formulation $[W_3S_4D_2H(edpp)_3]^+$ (Figure S1). Additionally, comparison of the FT-IR spectra of 1^+ and the deuterium labelled derivative 1^+-d_2 showed significant changes. In particular, the signal at 1760 cm^{-1} for the W-H bond is shifted to 1656 cm^{-1}. Although some low intensity bands appeared in the range expected for the W-D bonds, *ca.* 1240 cm^{-1} (Figure S3), these are hidden under other bands making the assignment unfeasible. An ORTEP drawing of this cation is represented in Figure 2 together with some relevant bond distances.
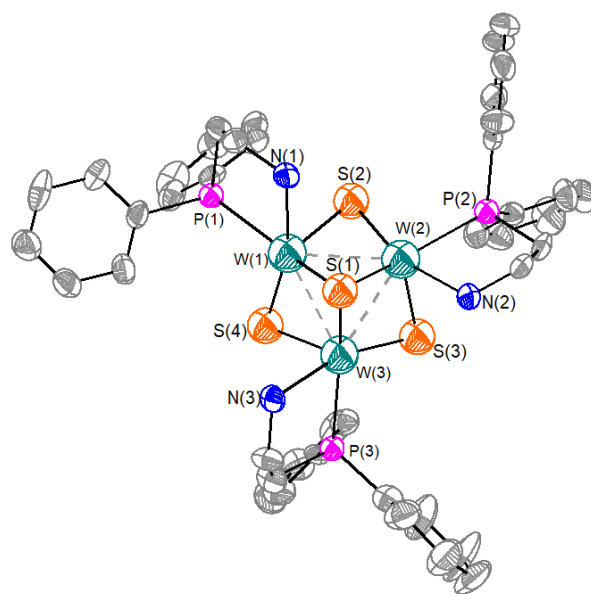

Figure 2. ORTEP representation (ellipsoids at 50% probability) of the cationic cluster 1^+-d_2. Hydrogen atoms have been omitted for clarity. Average distances: W–W = 2.750[7] Å, W–(μ_3-S(1)) = 2.356[3] Å, W–(μ-S)$_{trans-H}$ = 2.361[1] Å, W–(μ-S)$_{trans-N}$ = 2.300[6] Å, W – N = 2.303[1] Å, W–P = 2.494[3] Å. Standard deviations of average distances are given in brackets.

The cluster shares the structural features of its $[W_3S_4Br_3(edpp)_3]^+$ precursor.[13] The nature of the W_3S_4 core in 1^+-d_2 is such that the bridging and capping sulfur atoms occupy a set of facial positions around the octahedrally coordinated tungsten atoms leaving the three outer positions for the nitrogen and the phosphorous atom (*trans* to the capping sulfur) of the edpp ligand. The apparently empty site must be occupied by the hydrogen/deuterium atoms to balance the cluster charge. Replacement of the bromide atoms in the $[W_3S_4Br_3(edpp)_3]^+$ precursor by the hydride ligands is reflected in an elongation of 0.05 Å of the W-μ-S distance *trans* to the hydride. This lengthening has been previously observed in other hydrido clusters and interpreted in terms of the higher *trans* influence of the hydride.[8-10]

The NH_2 groups and hydrido ligand coordinated to the same metal center lie on the same side of the trimetallic plane, as shown in Figure 1 and Figure S4. The shorter W-H···H(-NH) distances of 2.5 Å correspond to interactions between ligands located in geminal positions. Distances have been calculated considering a

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W-H bonds length of 1.74 Å. Interactions between hydrogen atoms of ligands in vicinal positions are ca. 0.3 Å longer.

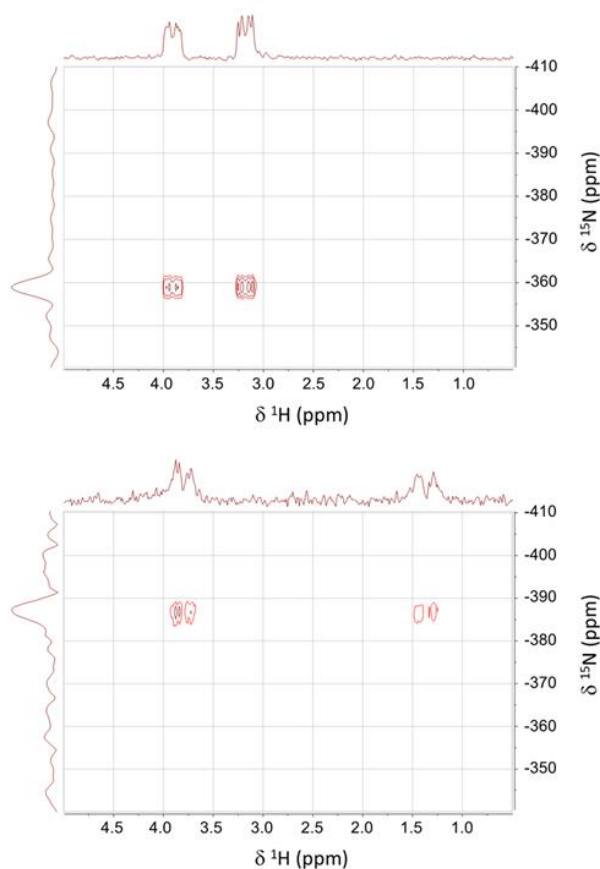**Figure 3.** ^1H-^{15}N HSQC spectra of $[W_3S_4Br_3(edpp)_3]^+$ (top) and $\mathbf{1^+}$ (bottom) in CD$_3$CN.

**The behavior of $[W_3S_4H_3(edpp)_3]^+$ in solution**

The occurrence of a very fast dynamic process among the amino protons of the edpp the ligand and the hydrides can be inferred from the ^1H NMR spectra recorded using different solvents and temperatures. Although no hydride signal was observed in the proton spectrum of $\mathbf{1^+}$, the $^{31}P\{^1H\}$ NMR of the deuterated crystals (Figure S2 (bottom)) revealed a second signal attributable to the presence of the deuterium atoms in the $[W_3S_4D_2H(edpp)_3]^+$ cluster when compared with that of compound $\mathbf{1^+}$ (Figure S2 (top)).[14]

Relevant information is inferred by comparing the ^1H-^{15}N HSQC spectra of $\mathbf{1^+}$ with that of its cluster precursor (Figure 3). The spectrum of $[W_3S_4Br_3(edpp)_3]^+$ (Figure 3 top) shows a nitrogen signal at -359 ppm ppm that correlates with two proton signals at 3.2 and 3.9 ppm, both of them appearing as a doublet of doublets, with coupling constants of $^2J_{H,H}$ = 21 Hz and $^1J_{H,N}$ = 63 and 56 Hz, respectively.[15] In the monodimensional ^1H NMR spectrum, those proton signals appear as two broad unresolved signals with the same integral. On the other hand, the ^1H-^{15}N HSQC spectrum of $\mathbf{1^+}$ (Figure 3 bottom) shows a nitrogen signal at -387 ppm that correlates with two proton signals at 1.4 and 3.8 ppm, which show $^2J_{H,H}$ = 22 Hz and $^1J_{H,N}$ coupling constants of 93 and 70 Hz, respectively. Interestingly, the intensity of both signals is now different in the proton NMR spectrum, the integral of the 1.4 ppm signal doubling that of the 3.8 ppm signal.

Notice that the existence of the proton-nitrogen coupling in the hydrido $\mathbf{1^+}$ cluster rules out any dynamic process involving nitrogen decoordination. On the other hand, the upfield shift of the bromo cluster as wells as its higher intensity (2x) suggest that one of the hydrogen atoms in the NH$_2$ group is rapidly exchanging with the hydride, which typically shows chemical shifts in the 1 to -3 ppm range in this kind of hydride clusters.[9,10] This hypothesis is also supported by the absence of phosphorus-proton coupling in the ^1H-^{15}N HSQC spectra, which again points out to the participation of the coordinated hydride in a dynamic process that cancels out the coupling to phosphorus.

The reaction of $[W_3S_4H_3(edpp)_3]^+$ with acids

Cuboidal diphosphino W$_3$S$_4$ hydrido clusters react with HX (X= Cl or Br) acids to form W-H···H-X dihydrogen species that upon hydrogen release afford the hydride-for-halide substitution product.[6,7] The reaction of $\mathbf{1^+}$ with HCl or HBr in CH$_3$CN or CH$_2$Cl$_2$ also affords the corresponding substitution products, as represented in Eq.(2).

$$[W_3S_4H_3(edpp)_3]^+ \ (\mathbf{1^+}) + HX(excess) \rightarrow [W_3S_4X_3(edpp)_3]^+ \qquad (2)$$
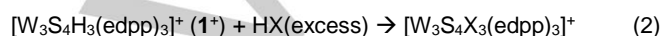
The $[W_3S_4X_3(edpp)_3]^+$ products have been identified by its UV-vis spectra with their characteristic band at *ca.* 565 nm and one phosphorous signal in their $^{31}P\{^1H\}$-NMR spectra.[13] However, differences in the solution behavior between $[W_3S_4H_3(diphospine)_3]^+$ and the aminophosphino $\mathbf{1^+}$ anticipates a different reaction kinetics. With this idea in mind, we undertook a kinetic study of the reaction in Eq.(2) using stopped flow techniques. Typical stopped-flow spectral changes for the reaction of $\mathbf{1^+}$ with HBr in acetonitrile at 25ºC are illustrated in Figure 4.
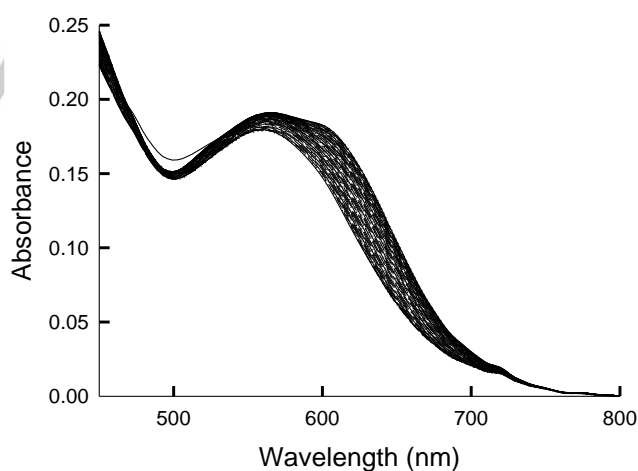

Figure 4. Typical spectral changes during 1000 seconds for the reaction of $[W_3S_4H_3(edpp)_3]^+$ (1.8×10^{-4} M) with HBr (0.036 M) in acetonitrile solution at 25.0ºC.

The initial spectrum in these experiments shows a band at 535 nm that differs from that of $\mathbf{1^+}$ (522 nm), thus evidencing the existence of a rapid step occurring within the stopped-flow mixing time even at the lowest concentrations of acid used. The subsequent changes span for more than 1000 s and show a

gradual shift of the 535 nm band to 565 nm, the value expected for $[W_3S_4Br_3(edpp)_3]^+$. However, the reaction does not stop at this point but continues to form a different species with a band at 602 nm. The fit of those spectral changes proved to be very complex, and a satisfactory fit could be only obtained using a polyphasic model with the values of the rate constants included in Table 1; the spectra calculated for the different intermediates are shown in Figure S5.

Table 1. Values of the rate constants at 25.0ºC for the reaction of $[W_3S_4H_3(edpp)_3]^+$ with acids.[a]

	HBr[b]	HCl[b]	DCl[b]	kie	HCl[c]
k_1 (s^{-1})	[d]	[d]	[d]		[d]
k_2 (s^{-1})	25(4)	24(5)	26(3)	0.9(2)	8±5
k_3 (s^{-1})	1.9(6)	1.7(2)	1.9(3)	0.9(2)	1.6±0.3
k_4 (s^{-1})	0.18(1)	0.11(2)	0.11(2)	1.0(3)	0.16±0.03
k_5 (s^{-1})	0.028(5)	0.012(3)	8.9(3)·10^{-3}	1.3(3)	3(1)·10^{-3}
k_6 (s^{-1})	4(1)·10^{-3}	3(1)·10^{-3}	[e]		1.4(4)·10^{-4}
k_7 (s^{-1})	2.3(3)·10^{-3}	[e]	[e]		[e]

[a] The numbers in parentheses represent the standard deviation in the last significant digit. In all cases the rate constants were found to be independent of the acid concentration in the range 0.009-0.054. [b] Experiments in CH_3CN solution. [c] Experiments in CH_2Cl_2 solution. [d] Too fast, it occurs within the stopped-flow mixing time. [e] Not resolved.

Despite the complexity of the kinetic analysis, all rate constants appear to be independent of the acid concentration. Thus, the order of reaction with respect to the acid is zero for all the resolved kinetic steps, an unprecedented kinetic behavior in this kind of reaction that suggests a mechanistic change with respect to the pathways observed for related diphosphino clusters for which order one and two have been observed depending on the nature of the solvent.[6,7] The effect of the solvent was examined by carrying out kinetic studies with HCl in CH_3CN and CH_2Cl_2, (see Table 1). In this case, the rate constants show little dependence on the solvent. Next, the effect of isotopic substitution was investigated and the reaction kinetics towards DCl in acetonitrile was measured without any noticeable kinetic isotope effect (kie). This tendency follows that of the $[W_3S_4H_3(diphosphine)_3]^+$ clusters but it contrasts with the significant inverse kie observed in the reaction with acids of mononuclear hydride complexes.[6,16]

Conclusion

An aminophosphine cuboidal $[W_3S_4H_3(edpp)_3](BPh_4)$ cluster hydride with an acidic –NH_2 functionality has been prepared in high yield by reacting its bromide precursor with borohydride. This cluster complex is air stable in solution and its crystal structure shares common features with its parent bromide complex. Interestingly, one of the hydrogen atoms in the NH_2 group is rapidly exchanging with the hydride. This exchange is probably so fast that no separate ^1H NMR signals for both types of hydrogen atoms could be obtained. Kinetic studies also reveal that the acid-promoted substitution of the coordinated hydrides goes through a mechanism different from those previously reported for their

diphosphine analogues for which first and second order dependence on the acid concentration has been observed, depending on the solvent nature. For the reaction of the aminophosphino $[W_3S_4H_3(edpp)_3]^+$ cluster hydride with acids, the similar kinetics observed in acetonitrile and dichloromethane solutions together with the zero order acid concentration kinetics suggest that the hydride /NH_2 proton exchange may be relevant in determining the reaction pathway.

Experimental Section

General remarks.

All reactions were carried out under a nitrogen atmosphere using standard Schlenck techniques. Compound $[W_3S_4Br_3(edpp)_3]Br$ was prepared according to literature methods.[14] Addition of $Na(BPh_4)$ to concentrated methanol solutions of $[W_3S_4Br_3(edpp)_3]Br$ causes precipitation of the corresponding tetraphenylborate salts.The remaining reactants were obtained from commercial sources and used as received. Solvents were purified by using an MBRAUN SPS-800 system.

Physical measurements.

^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker Avance III HD 400 MHz using CD_3CN as solvent and referenced to the residual protons of the deuterated solvent. ESI-mass spectra were recorded using a Premier Q-TOF (quadrupole-hexapole-TOF) mass spectrometer with an orthogonal Z-spray electrospray source (Waters, Manchester, UK). Samples solutions of $[W_3S_4D_2H(edpp)_3](BPh_4)$ (**1-d$_2$**) and $[W_3S_4H_3(edpp)_3](BPh_4)$ (**1**) in CH_3CN were freshly prepared for the measurements. The temperature of the source block was set at 120 ºC and the desolvation temperature at 225 ºC. A capillary voltage of 3.3 kV was used in the negative scan mode, and the cone voltage was set to $Uc = 20$ V for both compounds. Time-of-flight (TOF) mass spectra were acquired in the V-mode at a resolution of ca. 5000 [full width at half-maximum (FWHM)]. Sample solutions were injected with a syringe pump directly connected to the ESI source at a flow rate of 10 μL·min^{-1}. The observed isotopic pattern of each compound perfectly matched the theoretical isotope pattern calculated from their elemental composition by using the MassLynx 4.1 program.[17] Infrared spectra were measured in a Jasco FT/IR-6200 spectrometer.

$[W_3S_4H_3(edpp)_3](BPh_4)$, 1(BPh$_4$)

An excess of $NaBH_4$ (0.045 g, 0.118 mmol) was added to a blue solution of $[W_3S_4Br_3(edpp)_3](BPh_4)$ (0.030 g, 0.0156 mmol) in 20 mL of THF. After 18 hours the reaction mixture was filtered and the pink-reddish filtrate was evaporated to dryness. The solid product was dissolved in CH_2Cl_2 and filtrated to eliminate the excess of $NaBH_4$ and the inorganic salts formed during the reaction. The filtrate was taken to dryness yielding 0.025 g (92%) of a pink solid. $^{31}P\{^1H\}$ NMR (161.9 MHz, CD_3CN) δ = 28.1 (s, 3P), IR (KBr) ν = 1760 cm^{-1} (W-H), Q-TOF-MS (CH_3CN, 20 V) m/z calcd for $W_3S_4P_3N_3C_{42}H_{51}$: 1370.0726 [M$^+$]; found 1370.0759; Elemental Analysis calcd (%) for $W_3S_4P_3N_3C_{66}H_{71}B$: C 46.9, H 4.2, N 2.5; found C 47.1, H 4.5, N 2.7.

$[W_3S_4D_2H(edpp)_3](BPh_4)$, (1-d$_2$)(BPh$_4$)

This compound was prepared following the same procedure above but using the deuterated $NaBD_4$. Yield: 80%. $^{31}P\{^1H\}$ NMR (161.9 MHz, CD_3CN) δ = 28.15 (s, 1P), 28.23 (s, 2P); IR (298 K) ν = 1656 cm^{-1} (W-D), Q-TOF-MS (CH_3CN, 20 V) m/z calcd for $W_3S_4P_3N_3C_{42}H_{51}$: 1372.0868 [M$^+$]; found 1372.0784.

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Structure determination

Suitable single crystals of $[W_3S_4D_2H(edpp)_3](BPh_4)\cdot2[CH_3CH_2)_2O]$ for X-ray analysis were obtained by slow evaporation of a CH_2Cl_2/Et_2O mixture. The diffraction data were collected on an Agilent Supernova diffractometer equipped with an Atlas CCD detector using Mo-K_α radiation ($\lambda = 0.71073$ Å).[18] No instrument or crystal instabilities were observed during data collection. Absorption corrections based on the multiscan method were applied.[19] A reddish pink needle with dimensions $0.044 \times 0.062 \times 0.194$ mm^3 was selected and kept at a steady $T = 199.9(4)$ K during data collection. The structure was solved with the olex2.solve 1.3-alpha structure solution program using the Charge Flipping solution method and by using Olex2 as the graphical interface.[20,21] The model was refined with version 2018/3 of ShelXL using Least Squares minimization.[22] The compound crystallizes with two $(CH_2CH_3)_2O$ crystallization solvent molecules. One of these molecules is highly disordered so had to be refined isotropically restraining all distances to a fixed value. Hydrogen atoms were isotropically refined in their geometrically calculated positions using a riding model for this purpose. Three peaks of $ca.$ 3.4-2.9 eÅ^{-3} remained in the last Fourier map of structure. This residual density, below the 7.5% of the higher Z value in the structure, has not been included in the model. The structural figures were drawn using the Diamond visual crystal structure information system software.[23] CCDC 2099731 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Crystal Data for $[W_3S_4D_2H(edpp)_3](BPh_4)\cdot2(CH_3CH_2)_2O$

$C_{74}H_{78}BN_3O_2P_3S_4W_3$, $Mr = 1824.88$ g/mol, triclinic, space group P-1, a = 11.5952(4) Å, b = 18.2064(6) Å, c = 18.5375(5) Å, $\alpha = 75.248(3)°$, $\beta = 77.941(3)°$, $\gamma = 78.766(3)°$, $V = 3659.2(2)$ Å^3, $T = 199.9(4)$ K, $Z = 2$, μ(Mo K_α) = 4.929 mm^{-1}. Reflections collected/unique = 45266/14958 (R_{int} = 0.0763) which were used in all calculations. Final refinement converged with $R_1 = 0.0887$ and $wR_2 = 0.1364$ for all data, GOF = 1.045, max/min residual electron density 3.4/–1.9 e/Å^3.

Kinetics Experiments

The kinetic experiments were carried out with an Applied Photophysics SX-18MV stopped-flow spectrometer provided with a PDA1 photodiode array (PDA) detector. Experiments were carried out at 25.0 °C under an atmosphere of argon by mixing a solution of the cluster with an excess of the acid in the same solvent. In all cases, pseudo-first-order conditions of acid excess were used, and preliminary experiments at two different concentrations of the complex were carried out to confirm the first order dependence of the observed rate constants on the complex concentration. In all cases the spectral changes were measured over a wide wavelength range and analyzed with the Specfit program.[24]

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Entry for the Table of Contents

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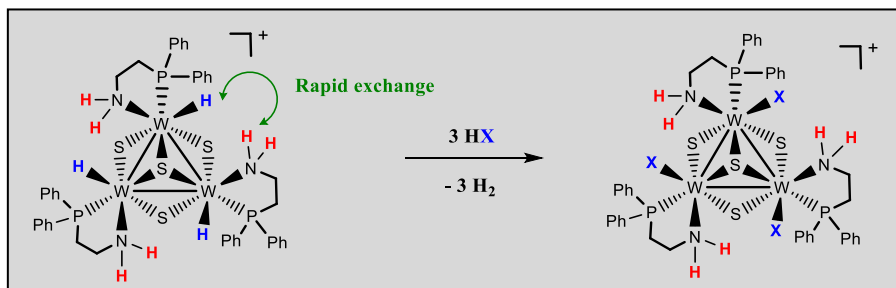
A novel $[W_3S_4H_3(edpp)_3]^+$ cluster hydride with an acidic –NH$_2$ functionality has been prepared and characterized. NMR studies evidence a rapid exchange between the hydride and one of the hydrogen atoms of the NH$_2$ group. The cluster reacts with HX acids to afford the corresponding substitution product with a zero-order kinetics with respect to the acid concentration and independent of the solvent nature.

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