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Article

Chiral [Mo₃S₄H₃(diphosphine)₃]⁺ Hydrido Clusters and Study of the Effect of the Metal Atom on the Kinetics of the Acid-Assisted Substitution of the Coordinated Hydride: Mo vs W

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The molybdenum(IV) cluster hydrides of formula [Mo₃S₄H₃(diphosphine)₃]⁺ with diphosphine = 1,2-(bis)dimethylphosphinoethane (dmpe) or (+)-1,2-bis-(2R,5R)-2,5-(dimethylphospholan-1-yl)ethane ((R,R)-Me-BPE) have been isolated in moderate to high yields by reacting their halide precursors with borohydride. Complex [Mo₃S₄H₃((R,R)-Me-BPE)₃]⁺ as well as its tungsten analogue are obtained in optically pure forms. Reaction of the incomplete cuboidal [M₃S₄H₃((R,R)-Me-BPE)₃]⁺ (M = Mo, W) complex with acids in CH₂Cl₂ solution shows kinetic features similar to those observed for the related incomplete cuboidal [W₃S₄H₃(dmpe)₃]⁺ cluster. However, there is a decrease in the value of the rate constants that is explained as a result of the higher steric effect of the diphosphine. The rate constants for the reaction of both clusters [M₃S₄H₃((R,R)-Me-BPE)₃]⁺ (M = Mo, W) with HCl have similar values, thus indicating a negligible effect of the metal center on the kinetics of reaction of the hydrides coordinated to any of both transition metals.

Introduction

Molybdenum and tungsten are essential elements in biological systems with oxidation numbers in the range from +4 to +6 in their reaction cycles.[1] The aqueous chemistry of these elements in their +4 oxidation state is dominated by the presence of trinuclear species, such as the incomplete cuboidal M₃O₄⁴⁺ aquo ion, for which their sufides analogues exist.[2,3] The motivation for studying these M₃S₄ complexes has come in part from their structural relation to the mixed metal sulfido clusters present in nitrogenase.[4,5] Detailed studies by Sykes and Hernandez-Molina on the kinetics and reaction mechanism of the substitution of the terminal water ligands in the [M₃Q₄(H₂O)₉]⁴⁺ aquo ions (M = Mo, W and Q = S, Se) show a similar behavior for Mo and W.[6] In the recent past, our groups have carried out a complete investigation on the kinetics and reaction mechanism of the reaction of trinuclear cluster hydrides of formula [W₃Q₄H₃(diphosphine)₃]⁺ with acids.[7–9] These studies include aspects such as solvent effects, ion pairing, phosphine basicity, and chalcogen substitution. However, the effect of the nature of the metal atom, Mo versus W, remains an open question because the corresponding molybdenum hydride complexes could not be isolated in pure form. The only evidence of the existence of an incomplete cubane-type Mo₃Q₄ hydride cluster comes from Cotton's group and goes back to the late 1980s.[10] The formulation of the [Mo₃S₄H₃(diphosphine)₃]⁺ complex obtained by reaction of its halide precursor with borohydride is only based on spectroscopic evidence. In this work, we report the isolation of two [Mo₃S₄H₃(diphosphine)₃]⁺ cluster salts, one of them in its optically pure form, a circumstance that has allowed us to investigate the influence of the group 6 metal atoms on the kinetics of acid-assisted substitutions in these trinuclear cluster hydrides.

The reaction of transition metal hydrides with acids is a complex process that may involve different reaction

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intermediates because the actual reaction pathway depends not only on the nature of the proton donor and acceptor but also on the solvent and the presence and identity of the counterion.[11,12] In spite of the existing chemical analogies between molybdenum and tungsten, differences arise regarding bonding energies, acidity/basicity, and stability. An increase in the homolytic M–H dissociation energies in mononuclear cationic $L_nM–H^+$ complexes when descending within group 6 has been estimated.[13] Relativistic effects are considered to be the key factor responsible for the stronger bond in the tungsten complex.

Lledos et al. have compared basicity, hydrogen bonding, and the mechanism of reaction with acids for two homologues, Mo(IV) and W(IV) metal hydrides of formula [Cp*M(dppe)-H_3].[14] Both experimental and theoretical results show a greater metal basicity for the tungsten system, although the two compounds are reversibly protonated to yield an identical classical tetrahydride product, $[Cp*M(dppe)H_4]^+$, without the detection of a dihydrogen intermediate. Contrary to the molybdenum system, a direct proton transfer to the metal assisted by the hydride ligand has been invoked for the reaction of $[Cp*W(dppe)H_3]$ with acids. Regarding stability, the molybdenum hydride complex loses H_2 in coordinating solvents or in the presence of co-ordinating anions, while its tungsten counterpart is stable under the same conditions.[11] Recent experiments by the same authors indicate that the reaction of $[Mo(CO)Cp*H(PMe_3)_2]$ with $Et_2O·HBF_4$ leads to a dihydrogen complex in tetrahydrofurane and to a classical dihydride in dichloromethane, thus showing again the important role of the solvent in this kind of reaction.[15] An essentially identical mechanism has been found for the reaction between the Mo(IV) and W(IV) hydrides [Cp_2MH_2] with acids.[16] For both Mo and W complexes, acid attack occurs in this case at the hydride site to generate dihydrogen species; however, for the molybdenum product, the subsequent cleavage of the dihydrogen ligand yields to the formation of dinuclear species. Again, the higher instability of the Mo(IV) hydrides in front of their tungsten homologues is evidenced.

Despite the precedents above, systematic knowledge on the kinetics of reaction with acids of transition metal hydrides of the same stoichiometry for metals within the same group is still scarce. With the isolation of the $[Mo_3S_4H_3(diphosphine)_3]^+$ cluster salts with two different diphosphines, dmpe or (R,R)-Me-BPE, the limitation that precluded such systematic study has been overcome. In this work, we report not only the isolation of the first Mo_3S_4 cluster hydrides but also a complete study on the kinetics of their reaction with acids (HCl) in dichloromethane. The kinetics of the reaction are compared with data obtained for their tungsten counterparts. The study is also extended to the analysis of the phosphine nature on the reaction kinetics and mechanism.

Experimental Section

General Remarks. $[Mo_3S_4Cl_3(dmpe)_3](BPh_4)$ and $[Mo_3S_4Cl_3-((R,R)-Me-BPE)_3]Br$ were prepared according to literature

methods.[17,18] Diphosphine (R,R)-Me-BPE was purchased from Strem Chemicals. Solvents for synthesis and electrochemical measurements were dried and degassed by standard methods before use.

Physical Measurements. Elemental analyses were performed on an EA 1108 CHNS microanalyzer at the Universidad de La Laguna. $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Mercury 300 MHz apparatus and were referenced to external 85% H_3PO_4. ^1H, $^{13}C\{^1H\}$, and $^1H–^{13}C$ gHSQC spectra were recorded on a Varian INOVA 500 MHz apparatus using CD_2Cl_2 or acetone-d_6 as the solvent. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR using KBr pellets. Signal intensities are denoted as s = strong, m = medium, and w = weak. Electronic absorption spectra were obtained on a Perkin-Elmer Lambda-19 spectrophotometer in dichloromethane. Circular dichroism measurements were recorded on a JASCO J-810 spectropolarimeter. Electrospray mass spectra were recorded with a Quattro LC (quadrupole-hexapole-quadrupole) mass spectrometer with an orthogonal Z-spray electrospray interface (Micromass, Manchester, U.K.). The cone voltage was set at 20 V unless otherwise stated using CH_3CN as the mobile phase solvent. Nitrogen was employed as a drying and nebulizing gas. Isotope experimental patterns were compared with theoretical patterns obtained using the MassLynx 4.0 program.[19]

Synthesis. $[Mo_3S_4H_3(dmpe)_3](BPh_4)$, **[1](BPh_4).** To a green solution of $[Mo_3S_4Cl_3(dmpe)_3](BPh_4)$ (0.168 g, 0.130 mmol) in THF (20 mL) was added an excess of $NaBH_4$ (0.044 g, 1.164 mmol) under nitrogen. The solution color turned purple within 30 min. After the mixture was stirred for 2.5 h, it was taken to dryness, redissolved in CH_2Cl_2, and filtered in order to eliminate the excess of $NaBH_4$ and other inorganic salts. Finally, a microcrystalline purple solid was obtained by slow diffusion of diethyl ether into the filtrate (0.124 g, yield: 80%). Found $Mo_3S_4P_6C_{42}H_{71}B$ (%): S, 10.71; C, 42.26; H, 5.93. Requires (%): S, 10.79; C, 42.44; H, 6.02%. RMN $^{31}P\{^1H\}/\delta$: −144.00 (sept, $^1J(P–F)$ 710.58 Hz), 24.00 (d, $^2J(P–P)$ 15.9 Hz) and 41.12 (d, $^2J(P–P)$ 15.9 Hz). RMN $^1H/\delta$: −2.95 (3H *hydride*, dd, $^2J(P–H)$ 62.8, $^2J(P'–H)$ 36.5 Hz), 0.40 (9H, CH_3, d, $^2J(P–H)$ 8.5 Hz), 1.51 (9H, CH_3, d, $^2J(P–H)$ 8.5 Hz), 1.89 (3H, CH_2, m,), 2.00 (9H, CH_3, d, $^2J(P–H)$ 8.5 Hz), 2.07 (3H, CH_2, m), 2.19 (9H, CH_3, d, $^2J(P–H)$ 8.5 Hz), 2.51 (3H, CH_2, m), 2.60 (3H, CH_2, m,). RMN $^{13}C\{^1H\}/\delta$: 14.71 (CH_3, d, $^1J(C–P)$ 66.5 Hz), 20.66 (CH_3, d, $^1J(C–P)$ 136.5 Hz), 21.60 (CH_3, d, $^1J(C–P)$ 78.0 Hz), 21.82 (CH_3, d, $^1J(C–P)$ 62.0 Hz), 28.59 (CH_2, m), 28.86 ppm (CH_2, m). ESI-MS (CH_3CN, 20 V): *m/z* (%) 868.9 (100) [M$^+$].

$[Mo_3S_4H_3((R,R)-Me-BPE)_3]Cl$ (**[2]Cl**). To a suspension of $[Mo_3S_4Cl_3((R,R)-Me-BPE)_3]Cl$ (0,150 g, 0,112 mmol) in dry THF (15 mL) was added $LiBH_4$ (0.074 g, 3.398 mmol), and then the mixture was stirred under a nitrogen atmosphere. After 48 h, the reaction mixture was filtered to remove the excess reducing agent and inorganic salts formed. Then, solvent was removed under a vacuum, and the solid was recrystallized from CH_2Cl_2/ether mixtures. The resulting solid was washed with water, isopropanol, and ether to yield 78 mg of the hydride product (yield: 56.4%). Found $Mo_3ClS_4P_6C_{42}H_{87}$ (%): C, 41.03; H, 7.15. Requires (%): C, 40.70; H, 6.91%. RMN $^{31}P\{^1H\}$ (CDCl_3, 121 MHz) δ: 59.56 (d, 3P), 86.84 ppm (d, 3P). RMN ^1H (CD_2Cl_2, 300 MHz) δ: −2.37 (dd, 3H *hydride*, $^2J(P–H)$ 36.44, $^2J(P'–H)$ 63.37 Hz). RMN $^{13}C\{^1H\}$ (CD_2Cl_2, 300 MHz) δ: 13.19 (CH_3, d), 14.73 (CH_3, d), 17.87 (CH_3, d), 18.04 (CH_3, d), 24.98 (CH, d), 25.12 (CH, d), 26.03 (CH, d), 26.13 (CH, d), 35.12 (CH_2, d), 35.75 (CH_2, d), 38.37 (CH_2, d), 39.0 (CH_2, d), 40.14 (CH_2, d), 41.87 ppm (CH_2, d). IR (KBr) cm^{-1}: 2923 (i), 2862 (i), 1450 (i), 1407 (m), 1369 (m), 1068 (m), 696 (m),

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Table 1. Crystallographic Data for $[Mo_3S_4H_3(dmpe)_3](BPh_4)\cdot1/2CH_2Cl_2$ ([**1**]$BPh_4\cdot1/2CH_2Cl_2$), $[W_3S_4Br_3((R,R)\text{-Me-BPE})_3]Br\cdot1/2CH_2Cl_2$ ([**3**]$Br\cdot1/2CH_2Cl_2$), and $[W_3S_4H_3((R,R)\text{-Me-BPE})_3]Br$ ([**4**]Br)

compound	[**1**](BPh₄)·1/2CH₂Cl₂	[**3**]Br·1/2CH₂Cl₂	[**4**]Br
empirical formula	$C_{42.50}H_{69}BClMo_3P_6S_4$	$C_{42.50}H_{85}Br_4ClP_6S_4W_3$	$C_{42}H_{87}W_3S_4P_6Br$
fw	1228.12	1816.81	1534.61
cryst syst	triclinic	monoclinic	trigonal
a, Å	15.2759(17)	12.0152(9)	14.9636(10)
b, Å	15.9639(18)	19.7370(15)	
c, Å	16.1002(18)	15.0015(12)	23.254(3)
α, deg	119.268(2)		
β, deg	105.991(3)	98.948(2)	
γ, deg	98.261(3)		
V, Å³	3105.8(6)	3520.7(5)	4509.2(7))
T, K	293(2)	293(2)	293(2)
space group	$P\bar{1}$	$P2(1)$	$R3$
Z	2	2	3
μ(Mo Kα), mm^{-1}	0.953	7.476	6.714
reflns collected	16886	19168	8163
ϕ range for data collection	1.47 to 25.00	1.37 to 25.00	1.80 and 26.00
unique reflns/R_{int}	10441 [R(int) = 0.0338]	11606 [R(int) = 0.0544]	3780 [R(int) = 0.0275]
Goodness-of-fit on F²	1.125	0.960	1.056
R1^a/wR2^b	R1 = 0.0745, wR2 = 0.2252	R1 = 0.0564, wR2 = 0.1484	R1 = 0.0301, wR2 = 0.0820
R1^a/wR2^b (all data)	R1 = 0.1010, wR2 = 0.2459	R1 = 0.0815, wR2 = 0.1684	R1 = 0.0350, wR2 = 0.0863
residual ρ/e A^{-3}	3.063 (0.99 Å from Mo) and −0.662	3.943 (0.96 Å from W) and −1.502	1.646 and −1.041

^{a} R1 = $\sum||F_o| - |F_c||/\sum F_o$. ^{b} wR2 = $[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

635 (m), 458 (d). CD (1.15×10^{-4} M, CH₂Cl₂) λ nm (mdeg): 531 (−36), 347 (−9), 288 (53), 240 (−74), 231 (43). UV−vis (CH₂Cl₂): λ (ε) 548 (1414), 436 (3545), 387 (3975.41), 244 nm (40 540 mol^{-1} m³ cm^{-1}). ESI-MS (CH₃CN, 20 V): m/z (%) 1193 (100) [M$^+$].

[W₃S₄Br₃((*R,R*)-Me-BPE)₃]Br ([3]Br). This compound was prepared by an excision reaction of the polymer {W₃S₇Br₄}$_n$ (0.200 g, 0.183 mmol with (*R,R*)-Me-BPE (0.212 g, 0.821 mmol)) in 20 mL of dried CH₃CN under reflux. After 24 h, the reaction mixture was filtered, the filtrated was taken to dryness under a vacuum, and the solid was dissolved in dichloromethane. The addition of ether (30 mL) caused the complete precipitation of a blue solid, which was recrystallized from CH₂Cl₂/ether mixtures and washed with toluene/acetone (95:5) mixtures to afford 307 mg of the desired product (yield: 95%). Found W₃Br₄S₄P₆C₁₈H₄₈ (%): S, 7.22; C, 28.43; H, 4.78. Requires (%): S, 6.93; C, 28.37; H, 4.72. RMN ^{31}P{^{1}H} (CD₂Cl₂, 121 MHz) δ: 31.69 (dd, 3P, $^2J_{\text{P-Pgem}}$ = 2.56 Hz, $^3J_{\text{P-Ptrans}}$ = 3.70 Hz), 35.90 (dd, 3P, $^2J_{\text{P-Pgem}}$ = 2.64 Hz, $^3J_{\text{P-Ptrans}}$ = 3.45 Hz) (AA′A″BB′B″ system). RMN ^{13}C{^{1}H} (CD₂Cl₂, 300 MHz) δ: 15.41 (CH₃, d), 16.85 (CH₃, d), 19.12 (CH₃, d), 20.79 (CH₃, d), 25.47 (CH, d), 25.61 (CH, d), 27.81 (CH, d), 27.99 (CH, d), 32.60 (CH₂, d), 35.5 (CH₂, s), 35.8 (CH₂, d), 39.75 (CH₂, d), 41.96 (CH₂, d), 43.10 ppm (CH₂, d). IR (KBr) cm^{-1}: 2923 (i), 2858 (i), 2130 (d), 1453 (i), 1410 (m), 1066 (m), 924 (i), 730 (d), 630 (m), 453 (m). CD (1.13×10^{-4} M, CH₂Cl₂) λ nm (mdeg): 543 (−33), 405 (−62), 326 (89), 292 (−28), 271 (143), 248 (175). UV−vis (CH₂Cl₂): λ (ε) 325 (13 360), 278 (20 190), 238 nm (31 580 mol^{-1} m³ cm^{-1}). ESI-MS (CH₂Cl₂, 20 V): m/z(%) = 1694 (100) [M$^+$].

[W₃S₄H₃((*R,R*)-Me-BPE)₃]Br ([4]Br). This compound was prepared following the same procedure for [**2**]Cl but in this case using *P*-[W₃S₄Br₃((*R,R*)-Me-BPE)₃]Br (0.060 g, 0.034 mmol) as a starting material and LiBH₄ (0.022 g, 1.010 mmol) in 10 mL of dry THF. The reaction occurred with a color change from blue to pink, and after 6 h the mixture was filtered. The filtrate was taken to dryness and then was dissolved in a minimum of dichloromethane. The addition of ether caused the complete precipitation of the pink product, which was then washed with water, isopropanol, and ether successively to afford 39 mg of *P*-[W₃S₄H₃((*R,R*)-Me-BPE)₃]Br (yield: 75%). Found W₃S₄P₆C₄₈H₈₇Br (%): S, 8.32; C, 32.80; H, 5.71. Requires (%): S, 7.82; C, 32.45; H, 5.63. RMN ^{31}P{^{1}H} (CD₂Cl₂, 121 MHz) δ: 27.04 (s, 3P), 56.58 (s, 3P). RMN ^{1}H (CD₂Cl₂, 300 MHz) δ: −0.408 (dd, 3H *hydride*, ^{2}J(P−H) 29.91, ^{2}J(P′−H) 47.65 Hz). RMN ^{13}C{^{1}H} (CD₂Cl₂, 300 MHz) δ: 12.48 (CH₃, d), 14.01 (CH₃, d), 16.99 (CH₃, d), 18.66 (CH₃, d), 25.88 (2 CH, c), 27.03 (2 CH, c), 34.79 (CH₂, d), 35.05 (CH₂, s), 37.91 (CH₂, d), 39.61 (CH₂, d), 40.25 (CH₂, d), 43.17 ppm (CH₂, d). IR (KBr) cm^{-1}: 1709 (m,

W−H), 953 (i), 940 (i), 848 (i), 557 (d), 439 (d, W-μ_3S), 423 (d, W-μ_3S), 355 (d). CD (1.18×10^{-4} M, CH₂Cl₂) λ nm (mdeg): 482 (−52), 394 (28), 308 (−45), 269 (+11), 235 nm (−47). UV−vis (CH₂Cl₂): λ (ε) 502 (1654), 311 (8426), 236 nm (27891 mol^{-1} m³ cm^{-1}). ESI-MS (CH₃CN, 10 V) m/z (%): 1457 (100) [M$^+$].

Kinetic Experiments. The kinetics of reaction of the **2**$^+$ and **4**$^+$ clusters with acids were studied at 25.0 °C using an Applied Photophysics SX17MV stopped-flow instrument provided with a PDA1 diode-array detector, and the results were analyzed with the SPECFIT program.[20] All experiments were carried out in dichloromethane solutions of the cluster salt and the acid. The complex solutions were prepared at concentrations $(0.8−9.0) \times 10^{-4}$ mol· dm^{-3}, and preliminary experiments at two or three different concentrations were carried out in all cases to confirm the first order dependence of the observed rate constants with respect to the complex concentration. Solutions of HCl in dichloromethane were prepared by mixing the required amounts of chlorotrimethylsilane and methanol. The acid solutions were used within 2−3 h from preparation, and their concentrations were determined by titration with KOH (phenolphthalein indicator) of solutions resulting from adding an aliquot (3 mL) to 50 mL of water and stirring vigorously for 20 min. Most experiments were carried out under pseudo-first-order conditions of acid excess, and the analysis required the use of a multistep kinetic model.

X-Ray Studies. The crystals are air stable and were mounted on the tip of a glass fiber with the use of epoxy cement. X-ray diffraction experiments were carried out on a Bruker SMART CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å) at room temperature. The data were collected with a frame width of 0.3° in ω and a counting time of 10 s per frame. The diffraction frames were integrated using the SAINT package and corrected for absorption with SADABS.[21,22] The structures were solved by direct methods and refined by the full-matrix method based on F² using the SHELXTL software package.[23] The crystal parameters and basic information relating data collection and structure refinement for compounds [**1**](BPh₄)·1/2CH₂Cl₂, [**3**]Br·1/2CH₂Cl₂ and [**4**]Br are summarized in Table 1.

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For compound [**1**](BPh$_4$)·1/2CH$_2$Cl$_2$, all atoms in the **1**$^+$ cluster cation and the BPh$_4$$^-$ anion were refined anisotropically. The positions of all hydrogen atoms in the diphosphine ligands and BPh$_4$$^-$ anion were generated geometrically, assigned isotropic thermal parameters, and allowed to ride on their respective parent carbon atoms. In the last stages of the refinement, half a molecule of CH$_2$Cl$_2$ was located and refined isotropically as a rigid group. Hydrogen atoms from this CH$_2$Cl$_2$ molecule were fixed at calculated positions and included in the refinement. For compound [**3**]Br·1/2CH$_2$Cl$_2$, all atoms in the **3**$^+$ cluster cation and the bromine anion were refined anisotropically. Several C—C bond distances of the noncrystallographically equivalent five-membered rings of the Me—BPE ligands (C(7)—C(8), C(9)—C(10), C(11)—C-(12), C(13)—C(14), C(18)—C(19), C(24)—C(25), C(26)—C(27), and C(29)—C(30)) were constrained to a fixed value (typically 1.48 Å). The positions of all hydrogen atoms in the diphosphine ligands were generated geometrically, assigned isotropic thermal parameters, and allowed to ride on their respective parent carbon atoms. In the last stages of the refinement, half a molecule of CH$_2$Cl$_2$ was located and refined isotropically as a rigid group. Hydrogen atoms from this CH$_2$Cl$_2$ molecule were fixed at calculated positions and included in the refinement. For compound [**4**]Br, all atoms in the **4**$^+$ cluster cation and the bromine anion were refined anisotropically. The C(3)—C(4) bond distance of one five-membered ring of the Me—BPE ligands was constrained to a fixed value (typically 1.48 Å). The positions of all hydrogen atoms in the diphosphine ligands were generated geometrically, assigned isotropic thermal parameters, and allowed to ride on their respective parent carbon atoms. A high electronic positive residual density ca. 3.0 e/Å^3 for [**1**]BPh$_4$ and ca. 3.9 e/Å^3 for [**3**]Br stage remained in the last refinement, and in both cases these residual peaks were located at distances below 1 Å from the Mo(3) atom and W(1), respectively. A common feature of all three crystal structures is a moderate to high difference of the thermal parameters between neighbor atoms in the diphosphane backbone, dmpe for **1**$^+$ and Me-BPE for **3**$^+$ and **4**$^+$. Such differences are attributed to the commonly found solid state disorder in diphosphane—ethane complexes, which exists with two limit configurations: one with the two diphosphine backbone carbon located on different sides of the MoP(1)P(2) plane and the other with one of these two carbon atoms situated essentially in the MoP(1)P(2) plane.[24]

Results and Discussion

Synthesis, Structure, and Reactivity. Molybdenum hydride complexes are proved more difficult to isolate than their tungsten congeners as a result of their inherent instability.[25] The first reported synthesis of a cuboidal W$_3$S$_4$ trinuclear cluster hydride appeared in 1989 by conversion of the chloro [W$_3$S$_4$Cl$_3$(diphoshine)$_3$]$^+$ (diphosphine = dmpe, depe) species to hydrido species according to eq 1.[26]

$$[W_3S_4Cl_3(\text{diphosphine})_3]^+ + BH_4^- \text{ (excess)}$$
$$\rightarrow [W_3S_4H_3(\text{diphosphine})_3]^+ \qquad (1)$$
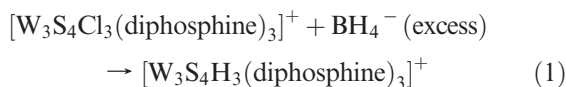
Attempts to extend this procedure to the analogous molybdenum system have not provided a definite proof of the existence of these molybdenum hydrides, although spectroscopic evidence of the formation of [Mo$_3$S$_4$H$_3$(dmpe)$_3$]$^+$ (**1**$^+$) cations using ^{31}P{^{1}H} NMR has been pointed out.[10] We have now been able to isolate the [Mo$_3$S$_4$H$_3$(dmpe)$_3$]-(BPh$_4$) salt in 80% yields by reacting its chloro precursor

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(26) Cotton, F. A.; Llusar, R.; Eagle, C. T. *J. Am. Chem. Soc.* **1989**, *111*, 4332–4338.
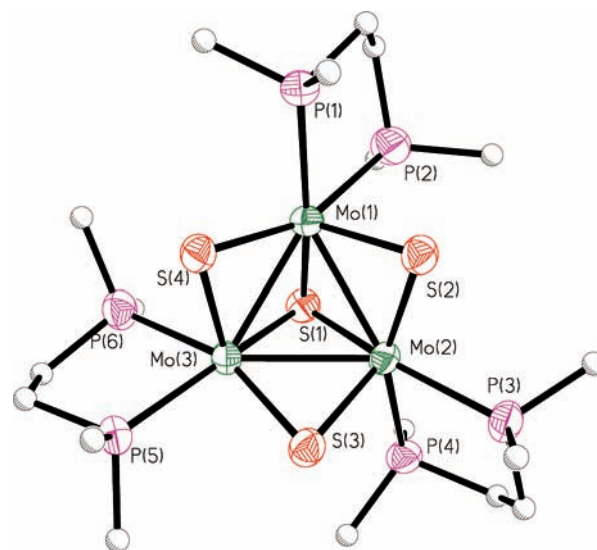

Figure 1. ORTEP representation of the cationic cluster [Mo$_3$S$_4$H$_3$-(dmpe)$_3$]$^+$ (**1**$^+$).

Table 2. Selected Averaged Bond Distances (Å) for Compounds [Mo$_3$S$_4$H$_3$-(dmpe)$_3$](BPh$_4$)·1/2CH$_2$Cl$_2$ ([**1**]BPh$_4$·1/2CH$_2$Cl$_2$), [W$_3$S$_4$Br$_3$((R,R)-Me-BPE)$_3$]Br·1/2CH$_2$Cl$_2$ ([**3**]Br·1/2CH$_2$Cl$_2$), and [W$_3$S$_4$H$_3$((R,R)-Me-BPE)$_3$]Br ([**4**]Br)

dist. (Å)^a	[**1**](BPh$_4$)	[Mo$_3$S$_4$Cl$_3$ (dmpe)$_3$(PF$_6$)^b	[**3**]Br	[**4**]Br
M—M	2.744[5]	2.766(4)	2.793[4]	2.7753(5)
M—(μ_3-S)	2.346[4]	2.360(9)	2.371[4]	2.364(3)
M—(μ-S)^c	2.329[4]	2.336(7)	2.289[5]	2.350(2)
M—(μ-S)^d	2.324[2]	2.290(7)	2.311[6]	2.334(2)
M—P(1)^e	2.467[12]	2.534(8)	2.559[3]	2.491(2)
M—P(2)^f	2.524[9]	2.605(8)	2.633[7]	2.548(2)

^{a}Standard deviations for averaged values are given in brackets. ^{b}Data taken from ref 26. ^{c}Distance *trans* to the Mo—P bond. ^{d}Distance *trans* to the Mo—X bond. ^{e}Distance *trans* to the M—(μ_3-S) bond. ^{f}Distance *trans* to the M—(μ-S) bond.

with a 9-fold excess of NaBH$_4$ in THF. An ORTEP drawing of the **1**$^+$ cation is represented in Figure 1.

The molybdenum and sulfur atoms in **1**$^+$ occupy adjacent vertices in a cube with a metal position missing, which results in an incomplete cubane-type structure. The three metal atoms define an approximately equilateral triangle with Mo—Mo bond distances of 2.744 [5] Å in agreement with the presence of a single metal—metal bond and a +4 oxidation state for the metal. The nature of the Mo$_3$(μ_3-S)-(μ-S)$_3$ core in **1**$^+$ is such that the bridging and capping sulfur atoms occupy a set of facial positions around the octahedrally coordinated metal atoms, leaving the three outer facial sites available for the two phosphorous atoms of the diphosphine and an apparently empty site occupied by a hydrogen atom. The existence of three hydride ligands, one on each Mo atom, has been fully supported by ^{1}H NMR spectroscopy. The proton spectrum of [Mo$_3$S$_4$H$_3$-(dmpe)$_3$]$^+$ shows a doublet of doublets in the hydride region centered at $\delta = -2.95$ ppm, attributed to the splitting of the two nonequivalent phosphorous atoms bonded to the same metal with ^{2}J(P—H) coupling constants of 62.8 and 36.5 Hz. Table 2 contains a list of important bond distances and angles. The metal—metal and metal—sulfur distances within the Mo$_3$S$_4$ cluster core follow the tendencies observed for other trinuclear M$_3$Q$_4$ (M = Mo, W; Q = S, Se) species. The Mo—(μ_3-S) distance in **1**$^+$ is approximately 0.02 Å
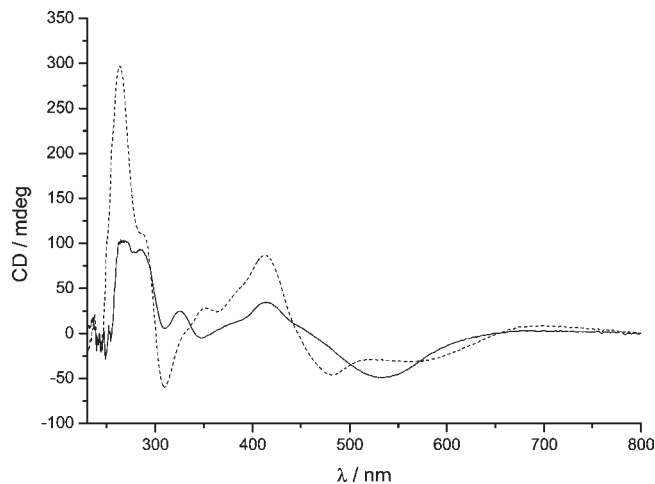
Figure 2. Circular dichroism spectra of *P*-[Mo$_3$S$_4$Cl$_3$((*R,R*)-Me-BPE)$_3$]-Cl (---) and *P*-[Mo$_3$S$_4$H$_3$((*R,R*)-Me-BPE)$_3$]Cl (*P*-[**2**]Cl; —) in dichloromethane at 25 °C.

Figure 3. Circular dichroism spectra of *P*-[W$_3$S$_4$Br$_3$((*R,R*)-Me-BPE)$_3$]-Br ([**3**]Br; ---) and *P*-[W$_3$S$_4$H$_3$((*R,R*)-Me-BPE)$_3$]Br ([**4**]Br, —) in dichloromethane at 25 °C.

longer than the average Mo−(μ-S) bond lengths, and there are two kinds of Mo−(μ-S) distances. The substitution of a chloride ligand in the [Mo$_3$S$_4$Cl$_3$(dmpe)$_3$]$^+$ starting material by hydrogen is reflected in the Mo−(μ-S) distance *trans* to that position that increases by approximately 0.034 Å in the hydrido cluster due to the higher *trans* influence of the hydride versus the chloride ligand. The specific coordination of the diphosphine ligand in **1**$^+$, with one phosphorous atom *trans* to the capping sufur atom and the other trans to the bridging sulfur atom, results in cubane-type sulfido clusters with backbone chirality. In this case, complex **1**$^+$ is obtained as a racemic mixture of the P and M enantiomers. The P and M symbols refer to the rotation of the H atom around the *C*$_3$ axis, with the capping sulfur atom pointing toward the viewer.

Following the same synthetic strategy used for the preparation of **1**$^+$, we have also been able to isolate the optically pure *P*-[Mo$_3$S$_4$H$_3$((*R,R*)-Me-BPE))$_3$]Cl salt ([**2**]Cl) also starting from its chloride precursor, this time by reaction with lithium borohydride, in 56% yield. Furthermore, the stereochemistry of the starting material is preserved in the final product as evidenced from the identical signal pattern of the circular dichroism spectra, represented in Figure 2. The circular dichroism spectrum of [**2**]Cl shows two signals at λ_{max}= 267 and 417 nm for +101 and +35 mdeg, respectively, as in the case of its *P*-[Mo$_3$S$_4$Cl$_3$((*R,R*)-Me-BPE))$_3$]$^+$ precursor that also shows two bands at λ_{max} = 265 and 416 nm for +290 and +35 mdeg, respectively.

For comparative purposes, the tungsten *P*-[W$_3$S$_4$H$_3$-((*R,R*)-Me-BPE)$_3$]Br ([**4**]Br) analogue was synthesized starting from its bromide precursor, which in turn was prepared by excision of the polymeric {W$_3$S$_7$Br$_4$}$_n$ phases in acetonitrile in the presence of the optically pure (*R,R*)-Me-BPE diphosphine. As reported for the molybdenum system, the reaction turned out to be enantioselective with the exclusive formation of the *P*-[W$_3$S$_4$Br$_3$((*R,R*)-Me-BPE)$_3$]Br ([**3**]Br) enantiomer as judged by X-ray single crystal analysis and circular dichroism spectroscopy.[18] The [**4**]Br tungsten hydride presents the same signal sequence as its halide [**3**]Br precursor in its circular dichroism spectrum (see Figure 3), as seen in the molybdenum
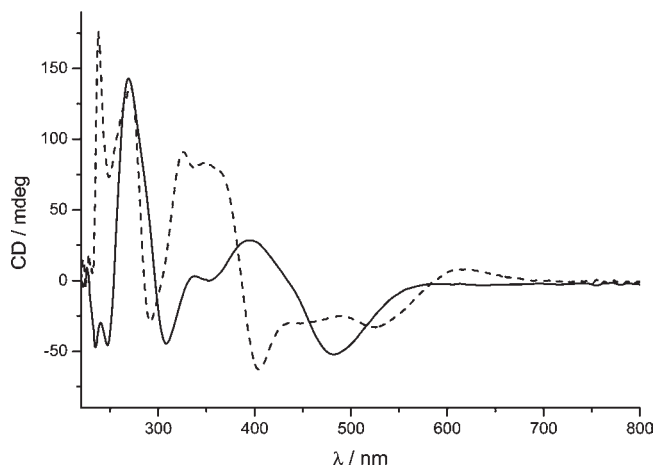
system, indicating that stereochemistry is preserved during the reaction. ORTEP views of **3**$^+$ and **4**$^+$ cluster *P* enantiomers, where the capping sulfur atoms point against the viewer, are represented in Figure 4. A summary of selected bond distances for [**3**]Br and [**4**]Br is given in Table 2. Again, we observe that substitution of a bromide ligand in **3**$^+$ by hydrogen produces an increase in the Mo−(μ-S) distance *trans* to that position of approximately 0.023 Å due to the higher *trans* influence of the hydride versus the bromide ligand. Complexes **3**$^+$ and **4**$^+$ share structural features with other [M$_3$Q$_4$X$_3$(diphosphine)$_3$]$^+$ compounds reported up to date.[3] The metal−metal distances are in the range (2.73−2.83 Å) found for other M$_3$S$_4$ complexes. The two types of W−P distances differ by 0.06−0.07 Å with the one *trans* to the capping sulfur atom being shorter.

The availability of a series of complexes [M$_3$S$_4$H$_3$-(diphosphine)$_3$]$^+$ with M = Mo and W containing two different diphosphine ligands, dmpe and (*R,R*)-Me-BPE, provides a unique opportunity to systematically investigate the influence of the metal and diphosphine basicity on the kinetics and reaction mechanisms of these hydrido species with acids. The kinetics of reaction with acids of [W$_3$Q$_4$H$_3$(dmpe)$_3$]$^+$ (Q = S, Se) cations in coordinating and noncoodinating solvents have been studied previously. In particular, when the reaction is carried out in dichloromethane, two competitive pathways showing a first and a second order dependence with respect to the acid are found, the second order pathway being the preferred one under pseudo-first-order conditions of acid excess.[7−9,12] Unfortunately, comparison with the Mo analogue was not possible because the reaction of the [Mo$_3$S$_4$H$_3$(dmpe)$_3$]$^+$ (**1**$^+$) hydride with acids could not be followed by stopped-flow techniques even under rigorous air-free conditions. No reproducible kinetic traces could be obtained for this reaction, most likely due to the lack of stability of the intermediates toward traces of oxygen. Fortunately, the molybdenum cluster **2**$^+$ containing the chiral diphosphine (*R,R*)-Me-BPE was more stable and allowed kinetic studies.

The molybdenum and tungsten trinuclear clusters [Mo$_3$S$_4$H$_3$((*R,R*)-Me-BPE)$_3$]$^+$ (**2**$^+$) and [W$_3$S$_4$H$_3$((*R,R*)-Me-BPE)$_3$]$^+$ (**4**$^+$) react with HCl in CH$_2$Cl$_2$ to form
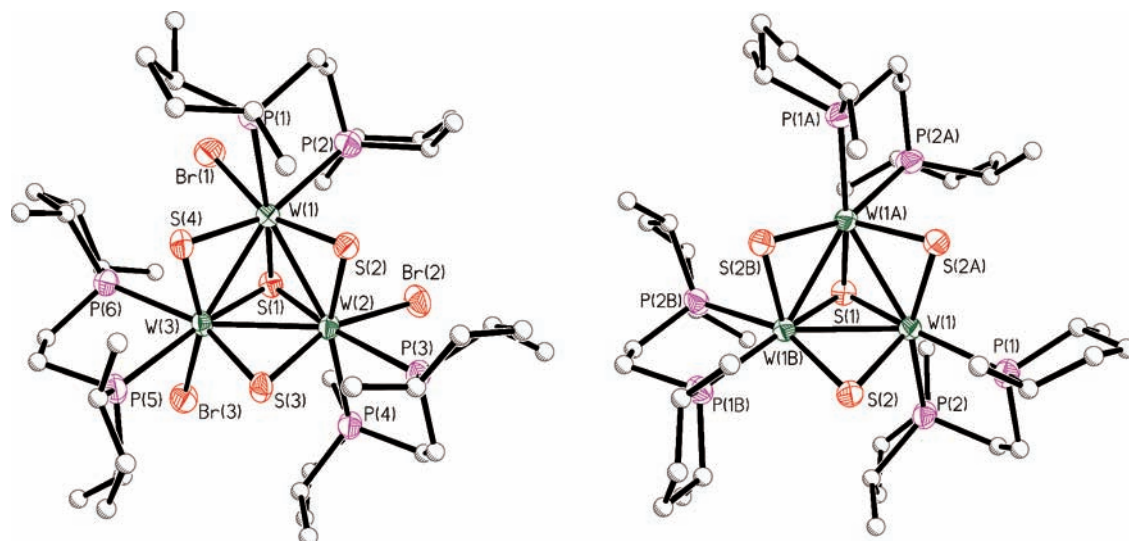
Figure 4. ORTEP representations of the cationic clusters P-[W$_3$S$_4$Br$_3$((R,R)-Me-BPE)$_3$]$^+$ (**3**$^+$; left) and P-[W$_3$S$_4$H$_3$((R,R)-Me-BPE)$_3$]$^+$ (**4**$^+$; right).
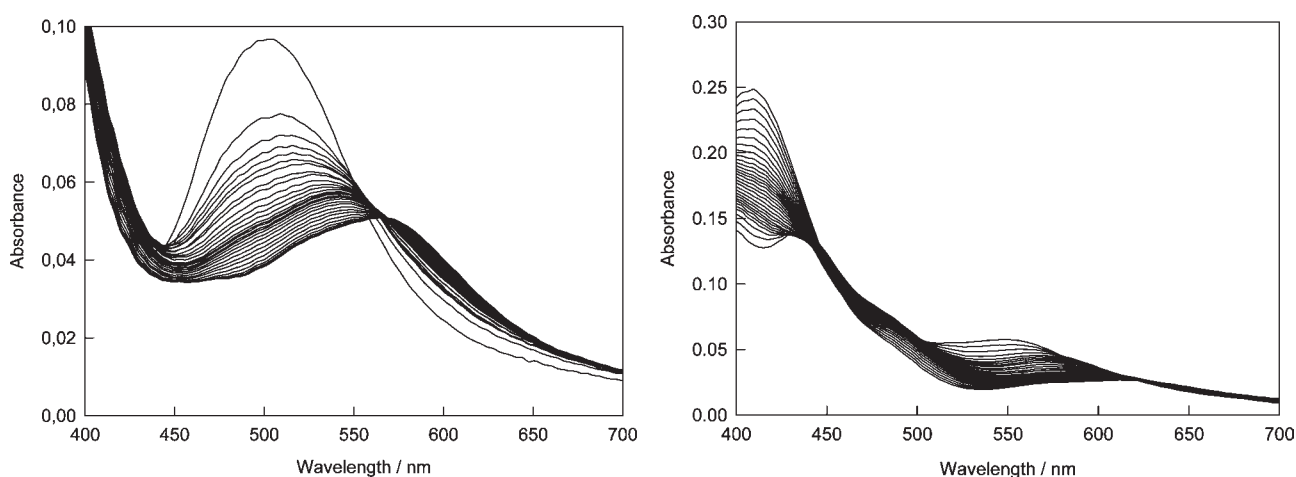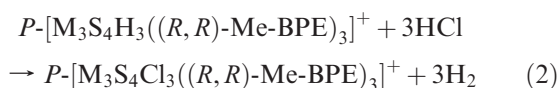

Figure 5. Typical spectral changes with time for the reaction of clusters **2**$^+$ (left) and **4**$^+$ (right) with HCl in CH$_2$Cl$_2$ solution at 25.0 °C.

[M$_3$S$_4$Cl$_3$((R,R)-Me-BPE)$_3$]$^+$, as represented in eq 2.

$$P\text{-}[M_3S_4H_3((R,R)\text{-Me-BPE})_3]^+ + 3HCl$$
$$\rightarrow P\text{-}[M_3S_4Cl_3((R,R)\text{-Me-BPE})_3]^+ + 3H_2 \quad (2)$$

No reaction is observed between these molybdenum and tungsten cluster hydrides and halide salts, as previously found for the [W$_3$Q$_4$H$_3$(dmpe)$_3$]$^+$ (Q = S, Se) system, suggesting that dihydrogen-bonded species are required to be formed as reaction intermediates in the course of the reaction. In contrast with the dmpe derivatives, the Mo and W hydride complexes containing the (R,R)-Me-BPE diphosphine ligand do not react with HCl in acetonitrile or acetonitrile/water mixtures, which shows that there is a significant basicity decrease in the hydride ligands when replacing dmpe for the less basic (R,R)-Me-BPE ligand. Fortunately, both compounds react with excess HCl in dichloromethane solutions, and this allowed a kinetic study on the effect of the nature of the metal center. Such a dramatic effect of solvent on the reactions of this kind of hydride clusters is not unprecedented, and the reasons that lead to the lack of reaction in acetonitrile solutions have

been discussed recently for the related [W$_3$PdS$_4$H$_3$(dmpe)$_3$-(CO)]$^+$.[27,28]

The Reaction of Clusters 2$^+$ and 4$^+$ with Acids: Kinetics of Reaction with HCl. In order to analyze the influence of the metal on the acid-assisted substitution process represented in eq 2, the kinetics of the reactions between clusters **2**$^+$ and **4**$^+$ with an excess of HCl in CH$_2$Cl$_2$ were investigated, and typical results of the stopped-flow experiments using a diode-array detector are illustrated in Figure 5. The formation of P-[M$_3$S$_4$Cl$_3$((R,R)-Me-BPE)$_3$]$^+$ (M = Mo, W) as the final reaction products was confirmed in independent NMR experiments. A detailed analysis of the spectral changes of the type shown in Figure 5 reveals that the reaction of both clusters with HCl occurs with three kinetically distinguishable steps with rate constants k_{1obs}, k_{2obs}, and k_{3obs}. For a given concentration of acid, no changes in the observed rate constants were observed when the concentration of any of both clusters was changed, which

(27) Basallote, M. G.; Algarra, A. G.; Feliz, M.; Fernandez-Trujillo, M. J.; Llusar, R.; Safont, V. S. *Chem.—Eur. J.* **2010**, 1613–1623.

(28) Algarra, A. G.; Basallote, M. G.; Feliz, M.; Fernandez-Trujillo, M. J.; Guillamon, E.; Llusar, R.; Vicent, C. *Inorg. Chem.* **2006**, *45*, 5576–5584.
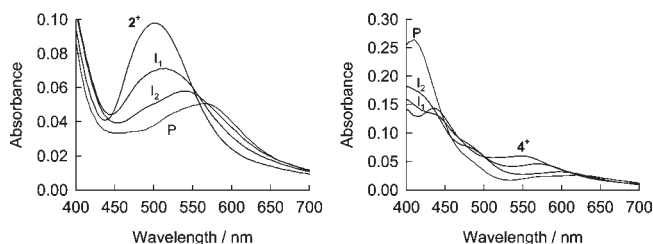
Figure 6. Electronic spectra calculated for the starting complex, the reaction intermediates, and the final reaction product from the spectral changes observed during the reaction of cluster 2^+ (left) and 4^+ (right) with HCl in CH_2Cl_2 solution at 25.0 °C.
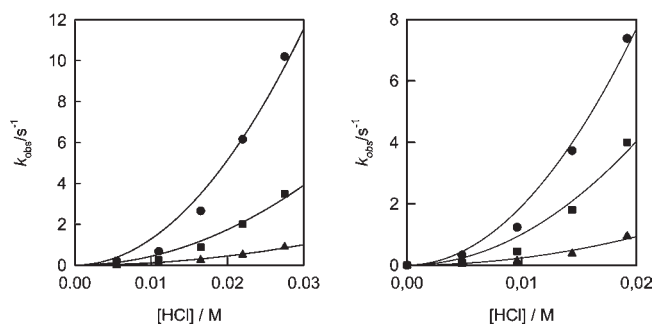

Figure 7. Plots of the observed rate constants versus [H$^+$] for the three steps in the reaction of 2^+ (left) and 3^+ (right) with HCl in CH_2Cl_2 solution at 25 °C.

Table 3. Rate Constants of the Different Steps Observed during the Protonation of 2^+ and 4^+ with HCl in CH_2Cl_2 at 25.0 °C^a

	2^+	4^+	$[W_3S_4H_3(dmpe)_3]^{+b}$
$10^{-4} \times k_1$ (M^{-2} s^{-1})	1.28 ± 0.07	1.9 ± 0.1	24.1 ± 0.6
$10^{-2} \times k_2$ (M^{-2} s^{-1})	4.3 ± 0.2	10 ± 3	103 ± 3
k_3 (M^{-2} s^{-1})	11.2 ± 0.5	23 ± 2	c
k_1/k_2	29.8	19	23.4
k_1/k_3	1143	826	
k_2/k_3	38.4	43.5	

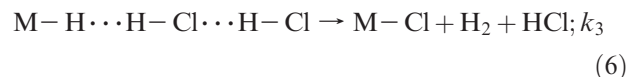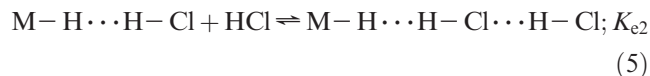^{a} For comparative purposes information about the cluster $[W_3S_4H_3(dmpe)_3]^+$ has also been included. ^{b} Data taken from ref 9. ^{c} The third step of this reaction is independent of the HCl concentration and has a value of 4 ± 1 10^{-3} s^{-1}.

indicates that all three steps show a first-order dependence on the cluster concentration. The analysis of the kinetic data also provides the electronic spectra calculated for the starting complexes (2^+ or 4^+), the reaction intermediates, and the final reaction products, which are shown in Figure 6. It is important to highlight, that in the case of the tungsten complex, all of the calculated spectra are very similar to those obtained for the reaction of the related $[W_3S_4H_3(dmpe)_3]^+$ cluster under the same conditions.[9]

For both complexes, the rate constants derived for the three steps change with the acid concentration according to eq 3 (see Figure 7), and the values of the corresponding third order rate constants as well as the k_1/k_2, k_1/k_3, and k_2/k_3 ratios are shown in Table 3. Attempts to improve the quality of the fits by including additional zero and first order terms with respect to the acid were unsuccessful because they led inevitably to negative values of those terms. On the other hand, alternative dependencies such as [H$^+$][Cl$^-$] can be ruled out[9] because HCl is a weak acid in organic solvents such as dichloromethane. The second order dependence with respect to the HCl concentration and the similarities between

the electronic spectra of the intervening species in the case of $[W_3S_4H_3(dmpe)_3]^+$ and 4^+ indicate that the mechanism of reaction between the acid and the coordinated hydride in 4^+ is the same as that for the previously studied $[W_3S_4H_3(dmpe)_3]^+$ cluster, with sequential participation of two HCl molecules in the initial formation of the dihydrogen-bonded species (eqs 4 and 5).[9] The second HCl molecule forms a hydrogen bond with the first one, which causes a decrease of the H$\cdots$H distance that facilitates H$_2$ release in the rate-determining step (eq 6).[9,12,27] If the initial equilibria are displaced toward the starting reagent, the rate law for the processes in eqs 4–6 has the same form as that of eq 3 with the equivalence $k_i = K_{e1}K_{e2}k_3$. As the process would be repeated for the three metal centers, three steps with a second order dependence with respect to the acid will be observed. It is interesting to note that significant deviations from statistically controlled kinetics are also observed; i.e., the rates of reaction at the three metal centers are in a ca. 1000:40:1 ratio, very far from the 3:2:1 ratio expected from statistical considerations. Although Sykes and Hernandez-Molina reported many examples that established firmly that substitution reactions in M_3S_4 aqua cluster complexes occur with statistically controlled kinetics,[6] we have found that deviations appear in some cases, especially when reactions are carried out in organic solvents. On the other hand, the values of k_1 in Table 3 for the W complexes 4^+ and $[W_3S_4H_3(dmpe)_3]^+$ indicate that substitution of dmpe by a bulkier diphosphine such as (R,R)-Me-BPE leads to a decrease in the rate of reaction of about 1 order of magnitude. With regard to the effect of the metal center, the values in Table 3 indicate that both clusters 2^+ and 4^+ react with similar rates with HCl, the quotient k_W/k_{Mo} between rate constants corresponding to the same resolved kinetic step, being in all cases close to 2.

$$k_{iobs} = k_i[HX]^2 \tag{3}$$

$$M-H + HCl \rightleftharpoons M-H\cdots H-Cl; K_{e1} \tag{4}$$

$$M-H\cdots H-Cl + HCl \rightleftharpoons M-H\cdots H-Cl\cdots H-Cl; K_{e2} \tag{5}$$

$$M-H\cdots H-Cl\cdots H-Cl \rightarrow M-Cl + H_2 + HCl; k_3 \tag{6}$$

Conclusions

In this paper, we report the synthesis of a novel hydride cluster of formula $[M_3S_4H_3((R,R)$-Me-BPE)$_3]^+$ (M = Mo, W; (R,R)-Me-BPE = (+)-1,2-bis-(2R, 5R)-2,5-(dimethylphos-pholan-1-yl)ethane). The molybdenum(IV) cluster hydride of formula $[Mo_3S_4H_3(dmpe)]^+$ (dmpe = (1,2-(bis)dimethylphos-phinoethane) has also been isolated. Both $[M_3S_4H_3((R,R)$-Me-BPE)$_3]^+$ (M = Mo, W) compounds react with HCl in CH_2Cl_2 in a way similar to that previously observed for $[W_3S_4H_3(dmpe)]^+$, three kinetically resolved steps being observed under acid excess and corresponding to the sequential substitution of the three hydride ligands by the anion of the acid. The values of the rate constants indicate that the steric effect associated with the bulkier (R,R)-Me-BPE chiral diphosphine

leads to a decrease in the rate constants as well as higher deviations of the kinetics with respect to the statistical behavior. The rate constants of the reaction between both $[M_3S_4H_3((R,R)\text{-Me-}BPE)_3]^+$ (M = Mo, W) compounds with HCl in CH_2Cl_2 are very similar, thus showing that the nature of the transition metal does not modify to a great extent the kinetics of the process. However, as the observed rate constants contain contributions from the initial formation of dihydrogen bonded adducts (eqs 4 and 5) and the rate-determining elimination of H_2 (eq 6), it is not possible to decide if the close values of the rate constants found for both metals indicate that there are no significant changes in any of the mechanistic steps or they result from compensating changes in the constants corresponding to the different contributions.

Supporting Information Available: Crystallographic data (excluding structure factors) for the structures reported in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.