Mechanism of the Catalytic Hydrodefluorination of Pentafluoropyridine by Group Six Triangular Cluster Hydrides Containing Phosphines: A **Combined Experimental and Theoretical Study**

Tomás F. Beltrán,[†] Marta Feliz,[†] Rosa Llusar,^{*,†} Jose A. Mata,[‡] and Vicent S. Safont.[†]

[†]Departament de Química Física i Analítica, Universitat Jaume I, Avenida Sos Baynat s/n, 12071 Castelló, Spain, and ‡ Departament de Química Inorgànica i Orgànica, Universitat Jaume I, Avenida Sos Baynat s/n, 12071 Castelló, Spain

Received October 15, 2010

The catalytic hydrodefluorination (HDF) of pentafluoropyridine in the presence of arylsilanes is catalyzed by the tungsten and molybdenum(IV) cluster hydrides of formula $[M_3S_4H_3(dmpe)_3]^+$, W-1⁺ for M = W and Mo-1⁺ for M = Mo (dmpe = 1,2-(bis)dimethylphosphinoethane). The reaction proceeds regioselectively at the 4-position under microwave radiation to yield the 2,3,5,6-tetrafluoropyridine. Catalytic activity is higher for the tungsten complexes with turnover numbers close to 100, while reactions catalyzed by molybdenum compounds are faster. A mechanism for the HDF reaction has been proposed that explains these differences based on DFT calculations. The mechanism involves partial decoordination of the diphosphine ligand that generates an empty position in the metal coordination sphere. This position together with its neighbor M-H site are used to activate the C-F bond of the pentafluoropyridine through a M-H/C-F σ -bond metathesis mechanism involving a four-center transition state to give 2,3,5,6-tetrafluoropyridine. Subsequent coordination of the dangling diphosphine affords the *para*-substituted product and the $[M_3S_4F_3(dmpe)_3]^+$. W-2⁺ for M = W and Mo-2⁺ for $M = M_0$, cluster fluoride. The structure of W-2⁺ has been determined by single-crystal X-ray diffraction experiments. In the presence of silanes the calculated mechanism for the cluster hydride regeneration also implies three steps: (i) partial decoordination of the diphosphine, (ii) M-F/Si-H σ -bond metathesis, and (iii) coordination of the dangling diphosphine, to afford the cluster hydride.

Introduction

Organofluorine compounds find widespread applications in pharmaceutical, agrochemical materials, and other industries.¹⁻³ High electronegativity, low polarizability, and the small covalent radius of the fluorine atom together with the great strength of the C-F bond make difficult the chemical modification of organic fluoro compounds, rendering catalytic selective functionalization of carbon-fluorine bonds a major challenge in synthetic chemistry.⁴⁻⁶ The majority of the corresponding catalysts are based on late transition metals, although in recent years they are competing with early transition metal complexes and Lewis-acidic maingroup species.⁷ The nature of the metal has a significant effect on the activation of C-F bonds with regard to activity

and chemo- and regioselectivity.8 In this regard it is of fundamental interest to gain a deeper understanding of the mechanism of the catalytic C-F bond transformation in order to design new transition metal complexes with a higher selectivity and discover unusual derivatization reactions.

ORGANOMETALLICS

In the case of fluoroaromatic and fluoroheteroaromatic compounds, group 10 metals have proved to be efficient in activating C-F bonds, for which the dominant mechanism involves oxidative addition of this bond to generate metal fluorine and metal carbon bonds.⁹⁻¹¹ Divergent behaviors are observed regarding the preference for C-F cleavage of pentafluoropyridine, and different reaction mechanisms have been proposed to account for differences in regioselectivity. For example, recent studies demonstrated that phosphino ligands in nickel complexes can participate as fluorine atom acceptors, providing alternative phosphine-assisted C-F activation pathways through a four-centered transition state, where the substitution at the 2-position of fluorinated pyridines

^{*}Corresponding author. Fax: +34 964 728066. Tel: +34 964 728086. E-mail: Rosa.Llusar@qfa.uji.es.

⁽¹⁾ Smart, B. E. J. Fluorine Chem. 2001, 109, 3-11.

⁽²⁾ Muller, K.; Faeh, C.; Diederich, F. Science 2007, 317, 1881–1886. (3) Purser, S.; Moore, P. R.; Swallow, S.; Gouverneur, V. Chem. Soc.

Rev. 2008, 37, 320-330.

⁽⁴⁾ Richmond, T. G. Angew. Chem., Int. Ed. 2000, 39, 3241-3244.

⁽⁵⁾ Albietz, P. J.; Houlis, J. F.; Eisenberg, R. Inorg. Chem. 2002, 41, 2001-2003.

⁽⁶⁾ Hughes, R. P.; Laritchev, R. B.; Zakharov, L. N.; Rheingold, A. L. J. Am. Chem. Soc. 2004, 126, 2308-2309.

⁽⁷⁾ Amii, H.; Uneyama, K. Chem. Rev. 2009, 109, 2119-2183.

⁽⁸⁾ Braun, T. In Comprehensive Organometallic Chemistry; Crabtree,

R. H., Mingos, D. M. P., Eds.; Elsevier: 2007; Vol. 1, pp 725–758.
 (9) Torrens, H. Coord. Chem. Rev. 2005, 249, 1957–1985.

⁽¹⁰⁾ Nova, A.; Erhardt, S.; Jasim, N. A.; Perutz, R. N.; Macgregor, S. A.; McGrady, J. E.; Whitwood, A. C. *J. Am. Chem. Soc.* **2008**, *130*, 15499-15511

⁽¹¹⁾ Schaub, T.; Fischer, P.; Steffen, A.; Braun, T.; Radius, U.; Mix, A. J. Am. Chem. Soc. 2008, 130, 9304-9317.

Article

is favored.¹² As previously mentioned, activation of C-F bonds is not restricted to electron-rich metals; to a lesser extent, electron-poor metal compounds such as zirconocenes also exhibit good performances for the hydrodefluorination (HDF) of pentafluoropyridine. Rosenthal and co-workers reported that zirconocene hydrides exhibit a significantly better performance for the hydrodefluorination of pentafluoropyridine than rhodium hydrido complexes, for which, in addition, high hydrogen pressures are required.¹³ Lentz et al. have also shown that, in the presence of silanes, titanocene dihalides can catalytically defluorinate fluoroalkenes, leading to less fluorinated compounds through a mechanism that implies the formation of the titanocene hydride and further olefin insertion followed by β -fluoride elimination.¹⁴ All these pieces of evidence point to the potential of electronically poor transition metal complexes in the catalytic activation of C-F bonds.

Metal hydrides play a crucial role in the catalytic HDF of organic fluorides promoted by early transition metals, where activation takes place at the hydride site to yield fluoride complexes.¹⁵ In the catalytic cycle, the fluoride ligand is replaced by a hydride ligand upon reaction with silanes, e.g., in Holland's catalytic cycle, shown in Schme 1, for the HDF of perfluoroaromatics and perfluoroalkenes promoted by β -dikeminate iron(II) fluoride species.¹⁶ The driving force for the reaction is the formation of a strong Si–F bond. Surprisingly, the iron hydride complexes obtained by reaction of iron fluoride with silanes do not show evidence for direct C–F activation in the absence of silane, preventing the complete elucidation of the reaction mechanism.

In the past years we have undertaken a full mechanistic study on the reaction of trinuclear cluster hydrides of formula $[M_3Q_4H_3(diphosphine)_3]^+$ (Q = S, Se; M = Mo, W) with acids.^{17–21} These studies include aspects such as solvent effects, ion pairing, phosphine basicity, and chalcogen and metal substitution. In the course of this work we found evidence that these trinuclear metal hydrides react with fluorinated inorganic compounds activating B–F bonds and potentially C–F bonds.²² We now report that HDF of pentafluoropyridine can be carried out catalytically using incomplete cuboidal group 6 transition metal cluster

Scheme 1. Holland's HDF Catalytic Cycle



chalcogenides. The isolation of M₃S₄ phosphino fluoride complexes combined with a complete DFT investigation of the potential reaction pathways has allowed us to propose a hydrodefluorination mechanism that explains the differences in activity between molybdenum and tungsten. To our knowledge, this study constitutes the first report on catalytic organofluoride HDF by group 6 transition metal cluster complexes. Examples of C-F bond activation by group 6 transition metal complexes are scarce. Nevertheless, the first organometallic system for activating C-F bonds at room temperature was based on a tungsten(0) carbonyl complex that reacts through an intramolecular chelate-assisted oxidative addition of a fluorinated aromatic ligand.^{23,24} Richmond et al. successfully extended this chemistry to include reactions at molybdenum(0).²⁵ C-F activation of fluoroarenes has also been observed by molybdenum and tungsten cyclopentadienyl complexes.²⁶ All these examples on group 6 metals refer to electronically rich complexes, in contrast with the high-valent character of the molybdenum and tungsten cluster hydrides reported in the present work.

Results and Discussion

Synthesis and Structure of Fluorinated $[M_3S_4F_3(dmpe)_3]^+$ (M = Mo, W) Cluster Cations. The incomplete cuboidal $M_3(\mu_3-S)(\mu-S)_3$ group 6 hydrides of formula $[M_3S_4H_3 (dmpe)_3]^+$, which we refer to as M-1⁺, react with HX (X = Cl and Br) under mild conditions in a variety of solvents, which results in a formal substitution of the hydride by the coordinating chloride or bromide ligands. In this reaction protons play an important role in the process, and mechanistic studies support the formation of dihydrogen species as intermediates or transition states.^{19,22} Reactions with noncoordinating acids such as HBF4 were investigated and allowed us to identify the solvated [M₃S₄(solv)₃-(dmpe)₃]⁴⁺ species as intermediates. However, the identification of these intermediates was somehow hindered, as there was a slow formation of the fluoride substitution products $[M_3S_4H_{3-x}F_x(dmpe)_3]^+$ obtained by abstraction of fluoride from the tetrafluoroborate anion. Fluoride clusters are scarce compared with their chloride and bromide analogues, the only example of a thiofluoride group 6 trinuclear cluster being the $[Mo_3S_4F_7(FHF)_2]^{5-}$ anion obtained as a potassium salt.²

⁽¹²⁾ Nova, A.; Reinhold, M.; Perutz, R. N.; Macgregor, S. A.; McGrady, J. E. Organometallics **2010**, *29*, 1824–1831.

⁽¹³⁾ Jager-Fiedler, U.; Klahn, M.; Arndt, P.; Baumann, W.; Spannenberg, A.; Burlakov, V. V.; Rosenthal, U. J. Mol. Catal. A: Chem. 2007, 261, 184–189.

⁽¹⁴⁾ Kuhnel, M. F.; Lentz, D. Angew. Chem., Int. Ed. 2010, 49, 2933-2936.

⁽¹⁵⁾ Braun, T.; Noveski, D.; Ahijado, M.; Wehmeier, F. Dalton Trans. 2007, 3820-3825.

⁽¹⁶⁾ Vela, J.; Smith, J. M.; Yu, Y.; Ketterer, N. A.; Flaschenriem, C. J.; Lachicotte, R. J.; Holland, P. L. J. Am. Chem. Soc. 2005, 127, 7857–7870.

⁽¹⁷⁾ Basallote, M. G.; Estevan, F.; Feliz, M.; Fernandez-Trujillo, M. J.; Hoyos, D. A.; Llusar, R.; Uriel, S.; Vicent, C. *Dalton Trans.* 2004, 530–536.

⁽¹⁸⁾ Algarra, A. G.; Basallote, M. G.; Feliz, M.; Fernandez-Trujillo, M. J.; Guillamon, E.; Llusar, R.; Vicent, C. *Inorg. Chem.* **2006**, *45*, 5576–5584.

⁽¹⁹⁾ Algarra, A. G.; Basallote, M. G.; Feliz, M.; Fernandez-Trujillo, M. J.; Llusar, R.; Safort, V. S. *Chem. Eur. J.* **2006**, *12*, 1413–1426.

⁽²⁰⁾ Algarra, A. S. G.; Basallote, M. G.; Fernandez-Trujillo, M. J.; Llusar, R.; Safont, V. S.; Vicent, C. *Inorg. Chem.* **2006**, *45*, 5774–5784.

⁽²¹⁾ Algarra, A. G.; Basallote, M. G.; Fernandez-Trujillo, M. J.; Feliz, M.; Guillamon, E.; Llusar, R.; Sorribes, I.; Vicent, C. *Inorg. Chem.* **2010**, *49*, 5935–5942.

⁽²²⁾ Basallote, M. G.; Feliz, M.; Fernandez-Trujillo, M. J.; Llusar, R.; Safont, V. S.; Uriel, S. *Chem. Eur. J.* **2004**, *10*, 1463–1471.

⁽²³⁾ Richmond, T. G.; Osterberg, C. E.; Arif, A. M. J. Am. Chem. Soc. 1987, 109, 8091–8092.

⁽²⁴⁾ Asplund, M. C.; Johnson, A. M.; Jakeman, J. A. J. Phys. Chem. B 2006, 110, 20–24.

⁽²⁵⁾ Kiplinger, J. L.; Richmond, T. G.; Osterberg, C. E. *Chem. Rev.* **1994**, *94*, 373–431.

⁽²⁶⁾ Chernega, A. N.; Graham, A. J.; Green, M. L. H.; Haggitt, J.; Lloyd, J.; Mehnert, C. P.; Metzler, N.; Souter, J. *J. Chem. Soc., Dalton Trans.* **1997**, 2293–2303.

⁽²⁷⁾ Mironov, Y. V.; Yarovoi, S. S.; Solodovnikov, S. F.; Fedorov, V. E. J. Mol. Struct. **2003**, 656, 195–199.



Figure 1. ORTEP representation of the $W-2^+$ cation.

 $\label{eq:composition} \begin{array}{l} Table 1. Selected Averaged Bond Distances for Compounds \\ [W_3S_4H_3(dmpe)_3]BPh_4 \ ([W-1]BPh_4) \ and \ [W_3S_4F_3(dmpe)_3]BPh_4 \\ \quad ([W-2]BPh_4) \end{array}$

distance $(\text{\AA})^a$	[W-1]BPh4 ^b	[W-2]BPh ₄	
W-W	2.751[4]	2.750[12]	
$W-(\mu_3-S)$	2.354[2]	2.367[6]	
$W - \mu - S)^{c'}$	2.329[6]	2.343[5]	
$W - (\mu - S)^d$	2.341[4]	2.306[3]	
$W - \dot{P}(1)^{e}$	2.476[9]	2.517[9]	
$W - P(2)^{f}$	2.516[5]	2.558[2]	

^{*a*} Standard deviations for averaged values are given in brackets. ^{*b*} Data taken from ref 33. ^{*c*} Distance *trans* to the Mo–P bond. ^{*d*} Distance *trans* to the W–X bond (X = H or F). ^{*e*} Distance *trans* to the W–(μ_3 -S) bond. ^{*f*} Distance *trans* to the W–(μ -S) bond.

The lack of solubility of this salt in all common solvents has prevented the derivatization of this anion with other ligands, i.e., diphosphines. However, complexes of formula $[M_3S_4F_3(dmpe)_3]^+$, which we refer to as **M-2**⁺, can be conveniently prepared by reacting their hydride precursors with fluoride-containing anions in the presence of acids. Achieving the reaction requires excess of the fluorinated anion and the presence of protons. Quantitative transformation of $[M_3S_4H_3-(dmpe)_3]^+$ to the fluoride-substituted product is achieved by reaction with aqueous solutions of HPF₆ in acetonitrile/water mixtures according to eq 1.

$$[M_{3}S_{4}H_{3}(dmpe)_{3}]^{+}$$

$$+ HPF_{6}(excess) \rightarrow [M_{3}S_{4}F_{3}(dmpe)_{3}]^{+} \qquad (1)$$

$$M_{2}^{+}$$

The structure of the fluoride $[W_3S_4F_3(dmpe)_3]^+$ (W-2⁺) complex has been determined by single-crystal X-ray diffraction methods. An ORTEP drawing of the W-2⁺ cation is represented in Figure 1.

The metal and sulfur atoms in $W-2^+$ occupy adjacent vertices in a cube with a vacant metal position, which results in an incomplete cubane-type structure. The three metal atoms define an approximately equilateral triangle with W–W bond distances of 2.750 [12] Å, in agreement with the presence of a single metal-metal bond and a +4 oxidation state for the metal. Table 1 contains a list of important bond distances and angles. The metal-metal and metal-sulfur distances within the M₃S₄ cluster core follow the trends observed for other trinuclear M₃Q₄ (M = Mo, W; Q = S, Se) species. The W–(μ_3 -S) distance in W-2⁺ is approximately 0.02 Å longer



Figure 2. ESI-MS monitoring of the reaction between $W-1^+$ and pentafluoropyridine: (a) Initial time, (b) after 1 h under MW radiation, (c) after 2 h.

than the average $W-(\mu-S)$ bond lengths, and there are two kinds of W–(μ -S) distances. The substitution of a hydride ligand in the $[W_3S_4H_3(dmpe)_3]^+$ starting material by fluorine is reflected in the W– $(\mu$ -S) distance *trans* to that position, which decreases by approximately 0.034 Å in the fluoride cluster due to the lower trans influence of the fluoride versus the hydride ligand. The W-F distances in W- 2^+ of 2.001[6] Å are slightly shorter than those found for the [Mo₃S₄F₇- $(FHF)_2$ ⁵⁻ anion (2.043–2.140 Å).²⁷ The specific coordination of the diphosphine ligand in $W-2^+$, with one phosphorus atom trans to the capping sufur atom and the other trans to the bridging sulfur atom, results in incomplete cubane-type sulfido clusters with backbone chirality. These complexes show two signals in the ³¹P NMR spectra that correspond to the two sets of phosphorus atoms located above and below the metal plane defined by the three Mo or W atoms.

Stoichiometric and Catalytic HDF of Pentafluoropyridine with $[M_3S_4H_3(dmpe)_3]^+$ (M = Mo, W). Reactivity of the molybdenum and tungsten triangular cluster hydrides of formula $[M_3S_4H_3(dmpe)_3]^+$ with fluorinated compounds is not restricted to acidic media, as under more severe conditions these metal hydrides react with an excess of pentafluoropyridine upon microwave (MW) irradiation at 180 °C to afford the fluoride-substituted cluster complex according to eq 2.



The reaction was followed by ESI mass spectrometry. Sequential substitution of hydride by fluoride ligands for W-1⁺ is observed by the appearance of peaks at m/z 1151 [W₃S₄H₂F(dmpe)₃]⁺, 1169 [W₃S₄HF₂(dmpe)₃]⁺, and 1187 [W₃S₄F₃(dmpe)₃]⁺ for the tungsten cluster during the

Table 2. Catalytic Hydrodefluorination of Pentafluoropyridine^a

entry	catalyst	reaction time (h)	silane	yield $(\%)^b$	TON
1		3	HSiMe ₂ Ph	0	0
2	W-1 ⁺	3	HSiMe ₂ Ph	90	90
3	W-1 ⁺	16	Ph ₂ SiH ₂	29	29
4	W-2 ⁺	3	HSiMe ₂ Ph	31	31
5	$W-2^+$	12	Ph_2SiH_2	25	25
6	$Mo-1^+$	2	HSiMe ₂ Ph	60	60
7	$Mo-2^+$	2	HSiMe ₂ Ph	51	51

^{*a*} Reaction conditions: 1% cat., 0.38 mmol of fluoroarene, 1.9 mmol of silane, 1 mL of CH₃CN. ^{*b*} Yield based on ¹⁹F NMR using fluorobenzene as internal standard. ^{*c*} TON (mol of HDF product/mol of cat.).

ESI-MS reaction monitoring, illustrated in Figure 2. Complete transformation of the cluster hydride into the fluoride is achieved within two hours for Mo and three hours for W. The same reaction monitoring was observed by ¹H and ¹⁹F NMR. In the case of the ³¹P NMR, overlap of the resonances for the different species makes this technique inappropriate to follow the reaction. The W-1⁺ hydride ¹H NMR signal appears as a doublet of doublets centered at -0.80 ppm. After 1 h of reaction, this signal disappears as two new sets of signals appear downfied centered at -0.48 and -0.08 ppm due to the di- and monohydride species, respectively. The ¹⁹F resonance of the $W-2^+$ trifluoride is also clearly observed after one hour of reaction together with a complicated pattern of signals associated with the mono- and bisubstituted fluoride derivatives. At the end of the reaction (3 h for W), the only observed signal is that of $W-2^+$ at -199.7 ppm. A similar situation is found for the conversion of the **Mo-1**⁺ hydride into the **Mo-2**⁺ fluoride.

For both metal complexes, molybdenum and tungsten, the reaction requires energetic conditions (ca. 180 °C) in spite of its exothermicity. Hence, the process is expected to take place through a transition structure with a high activation barrier. DFT calculations have been conducted modeling the HDF process on one metallic site, and the results obtained for activation and reaction energies (ca. 40 and ca. -45 kcal/mol, respectively) nicely agree with the experiment; see below.

The resulting organofluoride product was identified as the 2,3,5,6-tetrafluoropyridine by GC and confirmed by ¹⁹F NMR by the appearance of two signals at $\delta = -140.1$ and -92.2 ppm, which correspond to the two sets of fluorine atoms characteristic of 2,3,5,6-tetrafluoropyridine.

Catalytic Hydrodefluorination. The fluoride complex W-2⁺ can be potentially regenerated to the corresponding hydride in the presence of silanes, as seen for other transition metal halides, turning the C-F activation process, represented in eq 2, catalytic. To explore this possibility, the HDF of pentafluoropyridine was carried out in the presence of dimethyl phenyl silane under microwave radiation using different hydride and fluoride cluster catalysts. The results are summarized in Table 2. The reaction was followed by GC and ¹⁹F NMR and enabled us to confirm the formation of the hydrodefluorinated pyridine at the 4-position and the subsequent formation of the fluorinated silane coproduct. The two products were well characterized by GC and ¹⁹F NMR by comparison with pure commercial standards, $\delta = -140.1$ and -92.2 ppm for 2,3,5,6-tetrafluoropyridine and $\delta = -159.5$ ppm for Me₂PhSiF. All clusters show some activity under the reaction conditions used (MeCN, MW radiation, and 1% cat. loading). Complex W-1⁺ proved to be the most efficient catalyst, giving 90% yield and 90 turnovers (entry 2). In general, the

hydride clusters present a higher activity than their fluorinated analogues (entries 2, 4, 6, and 7). The HDF process is better achieved with the use of dimethyl phenyl silane than diphenyl silane. The catalytic role of the metal cluster is evidenced by the absence of direct reaction between the fluorinated pyridine and the silane. The reaction is highly selective, and only the 2,3,5,6-tetrafluoropyridine is detected. Degradation of the catalysts was not observed even at the end of the process. The fact that catalytic HDF conversion is observed for both the hydride or the fluoride cluster complexes gives full support to the catalytic cycle postulated by Holland (Scheme 1) for low-coordinate iron(II) complexes that in the case of the iron system could not be fully elucidated due to the lack of C-F bond activation of the iron hydride in the absence of silanes.¹⁶ In our case we have been unable to detect by ESI-MS and NMR techniques the formation of M-1⁺ hydrides in appreciable amounts from the reaction between $M-2^+$ fluorides and silanes, and the only evidence that reaction occurs comes from the detection of FSiMe₂Ph as reaction product by ¹⁹F NMR. We believe that the inefficient production of hydrides by reaction of the corresponding fluorides with silanes may be the reason for the lower catalytic activities found for the fluoride clusters in front of their hydride counterparts.

Mechanistic Studies

A theoretical study of the mechanism of hydrodefluorination of pentafluoropyridine at the 4-position promoted by group 6 trinuclear cluster hydrides containing phosphines (see eq 3) and the cluster regeneration reaction by silane HSiMe₂Ph (see eq 4) has been conducted by using DFT procedures. The mechanistic study was carried out at a single M-H site of the model cluster catalyst $M_3S_4H_3(PH_3)_6^+$, M'-1⁺ $(W'-1^+ \text{ for } M = W \text{ and } Mo'-1^+ \text{ for } M = Mo)$, in the gas phase. We use the prime symbol to designate the model compound used in our computational studies. In the case of $M_3S_4H_2F(PH_3)_6^+$, we name this model complex $M_{sc}'-2^+$ to emphasize the fact that calculations are carried out on a single metal center. This approach has been successfully employed in other theoretical studies involving reactions with acids of the $W_3S_4H_3(PH_3)_6^+$ $(W'-1^+)$ cluster hydride^{19,20} or the related hetobimetallic $W_3S_4PdH_3(PH_3)_6(CO)^+$ complex.²⁸



Considering the HDF reaction (eq 3), a single-step mechanism involving a direct fluorine/hydrogen exchange was first studied. However, all attempts made to find the corresponding transition state (TS) led to the dissociation of the phosphine ligand *trans* to μ -S. In this way, a coordinatively unsaturated intermediate, $[M_3S_4H_3(PH_3)_5]^+$, **M-1I**⁺, characteristic of a

⁽²⁸⁾ Algarra, A. G.; Basallote, M. G.; Feliz, M.; Fernandez-Trujillo, M. J.; Llusar, R.; Safont, V. S. *Chem. Eur. J.* **2010**, *16*, 1613–1623.



dissociative mechanism, has been found. The dissociation step going from the reactants (\mathbf{R}) to the intermediate $\mathbf{M'}$ -1 \mathbf{I}^+ is endothermic (16.7 and 14.9 kcal mol^{-1} for M = W and Mo, respectively); therefore, partial decoordination of the diphosphine in $M_3S_4H_3(dmpe)_3^+$ would be energetically accessible by microwave heating, in good agreement with the experiment. Previous calculations at the QM/MM level on the decoordination process of one of the phosphorus atoms of the diphosphine ligand in the P-[Mo₃S₄Cl₃(dppe)₃]⁺ (dppe = diphenylphosphinoethane) stereoisomer reported an activation energy of 24.4 kcal mol^{-1, ²⁹} As in the present case, the calculated energy demand was used to explain the cluster racemization observed in refluxing acetonitrile through a mechanism that implies the formation of a metal unsaturated intermediate generated upon phosphine decoordination. Our analysis of the HDF reaction (eq 3) is then better described as a threestep process (red lines in Scheme 2) in which the first and third step correspond to the decoordination and further coordination of one phosphine ligand in the $[M_3S_4H_3(PH_3)_6]^+$ model complex.

In a second step of the HDF reaction (eq 3), the intermediate $M'-II^+$ reacts with one equivalent of pentafluoropyridine between M–H and C–F bonds through a σ -bond metathesis mechanism, where the transition state $M'-1TS^+$ can be described as a four-center structure that brings together the fluorinated compound with the metal-vacant site, to finally afford the $M_3S_4FH_2(PH_3)_5^+$ (**M'-2I**⁺) cluster intermediate. This is the first example of a σ -bond metathesis mechanism for a F/H exchange reaction promoted by group 6 metal complexes and one of the few examples of this mechanism reported in the literature for C-F activation.³⁰ Recently, Whittlesey et al. have proposed a σ -bond metathesis transition state for the C-F aromatic fluorocarbon activation by a coordinatively unsaturated N-heterocyclic carbene Ru(II) complex, generated by facile dissociation of PPh₃.³¹ A fourmembered transition state has also been calculated in the case of the boryl-assisted mechanism for the activation of the C-F bond in pentafluoropyridine at the 2-position by

mononuclear boryl phosphino rhodium complexes.³² This transition state involves direct fluorine transfer onto the boron center and is stabilized by short $Rh \cdots N$ contacts.

The energies of $M'-1TS^+$ lie at 41.4 and 38.6 kcal mol⁻¹ above the reactants for W and Mo, respectively. These values are the maxima of both reaction profiles, stressing the ratelimiting-step nature of the HDF process. Although there is not a significant energetic difference (1.1 kcal mol⁻¹) between the activation barriers (24.8 kcal mol⁻¹ for W'-1TS⁺ and 23.7 kcal mol^{-1} for Mo'-1TS⁺), the higher stability of Mo'-1TS⁺ over W'-1TS⁺ (2.8 kcal mol⁻¹) explains the faster conversion observed experimentally when using the molybdenum cluster as catalyst. The 2,3,5,6-tetrafluoropyridine product and the coordinatively unsaturated reaction intermediates, M'-2I⁺, are obtained along the reaction coordinate as thermodynamically favorable processes, with an energy release of 76.8 kcal mol^{-1} for $W'-2I^+$ and 72.5 kcal mol⁻¹ for Mo'-2I⁺. It is interesting to point out that formation of $W'-2I^+$ is slightly more favorable $(1.5 \text{ kcal mol}^{-1})$ than Mo'-2I⁺, pointing out that there is an inversion of relative stabilities between the Mo and W intermediates $M'-2I^+$ and their corresponding $M'-1TS^+$ transition structures.

In the third reaction step, coordination of phosphine to $M'-2I^+$ gives $[M_3S_4H_2F(PH_3)_6]^+$ (which we name $M_{sc}'-2^+$, stressing the fact that a single metallic center is considered in our model) as the most stable fluorinated product. This stabilization is also confirmed by the isolation of various salts of the $[M_3S_4F_3(dmpe)_3]^+$ (M-2⁺) cations. In addition, higher stabilization of $W_{sc}'-2^+$ over $Mo_{sc}'-2^+$ by ca. 4 kcal mol^{-1} would explain the highest yields obtained by using the tungsten cluster as catalyst.

An inspection of the reactive site of $\mathbf{M'-1I^+}$ shows that hydride ligand lies in the plane defined by one phosphorus atom of the phosphine ligand, the metal, and the tricapped sulfur atom as shown in Figure 3 for $\mathbf{W-1I^+}$. The \mathbf{M}_3 subunit is slightly distorted, showing shorter intermetallic distances than its precursor (2.772 Å for $\mathbf{W-1^+}$ and 2.755 Å for $\mathbf{Mo-1^+}$) with deviations less than 0.05 Å.

A closer analysis of the M'-1TS⁺ transition structure allows us to identify a four-center plane defined by the metal, one hydrogen, one fluorine, and one of the carbon atoms of the fluorinated organic substrate; the plane is marked in dashed lines in Figure 3. The fluorine and hydrogen atoms occupy trans positions to the bridging sulfur atoms, and the aromatic ring lies perpendicular to the four-center plane defined above. An analysis of the interatomic distances shows a $M \cdots H$ bond elongation of ca. 0.2 Å for $M'-1TS^+$ with regard to the $M'-1I^+$ intermediate. The $M \cdots H$ and $M \cdots F$ distances are characteristic of a transient structure (1.96 and 2.36 Å, respectively). The $C \cdots F$ distance of the organic moiety is elongated by ca. 0.2 Å in relation to that of the pentafluoropyridine, and the C-C bonds close to the reactive carbon experience a slight elongation (ca. 0.04 Å), in agreement with the loss of the sp^2 character of the reactive carbon atom. Finally the structure of the $M'-2I^+$ intermediate shows close similarities to that of $M'-1I^+$, as shown in Figure 3. Scheme 3 summarizes the catalytic cycle at the same time that emphasizes the structure of the transition states referred to a single metal center.

Our experimental evidence suggests that the cluster catalyst can be regenerated by adding the silane HSiMe₂Ph to the

⁽²⁹⁾ Andres, J.; Feliz, M.; Fraxedas, J.; Hernandez, V.; Lopez-Navarrete, J. T.; Llusar, R.; Sauthier, G.; Sensato, F. R.; Silvi, B.; Bo, C.; Campanera, J. M. *Inorg. Chem.* **2007**, *46*, 2159–2166.

⁽³⁰⁾ Perutz, R. N.; Sabo-Etienne, S. Angew. Chem., Int. Ed. 2007, 46, 2578–2592.

⁽³¹⁾ Reade, S. P.; Mahon, M. F.; Whittlesey, M. K. J. Am. Chem. Soc. 2009, 131, 1847–1861.

⁽³²⁾ Teltewskoi, M.; Panetier, J. A.; Macgregor, S. A.; Braun, T. Angew. Chem., Int. Ed. 2010, 49, 3947–3951.

⁽³³⁾ Lide, D. R. *Handbook of Chemistry and Physics*, 80th ed.; CRC Press LLC: Boca Raton, FL, 2003.



Figure 3. Optimized geometries and some relevant characteristic distances of $W'-1I^+$ (left), $W'-1TS^+$ (center), and $W'-2I^+$ (right).

Scheme 3





reaction mixture. The computed regeneration reaction, referred to a single metal center, converting the fluoride into the hydride is represented in eq 4.



According to our computational analysis, regeneration takes place in three steps, highlighted in blue in Schemes 2 and 3. The monofluorinated M_{sc}' -2⁺ complex dissociates one phosphine ligand and gives the unsaturated $M'-2I^+$ intermediate with an energy increase of 11-13 kcal mol⁻¹. In the second step, the organosilane reacts with $M'-2I^+$ through a σ -bond metathesis mechanism, where the TS is associated to a F/H exchange between the silane and the fluorinated cluster, namely, $M'-2TS^+$, to give the unsaturated hydride cluster $[M_3S_4H_3(PH_3)_5]^+$ (M'-1I⁺). The activation energy for $M'-2TS^+$ shows that F/H exchange is a kinetically favorable process, with an energy barrier of ca. 5 kcal mol^{-1} for both the molybdenum and tungsten profiles. The $M'-2TS^+$ transition state renders the FSiMe₂Ph product and the $M'-1I^+$ intermediate in a thermodynamically favorable process, with an energy release of 8.6 and 11.9 kcal mol^{-1} for W and Mo,

respectively. In the last reaction step, coordination of the phosphine to the unsaturated $M-1I^+$ cluster affords the $M'-1^+$ cluster hydride, closing the catalytic cycle, with an energy release of 16.6 and 14.9 kcal mol⁻¹ for W and Mo, respectively.

Analysis of the geometry of the M'-2TS⁺ transition-state structure shows that the organosilane interacts with the M-H site, defining a four-center moiety with the π -orbitals of the aryl group pointing toward the hydrogen atoms of one phosphine ligand, as depicted for W'-2TS⁺ in Figure 4.

The interatomic $\mathbf{M} \cdots \mathbf{F}$ distance in $\mathbf{M'} \cdot \mathbf{2TS}^+$ shows bond elongation of ca. 0.2 Å with regard to the $\mathbf{M'} \cdot \mathbf{2I}^+$ intermediate. The $\mathbf{M} \cdots \mathbf{H}$ and $\mathbf{M} \cdots \mathbf{F}$ bond lengths are characteristic of a transient structure (1.81 and 2.12 Å, respectively). The Si \cdots H distance in $\mathbf{M'} \cdot \mathbf{2TS}^+$ is elongated by ca. 0.3 Å in relation to that of the dimethyl phenyl silane.

The transition states, $M'-1TS^+$ and $M'-2TS^+$, schematically represented in Scheme 3, are not reached through an oxidative addition mechanism, on the other hand, very unlikely for a d² metal configuration; instead, decoordination of one phosphine opens an empty site in the metal coordination sphere. This empty site next to the hydride or fluoride positions allows the interaction with the pentafluoropyridine or the silane molecules activating the C-F or the Si-H bonds, respectively.

Conclusions

In summary, addition of silane HSiMe₂Ph to the reactant mixture, NC_5F_5 and catalytic amounts of the $[M_3S_4H_3-(dmpe)_3]^+$ (M = W, Mo) complex, produces exclusively



Figure 4. Optimized geometry for W'-2TS⁺.

the *para*-substituted NC₅F₄H product and FSiMe₂Ph, at the same time recovering the metal cluster, turning the process catalytic. The reaction occurs through coordinatively unsaturated intermediates and a σ -bond metathesis mechanism that results in four-center transition states, as shown in Scheme 3. The reaction is highly exothermic, and the driving force of the reaction can be associated with the lower bond disruption enthalpy of the Si–H bond (ca. 72 kcal/mol) in comparison with that of the Si–F bond (ca. 132 kcal/mol).³³ The reaction profile for tungsten is more energy demanding than for molybdenum, which explains the faster conversion observed experimentally when using the molybdenum cluster as catalyst. The higher stability of the fluorinated $W_{sc'}$ -2⁺ cluster in contrast with their analogous $Mo_{sc'}$ -2⁺ complex supports the highest yields obtained by using the tungsten cluster as catalyst.

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 CH₃CN as the mobile phase solvent. Nitrogen was employed as drying and nebulizing gas. Isotope experimental patterns were compared with theoretical patterns obtained using the MassLynx 4.0 program.³⁴ ¹H, ¹⁹F, and ³¹P NMR spectra were recorded on a Varian Innova 300 and 500 MHz, using CD₃CN as solvents and referenced to TMS, CFCl₃, and 85% H₃PO₄. Electronic absorption spectra were obtained on a Perkin-Elmer Lambda-19 spectrophotometer in CH₃CN. Elemental analyses were carried out on a EuroEA3000 Eurovector analyzer. Gas chromatography analyses were performed on a Agilent 7820A GC system equipped with a FID and an Agilent capillary column (HP-5, 30 m \times 0.32 mm \times 0.25 μ m). MW-promoted reactions were carried out in a Discover Labmate (CEM Corp.) apparatus. Solvents were dried and degassed by standard methods before use.

Synthesis. Compounds $[W_3S_4H_3(dmpe)_3]X$ (X = PF₆⁻, SO₃CF₃⁻, [W-1]X) and $[Mo_3S_4(dmpe)_3H_3](SO_3CF_3)$, [Mo-1]-(SO₃CF₃) were prepared by following literature procedures for PF₆⁻ or BPh₄⁻ salt analogues.^{21,35}

Preparation of $[W_3S_4(dmpe)_3F_3]X$, [W-2]X (X = PF₆⁻, SO₃CF₃⁻). A 15% wt aqueous solution of HPF₆ (1.40 mL, 1.61 mmol) was added dropwise to a pink solution of $[W_3S_4-(dmpe)_3H_3]PF_6$ (100.6 mg, 0.079 mmol) in CH₃CN/H₂O (2:1, 30 mL), and the mixture was stirred at room temperature for 4 h.

The solvent was partially removed (ca. 20 mL) under reduced pressure, and the desired product was extracted with CH_2Cl_2 (30 mL) and washed with water (3 × 15 mL). The resulting violet organic phase was dried over anhydrous MgSO₄, filtered, and dried under vacuum to afford [W₃S₄(dmpe)₃F₃](PF₆) as an airstable violet solid (yield: 95 mg, 90%). Anion exchange, PF₆⁻ for SO₃CF₃⁻, was achieved by elution with a KSO₃CF₃ solution in acetone after absorption of a CH₂Cl₂ solution of [W-2](PF₆) solution in a silica gel column.

solution in a sinca get commin. ³¹P{¹H} NMR (CD₃CN, 121 MHz): δ –143.1 (septet, 1P, ¹J(³¹P, ¹⁹F) = 706.5 Hz), 9.69 (d, 3P, ²J(³¹P, ¹⁹F) = 101.9 Hz, ¹J(³¹P, ¹⁸³W) = 96.8 Hz), 12.77 (d, 3P, ²J(³¹P, ¹⁹F) = 61.5 Hz, ¹J(³¹P, ¹⁸³W) = 98.3 Hz. ¹⁹F NMR (CD₃CN, 282 MHz): δ –199.7 (dd, 3F, ²J(¹⁹F, ³¹P) = 96.6 Hz, ²J(¹⁹F, ³¹P) = 61.3 Hz), – 71.2 (d, 6F, ¹J(¹⁹F, ³¹P) = 707.7 Hz). IR (cm⁻¹, KBr): 1417 (s), 1286 (s) 940 (s), 901 (s), 842 (s, P–F), 558 (s, P–F), 440 (w, W-μ₃S), 418 (w, W-μ₃S). UV-vis (CH₃CN): λ (T) 548 (71.4), 305 (350.1), 253 nm (588.2 M⁻¹ cm⁻¹). ESI-MS (CH₃CN, 20 V): m/z 1187 [M+]. Anal. Calcd for W₃F₉S₄P₇C₁₈H₄₈: C, 16.23; H, 3.63. Found: C, 16.06; H, 3.80.

Preparation of $[Mo_3S_4(dmpe)_3F_3]X$, [Mo-2]X (X = PF_6^- , $SO_3CF_3^{-}$). This compound was prepared following the procedure described for $[W-2](PF_6)$ except that $[Mo_3S_4H_3(dmpe)_3]$ -(SO₃CF₃) (0.100 g, 0.098 mmol) and HPF₆ (15 wt %, 1.60 mL, 1.84 mmol) were used as starting materials. The resulting green solid was redissolved in an acetone/CH₂Cl₂ (2:1) mixture and loaded in a silica gel colum. Two bands separated in the column after elution with a KPF_6 (10 mg/L) solution in acetone. The first yellow band was rejected, and the second band (green) containing the desired product was collected and taken to dryness. The green solid was redissolved in CH₂Cl₂, filtered, and dried under vacuum to afford [Mo₃S₄(dmpe)₃F₃](PF₆) as an air-stable green solid (0.070 mg, 67%). Anion exchange, PF₆⁻ for SO₃CF₃⁻, was achieved by elution with a KSO₃CF₃ solution in a (2:1) acetone/ CH₂Cl₂ mixture after absorption of a (2:1) acetone/CH₂Cl₂ solution of [Mo-2](PF₆) in a silica gel column.

solution of [wb-2](**F** 6) in a since get comm. ³¹P{¹H} NMR (CD₃CN, 121 MHz): δ –143.3 (septet, 1P, ¹J(³¹P, ¹⁹F) = 706.4 Hz), 24.30 (d, 3P, ²J(³¹P, ¹⁹F) = 83.6 Hz, 35.63 (d, 3P, ²J(³¹P, ¹⁹F) = 49.8 Hz). ¹⁹F NMR (CD₃CN, 282 MHz): δ –198.2 (dd, 3F, ²J(¹⁹F, ³¹P) = 85.1 Hz, ²J(¹⁹F, ³¹P) = 50.3 Hz), – 71.2 (d, 6F, ¹J(¹⁹F, ³¹P) = 707.7 Hz). IR (cm⁻¹, KBr): 1417 (s), 1285 (s) 940 (s), 899 (s), 840 (s, P–F), 557 (s, P–F), 440 (w, Mo-µ₃S), 457 (w, Mo-µ₃S). UV–vis (CH₃CN): λ 610 (280.4), 382 (2261.7), 342 (2355.1), 305 nm (3439.3 M⁻¹ cm⁻¹). ESI-MS (CH₃CN, 20 V): *m*/*z* 923 [M+]. Anal. Calcd for Mo₃F₉S₄P₇C₁₈H₄₈: C, 20.23; H, 4.53. Found: C, 20.09; H, 4.67.

HDF of Pentafluoropyridine with [M-1](SO₃CF₃) (M = Mo, W). A 10 mL capped high-pressure vessel containing a stirrer bar was charged with pentafluoropyridine (0.46 mmol), anisole as internal reference (0.46 mmol), 10 mg of catalyst (0.0077 mmol for [W-1](SO₃CF₃) and 0.0098 mmol for [Mo-1]-(SO₃CF₃)), and 1 mL of acetonitrile. The solution was heated to 180 °C under MW irradiation for the appropriate time. Reaction monitoring was achieved by ESI-MS spectrometry and ³¹P{¹H} and ¹⁹F NMR for the inorganic species and GC chromatography and ¹⁹F NMR for the organic compounds. The inertness of the triflate anion as fluorinating agent under the present HDF conditions was confirmed by the lack of reaction between the anion and the M-1⁺cations.

X-ray Data Collection and Structure Refinement. Suitable crystals for X-ray studies of the tetraphenylborate salts of W-2⁺ were grown by slow diffusion of diethyl ether into a sample solution in CH₂Cl₂. Replacement of the PF₆⁻ ion was carried out by addition of an excess of Na(BPh₄) to methanol solutions of [W-2](PF₆), resulting in precipitation of the desired tetraphenylborate salts of the trinuclear cation W-2⁺. 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 K α radiation ($\lambda = 0.71073$ Å) at T = 293(2) K. The data were

⁽³⁴⁾ MASSLYNX, 4.0 ed.; Waters Ltd.: Milford, MA, 2005.

⁽³⁵⁾ Cotton, F. A.; Llusar, R.; Eagle, C. T. J. Am. Chem. Soc. 1989, 111, 4332–4338.

collected with a frame width of 0.3° in Ω and a counting time of 25 s per frame at a crystal-detector distance of 4 cm. SAINT software was used for integration of intensity reflections and scaling, and SADABS software was used for absorption correction.^{36,37} A total of 13 851 reflections were collected in the θ range 1.23–27.50°, of which 10 199 were unique ($R_{int} = 0.0550$). The structure was solved by direct methods and refined by the full matrix method based on F^2 using the SHELXTL software package.³⁸The non-hydrogen atoms were refined anisotropically; the positions of all hydrogen atoms were generated geometrically, assigned isotropic thermal parameters, and allowed to ride on their respective parent carbon atoms. Least-squares refinement on 522 parameters converged normally with R_1 ($I > 2\sigma(I)$) 0.0594, wR_2 (all data) = 0.1009 with a GOF = 1.040.

Crystal data: C₄₂H₆₈BF₃P₆S₄W₃, $M_r = 1506.38$, triclinic, space group $P\overline{1}$ (no. 2), a = 11.137(4) Å, b = 14.984(5) Å, c = 16.850(6) Å, $\alpha = 82.866(8)$, $\beta = 81.808(7)$, $\gamma = 88.481(7)^\circ$, V = 2761.5(16) Å³, Z = 2, $\mu = 6.596$ mm⁻¹.

Catalytic Studies. Catalytic experiments were carried out under aerobic conditions. The microwave power is dynamically adjusted to follow the defined temperature profile. All other reagents were used as received from commercial suppliers.

Catalytic Hydrodefluorination of Pentafluoropyridine. A 10 mL capped high-pressure vessel containing a stirrer bar was charged with pentafluoropyridine (0.38 mmol), silane (dimethylphenylsilane, phenylsilane) (1.9 mmol), anisole as internal reference (0.38 mmol), catalyst (1 mol %), and 1 mL of acetonitrile. The solution was heated to 180 °C under MW irradiation for the appropriate time. During the reaction monitoring, yields and conversions were determined by GC chromatography and ¹⁹F NMR. The confirmation of the nature of 2,3,5,6-tetrafluoropyridine and FSiMe₂Ph was performed by comparison with a pure commercial standard and by spectral comparison with literature data.

Computational Details. All calculations were performed with the Gaussian03 package³⁹ at the B3PW91 level.^{40,41} Transition metal atoms were represented by the relativistic effective core

(38) Sheldrick, G. M. *SHELXTL*, version 5.1; Bruker Analytical X-ray Systems: Madison, WI, 1997.

(39) Frisch, M. J.; et al. et al. *Gaussian 03*, revision D.02; Gaussian, Inc.: Wallingford, CT, 2004.

- (40) Becke, A. D. J. Chem. Phys. 1993, 98, 5648-5652.
- (41) Perdew, J. P.; Wang, Y. Phys. Rev. B 1992, 45, 13244-13249.

potential (RECP) from the Stuttgart group and its associated basis set,⁴² augmented by an f polarization function (Mo: $\alpha = 1.043$; W: $\alpha = 0.823$).⁴³ P, S, and Si atoms were represented by the relativistic effective core potential (RECP) from the Stuttgart group and the associated basis set,⁴⁴ augmented by a d polarization function (P: $\alpha = 0.387$; S: $\alpha = 0.503$; Si: $\alpha = 0.284$).⁴⁵ A 6-31G(d,p) basis set was used for all the other atoms (H, C, N, F).⁴⁶The geometry optimizations were performed in the gas phase without any symmetry constraint followed by analytical frequency calculations to confirm that a minimum or a transition state had been reached. The nature of the species connected by a given transition-state structure was checked by optimization as minima of slightly altered TS geometries along both directions of the transition-state vector.

Acknowledgment. The financial support of the Spanish Ministerio de Ciencia e Innovación (Grants CTQ2008-02670), Fundació Bancaixa-UJI (research project P1.1B2007-12), and Generalitat Valenciana (ACOMP/2010/276 and Prometeo/2009/053) is gratefully acknowledged. The authors also thank the Servei Central D'Instrumentació Cientifica (SCIC) of the Universitat Jaume I for providing us with the mass spectrometry, NMR, and X-ray facilities. Special thanks go to Dr. Cristian Vicent for collecting diffraction data. T.B. thanks the Spanish Ministerio de Ciencia e Innovación (MICINN) for a doctoral fellow-ship (FPI).

Supporting Information Available: Crystallographic data in cif format (excluding structure factors), DFT-computed Cartesian coordinates for the optimized molecules, their electronic energies, and imaginary frequencies for transition-state structures reported in this paper, and complete ref 39 can be obtained free of charge via the Internet at http://pubs.acs.org.

(46) Harihara, Pc; Pople, J. A. Theor. Chim. Acta 1973, 28, 213-222.

⁽³⁶⁾ *SAINT*, version 6.2; Bruker Analytical X-ray Systems: Madison, WI, 2001.

⁽³⁷⁾ Sheldrick, G. M. SADABS; University of Göttingen: Göttingen, Germany, 1996.

⁽⁴²⁾ Andrae, D.; Haussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123–141.

⁽⁴³⁾ Ehlers, A. W.; Bohme, M.; Dapprich, S.; Gobbi, A.; Hollwarth, A.; Jonas, V.; Kohler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 111–114.

⁽⁴⁴⁾ Bergner, A.; Dolg, M.; Kuchle, W.; Stoll, H.; Preuss, H. Mol. Phys. 1993, 80, 1431-1441.

⁽⁴⁵⁾ Hollwarth, A.; Bohme, M.; Dapprich, S.; Ehlers, A. W.; Gobbi, A.; Jonas, V.; Kohler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 237–240.