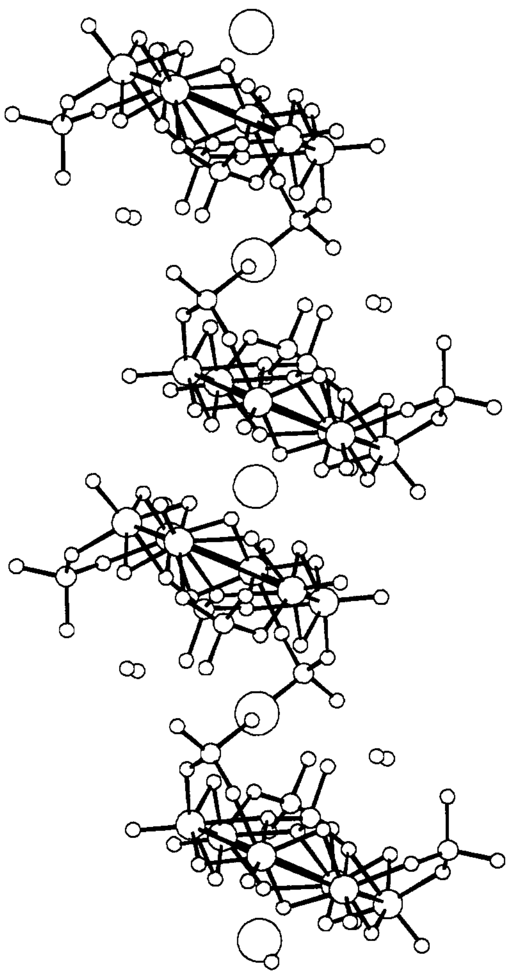

Figure 2. $[(H_3O)_2NaMo_6P_4O_{24}(OH)_7]^{2-}$ chains in **1**. The Na–O bonds are omitted for clarity.

served geometry, all Mo atoms are assigned an oxidation state of 5+. This charge assignment for the Mo requires the $Mo_6P_4O_{24}(OH)_7$ unit to have a 5– charge, which is compensated in the crystal by the two PPh_4^+ cations, the two Na^+ cations (both Na atoms lie on special positions with $\bar{1}$ symmetry and thus contribute $+^1/_2$ each to the overall charge in the lattice), and two H_3O^+ cations[12] that are located between the Mo_6P_4 cages.

In the crystals of **1**, the $Mo_6P_4O_{24}(OH)_7^{5-}$ clusters are bridged together into one-dimensional strings (Figure 2), which run parallel to the [001] direction, by two sodium ions, Na1 and Na2, both of which lie on inversion centers and are coordinated to oxygens in a distorted-octahedral fashion. The Na1 ion is coordinated to six μ_2-O atoms, while Na2 is bound to two μ_2-O and four phosphate OH oxygens. There are also two hydronium cations sandwiched between every other $Mo_6P_4O_{24}(OH)_7^{5-}$ cluster[12] (Figure 2). These $[(H_3O)_2NaMo_6P_4O_{24}(OH)_7]^{2-}$ clusters are hydrogen-bonded into two-dimensional sheets, which lie parallel to the *ac* face of the unit cell, by five additional water molecules per formula unit. These sheets are interleaved with layers of the PPh_4^+ cations to complete the three-dimensional structure.

These results, together with our recently determined structure of the huge $[Na_{12}Mo_{24}P_{17}O_{97}(OH)_{31}]^{8-}$ cluster,[6] demonstrate that it is possible to form novel metal–metal-bonded molybdenum phosphate clusters from aqueous phosphoric acid in the presence of a suitable reducing agent. Preliminary experiments indicate that reactions similar to those discussed here with sulfuric acid in place of phosphoric acid likewise yield reduced molybdates.

Supplementary Material Available: Tables of crystallographic parameters, positional and thermal parameters, and bond lengths and bond angles (19 pages); a table of observed and calculated structure factors (82 pages). Ordering information is given on any current masthead page.

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[12] Since all of the Mo atoms are assigned an oxidation state of 5+, as discussed in the text, the presence of two hydronium cations is required for charge balance. It was not possible to crystallographically locate the hydrogen atoms on any of the water/hydronium molecules in the structure, but it is assumed that the oxygen atoms between the $Mo_6P_4O_{24}(OH)_7^{5-}$ clusters are hydronium cations due to their proximity to the negative charges on the cluster.

[13] Chem-X is designed and distributed by Chemical Design, Ltd., Mahwah, NJ.

Regioselectivity in the Novel Conversion of an Aromatic C–F Bond into a C–H Bond via an Organonickel Intermediate

During an attempt to synthesize the phosphonium cation $[Ph_3(C_6F_5)P]^+$ by a procedure analogous to that reported in the literature for $[Ph_4P]^+$, we have discovered an unusual and unexpected C–F cleavage reaction. This cleavage reaction involves the formation of an organometallic intermediate whereby a C–Ni bond has replaced a C–F bond in the 4-position of the perfluoro ring. Subsequent hydrolytic cleavage of the C–Ni bond results in C–H bond formation.

The compound $[Ph_4P]Br$ has been previously prepared by the fusion reaction between triphenylphosphine, bromobenzene, and nickel bromide (eq 1).[1] Subsequent hydrolysis of the tetraphenylphosphonium nickelate salt gives the bromide salt $[Ph_4P]Br$.

$$2PPh_3 + PhBr + NiBr_2 \rightarrow [Ph_4P][NiBr_3(PPh_3)] \quad (1)$$

Our approach to the synthesis of the compound $[Ph_3(C_6F_5)P]Br$ is to carry out an analogous fusion reaction with triphenylphosphine, bromopentafluorobenzene, and nickel bromide. We find that the reaction mixture must be refluxed in an open vessel under a nitrogen flow because heating the mixture in a sealed tube gives triphenylphosphine oxide as the product after hydrolysis. Treating the fusion product from the open-vessel reaction with water results in the formation of the compound $[Ph_3(4\text{-}C_6F_4H)P]Br$ (eq 2), whereby the fluorine in the 4-position has been replaced by hydrogen.[2]

$$\begin{gathered} PPh_3 + C_6F_5Br + NiBr_2 \xrightarrow[N_2]{\sim 200\ ^\circ C} \text{solid} \\ \text{solid} + H_2O \rightarrow [Ph_3(4\text{-}C_6F_4H)P]Br \end{gathered} \quad (2)$$

This hygroscopic salt $[Ph_3(4\text{-}C_6F_4H)P]Br$ dissolves in water, and this solution gives a precipitate of silver bromide with aqueous silver nitrate solution. The $^{31}P\{^1H\}$ NMR spectrum of the salt shows a triplet centered at δ 16.2 ($^3J(PF)$ = 6.0 Hz). The ^1H NMR spectrum shows a complex multiplet in the phenyl region, and no individual C–H resonance on the fluoro aromatic ring can be identified. The ^{19}F NMR spectrum shows two multiplets of equal intensity centered at δ −123.5 (F^a) and δ −131.3 (F^b). Proton decoupling results in the simplification of each set of fluorine multiplets. Hydrolysis of the fusion product with D_2O rather than H_2O yields the deuterated derivative $[Ph_3(4\text{-}C_6F_4D)P]Br$. The ^2H NMR spectrum of this salt shows a broad multiplet in the phenyl region at δ 7.81, and the IR spectrum shows a band at 2196 cm^{-1} characteristic of ν(C–D). Final confirmation of the structure of these phosphonium salts is by spectral simulation of the ^{19}F NMR spectrum of $[Ph_3(4\text{-}C_6F_4H)P]Br$. Iterative fitting to the experimental spectra

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[1] Horner, L.; Mummenthey, G.; Moser, H.; Beck, P. *Chem. Ber.* **1966**, *99*, 2782–2788.

[2] Heating triphenylphosphine (3 g, 1 mol) with bromopentafluorobenzene (5.65 g, 2 mol) and nickel bromide (1.25 g, 0.5 mol) under nitrogen at reflux in an oil bath at 200 °C for 3 h gave an uncharacterized fused product. Subsequent hydrolysis resulted in the isolation of $[Ph_3(4\text{-}C_6F_4H)P]Br$ (1 g). Anal. Calcd for $C_{24}H_{16}BrF_4P$: C, 58.7; H, 3.28. Found: C, 58.8; H, 3.45.

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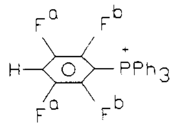


Figure 1. Labeling scheme for $Ph_3(4\text{-}C_6F_4H)P^+$.

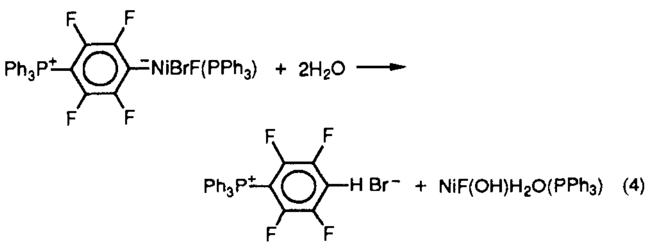
with the PANIC spectral simulation program[3] gives the following coupling constants: $^3J(PF^b) = 6.05$ Hz, $^3J(F^aF^b) = 9.00$ Hz, $^3J(HF^a) = 10.30$ Hz, $^4J(PF^a) = 0.05$ Hz, $^4J(HF) = 9.20$ Hz, $^5J(F^aF^b) = -13.50$ Hz, $^4J(F^aF^a) = -1.75$ Hz, $^4J(F^bF^b) = 9.00$ Hz.[3] The labeling scheme is shown in Figure 1.

The compound $[Ph_3(4\text{-}C_6F_4H)P]Br$ reacts with aqueous NaOH at ambient temperature to give quantitative conversion to triphenylphosphine oxide and 1,2,4,5-tetrafluorobenzene (eq 3). The

$$[Ph_3(4\text{-}C_6F_4H)P]Br + NaOH \rightarrow Ph_3PO + 1,2,4,5\text{-}C_6F_4H_2 + NaBr \quad (3)$$

^1H and ^{19}F NMR spectra of the product 1,2,4,5-tetrafluorobenzene correspond with those given in the literature.[4] If an aqueous solution of NaOD in D_2O is used, the *monodeuterated* compound $1,2,4,5\text{-}C_6F_4HD$ is obtained. This monodeuterated compound is also obtained upon treating the fusion product with D_2O, followed by reaction of the resulting salt $[Ph_3(4\text{-}C_6F_4D)P]Br$ with NaOH in water. The ^1H NMR spectrum of 1,2,4,5-tetrafluoro-3-deuterobenzene shows a triplet of triplets centered at δ 7.03 (^3J(HF), ^5J(HF): 9.7, 7.5 Hz). The ^{19}F NMR spectrum shows a multiplet centered at δ −139.3 for chemically equivalent but magnetically inequivalent fluorine nuclei. Reactions that allow the selective deuteration of equivalent positions are rather rare. The *doubly deuterated* product $1,2,4,5\text{-}C_6F_4D_2$ can also be synthesized by treatment of $[Ph_3(4\text{-}C_6F_4D)P]Br$ with a solution of NaOD in D_2O. The ^{19}F NMR spectrum shows a single peak at δ −138.4. No other isomers are observed.

In the formation of $[Ph_3(4\text{-}C_6F_4H)P]^+$ the selective cleavage of the C–F bond must occur in the fusion reaction with nickel bromide rather than in the subsequent hydrolysis step. Cleavage of the C–F bond in the hydrolysis step does not explain our results because a phosphonium ion substituent on the fluoro aromatic ring is expected to increase the susceptibility of the ring to *nucleophilic* attack. Such nucleophilic attack by water at $[Ph_3(C_6F_5)P]^+$ is expected to occur either at the 4-position of the perfluoro ring to give $[Ph_3(4\text{-}C_6F_4OH)P]^{+}$[5] or at phosphorus to give phosphine oxide.[6] The only reasonable explanation for this unusual chemistry is that C–F cleavage occurs in the reaction with nickel bromide and that the melt contains an organonickel complex of a phosphonium salt. On the basis of the precedent in ref 1, we propose a structure of the type $Ph_3(4\text{-}C_6F_4(NiBrF(PPh_3)^-))P^+$ for the organonickel complex formed after reductive elimination of Br_2. Hydrolysis of this complex results in the formation of $[Ph_3(4\text{-}C_6F_4H)P]Br$ and uncharacterized nickel-containing products (eq 4). This phosphonium product results from a regioselective reaction with water whereby the nickel center is more oxophilic than the carbon atom, resulting in hydrogen transfer to carbon rather than to nickel. A plausible pathway for the overall reaction involves insertion of a nickel center into the C–F bond.



(4)

The C–F bond in the 4-position is the sterically favored one, and recent examples of similar C–F oxidative additions have been reported.[7] This pathway is attractive because it explains why, under reaction conditions in an open container where the halogen formed in the reaction can escape, only small amounts of triphenylphosphine oxide are formed. Under sealed-tube conditions halogenation of triphenylphosphine occurs, and subsequent hydrolysis yields triphenylphosphine oxide as the major product.

The subsequent reaction of $[Ph_3(4\text{-}C_6F_4H)P]Br$ with hydroxide ion follows an atom-transfer regioselectivity whereby the oxygen migrates to phosphorus and the hydrogen to carbon. We observe no formation of phenols, or of compounds that contain P–H bonds, resulting from the opposite selectivity.

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(3) PANIC 83.3004 *Aspect 3000 NMR Software Manual*; Bruker Spectrospin: Karlsruhe, West Germany, 1985.

(4) *Aldrich Library of NMR Spectra*; Aldrich: Milwaukee, WI, 1983.

(5) Banks, R. E. *Fluorocarbons and Their Derivatives*, 2nd ed.; MacDonald; London, 1970; pp 218–221.

(6) We find that $[Ph_2(C_6F_5)MeP]^+$ reacts with OH^- to give primarily $Ph_2(C_6F_5)PO$.

(7) Richmond, T. G.; Osterberg, C. E.; Arif, A. M. *J. Am. Chem. Soc.* **1987**, *109*, 8091–8092. Gross, M. E.; Johnson, C. E.; Maroney, M. J.; Trogler, W. C. *Inorg. Chem.* **1984**, *23*, 2968–2973.

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Novel Cubane-Type Molybdenum–Tin Cluster Complexes $[(H_2O)_9Mo_3S_4SnS_4Mo_3(H_2O)_9]^{8+}$ and $Mo_3SnS_4(aq)^{6+}$

The sulfur-bridged incomplete cubane-type aqua ion $[Mo_3S_4(H_2O)_9]^{4+}$ (A) reacts not only with metallic tin but also with tin(II) ion to give $[(H_2O)_9Mo_3S_4SnS_4Mo_3(H_2O)_9]^{8+}$ (B) and $Mo_3SnS_4(aq)^{6+}$ (C), respectively. Although the aqua ion A reacts with metallic iron,[1] nickel,[2] copper,[3] mercury,[4] and magnesium,[5] it does not react with any 2+ ion of the metals.

Compounds containing both molybdenum and tin are relatively rare, though some very interesting reports have appeared.[6] No cubane-type compounds with a Mo_3SnS_4 core, to our knowledge, have been reported so far. We describe here the preparation, electronic spectra, and electrochemistry of B and C, together with the X-ray structure of the *p*-toluenesulfonate salt of B.

The preparation of $[(H_2O)_9Mo_3S_4SnS_4Mo_3(H_2O)_9](CH_3C_6H_4SO_3)_8\cdot 26H_2O$ (B′) is as follows: All the experiments were carried out under a dinitrogen atmosphere. Addition of tin metal (3 g) to A (0.15 M per Mo, 25 mL in 2 M HCl) rapidly changed the color of the solution from green to red-purple. After a couple of days at room temperature, the unreacted metal was removed from the solution and Dowex 50W-X2 column chromatography was used (2 × 85 cm). The resin was washed with 0.5 M HCl, and a small amount of yellow-green single-cubane C was eluted with 1 M HCl. A small amount of unreacted A may follow this species. A red-purple solution of B was obtained by use of 2 M

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(1) Shibahara, T.; Akashi, H.; Kuroya, H. *J. Am. Chem. Soc.* **1986**, *108*, 1342–1343.

(2) Shibahara, T.; Kuroya, H. *Abstracts of Papers*, 1987 International Miniconference for Young Chemists in Tokyo—Macrocyclic and Coordination Chemistry, Tokyo, July 1987; Japan Society of Young Coordination Chemists: Tokyo, 1987; Abstract D13. Shibahara, T.; Kuroya, H. *J. Coord. Chem.* **1988**, *18*, 233–236.

(3) Shibahara, T.; Akashi, H.; Kuroya, H. *J. Am. Chem. Soc.* **1988**, *110*, 3313–3314.

(4) Akashi, H.; Shibahara, T. *Abstracts of Papers*, XXVI International Conference on Coordination Chemistry, Porto, Portugal, Aug 1988; Universidade do Porto and Sociedade Portuguesa de Química: Porto, Portugal, 1988; Abstract A27.

(5) Shibahara, T.; Yamamoto, T.; Kanadani, H.; Kuroya, H. *J. Am. Chem. Soc.* **1987**, *109*, 3495–3496.

(6) For example, $Mo_2(Sn(SnMe_3)_3)_2(NMe_2)_4$: Chisholm, M. H.; Chiu, H.-T.; Folting, K.; Huffman, J. C. *Inorg. Chem.* **1984**, *23*, 4097–4102.

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