Communication

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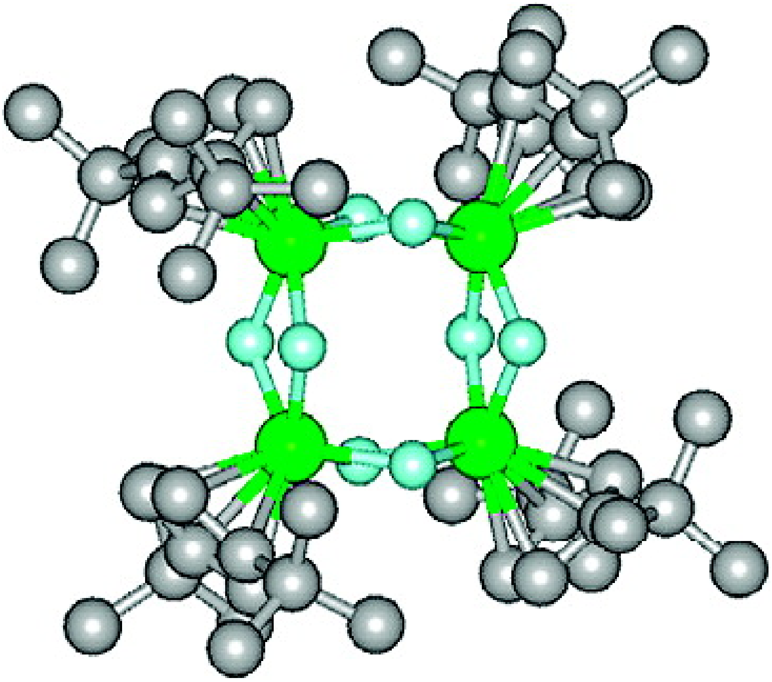
J. Am. Chem. Soc., **2005**, 127 (34), 11924-11925• DOI: 10.1021/ja052214s • Publication Date (Web): 04 August 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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Reactions of SF_6 with Organotitanium and Organozirconium Complexes: The “Inert” SF_6 as a Reactive Fluorinating Agent

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SF_6 has long served as the epitome for an inert molecular gas. Typical of descriptions one finds in standard texts are the following: “extremely inert”,[1] “extraordinary stability”,[2] “chemically very inert”,[3] “extreme thermal and chemical stability,” and “possibly the most inert non-ionic fluorine compound”.[4] Due to its inertness and high dielectric constant, SF_6 has found widespread application in high voltage transformers, as an inert gas to blanket molten magnesium, as a noise insulator in multipane windows, and previously even in some shoes.[5] Inevitably, much of this SF_6 finds its way into the atmosphere, which is problematic because it is a potent greenhouse gas,[6] having the highest global warming potential known (estimated at more than 22 000 times that of CO_2), in large part due to its estimated lifetime of 3200 years in the atmosphere. As a result, SF_6 is one of the gases falling under the Kyoto protocol.[7]

While SF_6 does react readily with ketyl solutions and the like[3,8] and has also been employed as a thermal electron scavenger,[9] it clearly may not be considered to have been established as a useful reagent.[10] Herein we wish to report that, with low valent organometallic compounds, SF_6 can not only be quite reactive at and even below room temperature, serving as a useful and selective fluorinating agent, but also quite surprisingly, its reactivities can rival or exceed those of some commonly employed fluorinating agents.

Initial attempts to prepare higher valent (pentadienyl)zirconium fluorides focused on analogues of recently isolated chloride, bromide, and iodide complexes such as the $Zr(6,6\text{-dmch})_2X_2$[11] and $Zr(C_5H_5)(6,6\text{-dmch})X_2$[12] compounds (6,6-dmch = 6,6-dimethylcyclohexadienyl). It was first observed that the Zr(II) starting materials $Zr(6,6\text{-dmch})_2(PMe_3)_2$ and $Zr(C_5H_5)(6,6\text{-dmch})(PMe_3)_2$ were able to activate C−F bonds, as has been demonstrated for early metallocenes,[13] presumably leading to compounds of interest. However, the reactions yielded products that were quite insoluble, perhaps a result of the notably weaker binding of pentadienyl ligands to metals in relatively high ($\geq +4$) oxidation states.[11,12,14] In such situations, these ligands exhibit a marked tendency to form only one short contact with the dienyl fragment through the central (C(3)) carbon atom, likely a result of a size mismatch between the wide pentadienyl fragments and the contracted metal orbitals. The C(2,4) and C(1,5) atoms then become located progressively further from the metal center, and these weak interactions could promote extensive bridging by any fluoride ligands. As the reactions tended to be somewhat slow and yielded insoluble products, alternative fluorinating agents were considered, including SF_6. Indeed, reactions of some of the Zr(II) starting materials with SF_6 were found to be rapid at and even below room temperature, leading to very warm reaction solutions, but again the metal-containing products exhibited very low solubilities.

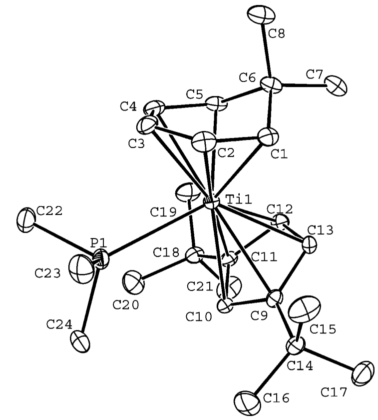

Figure 1. Perspective view of $Ti[1,3\text{-}(t\text{-Bu})_2C_5H_3](6,6\text{-dmch})(PMe_3)$.

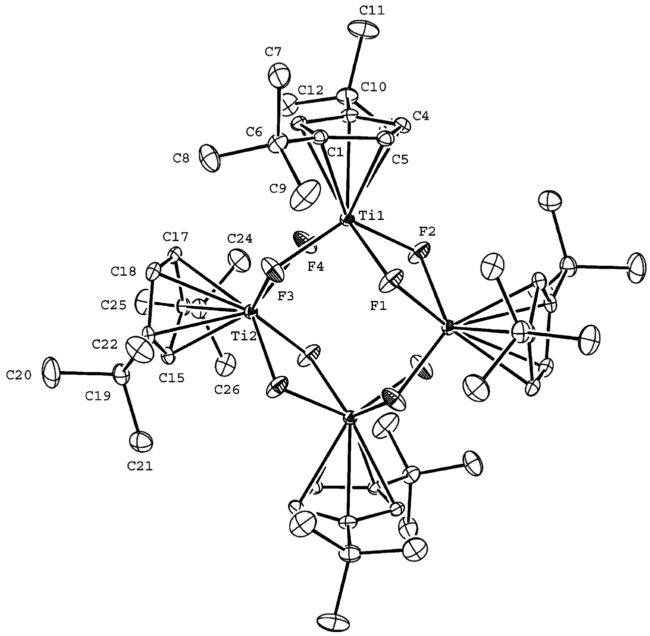

Figure 2. Perspective view of $\{Ti[1,3\text{-}(t\text{-Bu})_2C_5H_3]F_2\}_4$. The complex lies on a crystallographic center of inversion.

To favor the formation of a more soluble complex, resort was made to alkylated starting materials. The “half-open titanocene” $Ti[1,3\text{-}C_5H_3(t\text{-}C_4H_9)_2](6,6\text{-dmch})(PMe_3)$ was readily prepared and characterized (Figure 1). As is typical of other divalent half-open titanocenes,[15] the Ti−C distances for the electronically open pentadienyl ligand were found on the average to be substantially shorter than those for the cyclopentadienyl ligand, in this case the averages being 2.263 and 2.387 Å. This species was subjected to reactions with SF_6, which again proceeded quite readily, yielding a bright green product. Subsequent characterization revealed the product to be $\{Ti[1,3\text{-}C_5H_3(t\text{-}C_4H_9)_2]F_2\}_4$ (Figure 2). The tetrameric arrangement of this complex appears quite new for at least group IV organometallic complexes[16] and is based on a tetragonally distorted cube of fluoride ions, with $Ti[1,3\text{-}C_5H_3(t\text{-}C_4H_9)_2]$ units situated above four of the cube faces, with the other two (opposite) faces empty (Figure 2). The average Ti−F and Ti−F bond distances

10.1021/ja052214s CCC: $30.25 © 2005 American Chemical Society

are 2.362 and 2.017 Å, respectively, and the Ti−F vectors are bent down from the cyclopentadienyl ligand centroids by an average of 118.1°. The Ti−F bonds are substantially shorter than those of ca. 2.10 Å observed in bis(cyclopentadienyl)titanium(III) fluorides.[17] That the product is a Ti(III) complex, presumably formed via loss of its pentadienyl ligand from a Ti(IV) intermediate, was not surprising in view of the strong preference of pentadienyl ligands for metals in lower oxidation states.[11,14a,18]

The high reactivity observed between SF_6 and low valent organometallic compounds of titanium and zirconium is particularly notable given that under the same conditions, XeF_2 or CoF_3 required substantially longer times for their reactions. It is likely that the SF_6 reactions occur via coordination of one or more of the fluorine atoms to the transition metal center, followed by the transfer of the fluorine atom(s), resulting in the oxidation of the metal center, in what may be described alternatively as an inner-sphere electron transfer, or simply as an atom abstraction. In either case, the replacement of S−F bonds by much stronger M−F bonds provides a substantial driving force for these reactions. The results reported herein open up the potential for the utilization of SF_6 as a safe fluorinating source, especially for the selective preparation of new organometallic fluoride complexes,[19] which have been shown to have unique reactivities.[21] Although one could be concerned that the formation of highly toxic SF_4 as a byproduct could pose a hazard, the fact that substantial quantities of Me_3PS are observed even when large excesses of SF_6 are employed demonstrates that the lower sulfur fluorides are, as expected, far more reactive than SF_6. Thus, all the fluorine atoms on sulfur can be effectively utilized, which is not only economical but should also allow for any hazards to be minimized.

Acknowledgment. Acknowledgment is made to the Donors of the American Chemical Society Petroleum Research Fund, the U.S. Department of Energy (Contract DE-FC26-02NT41594), and the University of Utah for partial support of this work. We thank Mr. Kendric Nelson and Professor Joel Miller for their assistance in obtaining the magnetic moment of the fluoride compound.

Supporting Information Available: Synthetic procedures and spectroscopic data for the two new compounds, as well as positional coordinates and additional bonding parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) The products isolated may not always be those that would be expected. For example, reaction of SF_6 with $Zr(C_5H_5)_2(PMe_3)_2$ leads to two major products, one being the expected $Zr(C_5H_5)_2F_2$[20] (δ, $CDCl_3$: 6.45 ppm; δ, C_4D_8O: 6.39), favored when the reaction commences at room temperature. When the reaction commences at ca. −30°, however, the other, as yet unidentified, product dominates (δ, C_4D_8O: 6.27). Hence, SF_6 may prove useful for preparing species not normally obtained through other reactions. For comparison, reactions utilizing CoF_3 proceeded much more slowly even at room temperature, while little if any reaction with XeF_2 seemed to occur.

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JA052214S