

Communication

Early Transition-Metal Perfluoroalkyl Complexes

Felicia L. Taw, Brian L. Scott, and Jaqueline L. Kiplinger

J. Am. Chem. Soc., **2003**, 125 (48), 14712-14713 • DOI: 10.1021/ja038527+ • Publication Date (Web): 06 November 2003

Downloaded from <http://pubs.acs.org> on March 30, 2009

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 1 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



Early Transition-Metal Perfluoroalkyl Complexes

Felicia L. Taw, Brian L. Scott, and Jaqueline L. Kiplinger*

Chemistry Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

Received September 15, 2003; E-mail: kiplinger@lanl.gov

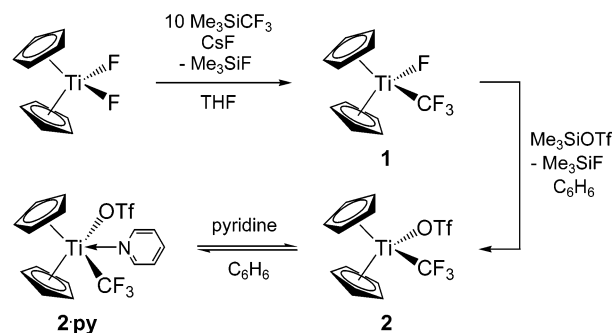
The first transition-metal perfluoroalkyl complex, $\text{Mn}(\text{CO})_5(\text{CF}_3)$, was reported in 1959¹ and led to a flourish of activity in the field of organometallic fluorocarbon chemistry. Today, metal CF_3 complexes are known for virtually all the middle- and late-row transition metals.² Despite persistent efforts, early transition-metal (groups 3, 4, and 5) perfluoroalkyl complexes have remained elusive for the last 44 years. Traditional methods^{2c} employed to prepare perfluoroalkyl complexes have repeatedly failed to provide early-metal analogues,³ and these failures have been attributed to facile α - and β -fluoride elimination pathways available to the early-metal fluoroalkyl complexes to give high lattice energy metal fluorides.⁴ Herein, we report the synthesis and characterization of the first early transition-metal perfluoroalkyl complexes, $\text{Cp}_2\text{Ti}(\text{CF}_3)(\text{F})$ (**1**) and $\text{Cp}_2\text{Ti}(\text{CF}_3)(\text{OTf})$ (**2**; $\text{OTf} = \text{OSO}_2\text{CF}_3$).

To synthesize complex **1**, Me_3SiCF_3 and CsF were added to a THF suspension of the previously reported complex Cp_2TiF_2 .⁵ The reaction proceeded at room temperature and was complete within 15 h (Scheme 1). Ruppert's reagent, Me_3SiCF_3 , has been used extensively to trifluoromethylate organic compounds.⁶ More recently, two cases have been reported in which Me_3SiCF_3 was successfully employed to transfer CF_3 groups to late transition metals.⁷ Our work establishes a synthetic methodology for the delivery of CF_3 groups to early-metal fluoride systems and illustrates that, under the proper reaction conditions, Me_3SiCF_3 is an effective reagent for the preparation of titanium–trifluoromethyl complexes.

Complex **1** was isolated in 60% yield as a bright yellow powder. In the solid state, **1** is unaffected by brief exposure to air; however, the complex is thermally sensitive, and degradation begins after 15 min at room temperature, whether under inert or aerobic conditions. As a solid, complex **1** can be stored indefinitely at -30 °C. Dissolved in THF, **1** is stable for several weeks at room temperature. In benzene or toluene solutions, slight decomposition was observed after 2 days, and in halogenated solvents such as dichloromethane or chloroform, decomposition occurred after several hours at room temperature to form intractable black solids. Brief exposure to air or the presence of small amounts of water did not accelerate the decomposition rate. These combined observations suggested that the titanium center in complex **1** could be stabilized in these solvents by the addition of Lewis bases such as THF, pyridine, or (dimethylamino)pyridine (DMAP). Indeed, addition of 1 equiv of DMAP to a dichloromethane solution of **1** resulted in no evidence of decomposition for 2 days at room temperature.

The ^1H NMR spectrum of complex **1** in $\text{THF-}d_8$ revealed a resonance for the equivalent Cp rings at δ 6.40 ppm (d, $^3J_{\text{F-H}} = 1.0$ Hz). Two resonances were observed in the ^{19}F NMR spectrum: a singlet at δ 206.3 ppm, corresponding to the fluoride ligand, and another singlet at δ -24.0 ppm for the CF_3 group (referenced to CFCl_3 at δ 0.00 ppm). The chemical shift of the fluoride ligand of **1** is significantly downfield from the fluoride resonances of other titanium–fluoride compounds (e.g. Cp_2TiF_2 exhibits a ^{19}F NMR resonance at δ 87.7 ppm) due to the presence of the highly electron-

Scheme 1



withdrawing trifluoromethyl group. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1** showed a resonance for the CF_3 group at δ 153.1 ppm, which is split into a quartet ($^1J_{\text{C-F}} = 382.6$ Hz) by the three adjacent fluorine atoms and split again into doublets ($^2J_{\text{C-F}} = 4.8$ Hz) by the fluoride bound to titanium. A singlet corresponding to the Cp groups appears at δ 117.4 ppm.

Solid-state IR studies of complex **1** showed C–F stretching frequencies in the range of 980–1080 cm^{-1} , which are typical of CF_3 ligands attached to transition metals.⁸ In general, these frequencies are approximately 100 cm^{-1} lower than the corresponding C–F stretching frequencies for CF_3I , indicating a weaker C–F bond in the metal complex.⁹

The identity of complex **1** as a titanium(IV) perfluoromethyl fluoride complex was unambiguously ascertained by a single-crystal X-ray diffraction study (Figure 1).¹⁰ The molecular structure of **1** reveals a typical bent-metallocene framework with a pseudotetrahedral coordination environment about the titanium metal center. The trifluoromethyl and fluoride ligands lie within the metallocene wedge. The Ti–F bond distance of 1.831(2) Å is in agreement with the average Ti–F bond distances (1.83 Å) reported for similar titanium difluoride complexes.¹¹ Comparisons for the metrical parameters of the Ti– CF_3 moiety can only be made to known middle- and late-row transition-metal trifluoromethyl complexes. Metal–carbon distances in middle and late transition-metal fluoroalkyl compounds are significantly shorter than those in hydrocarbon analogues.² In marked contrast, the Ti–C bond distance (2.221(3) Å) in complex **1** is substantially longer than the Ti–C bond lengths (1.988–2.181 Å)¹² reported for related Ti– CH_3 systems. For the trifluoromethyl group in complex **1**, the average C–F bond length (1.366(3) Å) and the average F–C–F bond angle (102.7(2)°) are quite similar to values found in known middle- and late-row transition-metal CF_3 complexes that are thermally stable.^{2c} Although direct quantitative comparisons are difficult, these observations are somewhat surprising as complex **1** displays low thermal stability. Of note is the absence of an α -fluoride interaction ($\text{Ti}\cdots\text{F}-\text{CF}_2$) between the electrophilic titanium(IV) metal center and any of the C–F bonds in the trifluoromethyl group, as evidenced in the X-ray crystal structure. In addition, variable-temperature NMR spectroscopic studies ($-80 \rightarrow +40$ °C) of **1** also

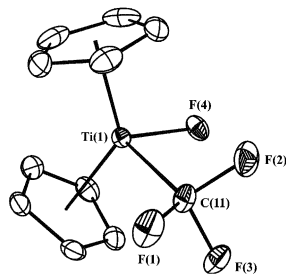


Figure 1. Molecular structure of **1** with thermal ellipsoids at the 25% probability level. Selected bond distances (Å) and angles (deg): Ti(1)–F(4) 1.831(2); Ti(1)–C(11) 2.221(3); C(11)–F(1) 1.362(3); C(11)–F(2) 1.365(4); C(11)–F(3) 1.370(3); F(4)–Ti(1)–C(11) 89.35(9); Ti(1)–C(11)–F(1): 118.4(2); Ti(1)–C(11)–F(2): 114.0(2); Ti(1)–C(11)–F(3): 114.5(2); F(1)–C(11)–F(2): 103.7(2); F(1)–C(11)–F(3): 102.3(2); F(2)–C(11)–F(3): 102.0(2).

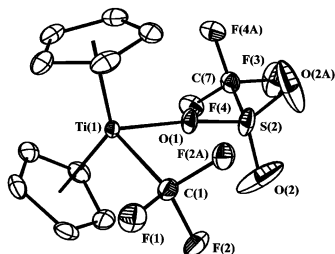


Figure 2. Molecular structure of **2** with thermal ellipsoids at the 25% probability level. Selected bond distances (Å) and angles (deg): Ti(1)–O(1) 1.985(4); Ti(1)–C(1) 2.222(5); C(1)–F(1) 1.367(6); C(1)–F(2) 1.362(4); C(1)–F(2A) 1.362(4); O(1)–Ti(1)–C(1) 88.3(2); Ti(1)–C(1)–F(1): 117.2(3); Ti(1)–C(1)–F(2): 114.2(2); Ti(1)–C(1)–F(2A): 114.2(2); F(1)–C(1)–F(2): 103.3(3); F(1)–C(1)–F(2A): 103.3(3); F(2)–C(1)–F(2A): 102.8(4).

preclude α -fluoride interactions in solution as no change in the CF_3 ^{19}F NMR shift or $^1J_{\text{C-F}}$ was observed.

The reaction chemistry of complex **1** was surveyed using a variety of substrates. The Ti– CF_3 linkage is remarkably robust; complex **1** displays no reaction chemistry (even under elevated temperatures) with nucleophiles such as acetonitrile, *tert*-butyllithium, carbon monoxide, triphenylphosphine, trimethyl phosphite, or benzophenone. However, reaction of complex **1** with the methide-abstracting agent $\text{B}(\text{C}_6\text{F}_5)_3$ resulted in the immediate formation of intractable products.

Complex **1** was successfully converted to the trifluoromethyl triflate **2** using Me_3SiOTf . Addition of 1 equiv of Me_3SiOTf to a benzene solution of **1** in the presence of pyridine led to formation of the pyridine-stabilized complex, $[\text{Cp}_2\text{Ti}(\text{CF}_3)(\text{OTf})\cdot(\text{pyridine})]$ (**2**·py; Scheme 1), which was characterized by NMR spectroscopy. Without the presence of a Lewis base, rapid decomposition occurred to form intractable solids. Addition of other electron-donating substrates such as DMAP, THF, or triphenylphosphine also served to stabilize $\text{Cp}_2\text{Ti}(\text{CF}_3)(\text{OTf})$, but were less effective than pyridine. Layering a toluene solution of **2**·py with hexanes at -30°C afforded orange-red X-ray quality crystals of complex **2** in 70% yield. A single-crystal X-ray diffraction study allowed assignment of the molecular structure of these crystals as $\text{Cp}_2\text{Ti}(\text{CF}_3)(\text{OTf})$ (**2**), with triflate coordinating to the Ti center in a monodentate fashion (Figure 2).¹⁰ Surprisingly, no pyridine or other solvent molecules were detected in the crystal lattice. Complex **2** is isostructural to complex **1**. The Ti– CF_3 bond distance of 2.222(5) Å is identical to the Ti– CF_3 bond distance in complex **1**. The C–F bond lengths

and the F–C–F bond angles are also similar in **1** and **2**. As in the case of **1**, no α -fluoride interaction is observed in **2** between the electropositive titanium(IV) metal center and any of the C–F bonds.

In the solid state, **2** is stable at room temperature for several hours. However, even brief exposure to air or moisture results in degradation. IR spectroscopic studies showed two distinct bands at 1082 and 1069 cm^{-1} , corresponding to C–F stretching frequencies of the trifluoromethyl group attached to titanium. When crystals of **2** were dissolved in benzene or toluene, decomposition occurred at room temperature within a few seconds. However, when 1 equiv of pyridine was added to the solvent before dissolution of **2**, the complex was again stable for several hours, and NMR spectroscopy identified the species in solution as **2**·py. In addition to the singlet observed at δ 6.76 ppm for the Cp rings in the ^1H NMR spectrum, the ^{19}F NMR spectrum of **2** (in $\text{THF-}d_8$) showed a singlet at δ -25.6 ppm, corresponding to the Ti– CF_3 group and a singlet at δ -80.0 ppm for the triflate ligand. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum exhibited a quartet at δ 151.8 ppm ($^1J_{\text{C-F}} = 382.9$ Hz), corresponding to Ti– CF_3 . Additional resonances were observed at δ 120.7 ppm (singlet) for the Cp rings and at δ 120.2 (q, $^1J_{\text{C-F}} = 317.3$ Hz) for the triflate.

In summary, we have demonstrated that stable early transition-metal perfluoroalkyl complexes can indeed be prepared. This work establishes new synthetic methodology for the delivery of CF_3 groups to early-transition-metal fluoride systems and suggests that a variety of early transition-metal perfluoroalkyl complexes will be accessible using other $\text{Me}_3\text{Si-R}_f$ reagents ($\text{R}_f = \text{fluoroalkyl}$). We anticipate that these novel perfluoroalkyl complexes will serve as useful platforms for the development of presently unknown catalytic systems capable of effecting fluorocarbon metathesis and polymerization.

Acknowledgment. For financial support of this work, we acknowledge the LANL Laboratory Directed Research and Development Program (J.L.K.). Finally, we thank Dr. Carol J. Burns (LANL) and Professor Thomas G. Richmond (University of Utah) for helpful discussions.

Supporting Information Available: Experimental procedures, characterization data, crystallographic information (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Coffield, T. H.; Kozikowski, J.; Closson, R. D. *Abstr. Proc. Int. Conf. Coord. Chem.*, 5th, Chemical Society: London, England, 1959; p 126.
- (2) (a) Bruce, M. I.; Stone, F. G. A. *Prepr. Inorg. React.* **1968**, *4*, 177. (b) Hughes, R. P. *Adv. Organomet. Chem.* **1990**, *31*, 183. (c) Morrison, J. A. *Adv. Organomet. Chem.* **1993**, *35*, 211.
- (3) (a) Ontiveros, C. D. Ph.D. Thesis, University of Chicago, Chicago, IL, 1986. (b) Jones, W. D. *Dalton Trans.* 2003. In press.
- (4) For example, α -fluoride elimination for transient $\text{CpMo}(\text{CO})_2(\text{CF}_3)$ could only be observed in a frozen matrix: Campen, A. K.; Mahmoud, K. A.; Rest, A. J.; Willis, P. A. *J. Chem. Soc., Dalton Trans.* **1990**, 2817.
- (5) (a) Wilkinson, G.; Birmingham, J. M. *J. Am. Chem. Soc.* **1954**, *76*, 4281. (b) Druce, P. M.; Kingston, B. M.; Lappert, M. F.; Spalding, T. R.; Srivastava, R. C. *J. Chem. Soc. A* **1969**, 2106.
- (6) Surya Prakash, G. K.; Yudin, A. K. *Chem. Rev.* **1997**, *97*, 757.
- (7) (a) Huang, D.; Koren, P. R.; Folting, K.; Davidson, E. R.; Caulton, K. G. *J. Am. Chem. Soc.* **2000**, *122*, 8916. (b) Vicente, J.; Gil-Rubio, J.; Bautista, C. *Inorg. Chem.* **2001**, *40*, 2636.
- (8) Brothers, P. J.; Roper, W. R. *Chem. Rev.* **1988**, *88*, 1293.
- (9) Cotton, F. A.; McCleverty, J. A. *J. Organomet. Chem.* **1965**, *4*, 490.
- (10) See Supporting Information for full crystallographic details.
- (11) Murphy, E. F.; Murugavel, R.; Roesky, H. W. *Chem. Rev.* **1997**, *97*, 3425.
- (12) (a) Bochmann, M.; Jaggar, A. J.; Wilson, L. M. *Polyhedron* **1989**, *8*, 1838. (b) Wöhrlé, T.; Thewalt, U. *J. Organomet. Chem.* **1993**, *456*, C21. (c) Thewalt, U.; Wöhrlé, T. *J. Organomet. Chem.* **1994**, *464*, C17.

JA038527+