

# Direct conversion of perfluoroalkanes and perfluoroarenes to perfluoro Grignard reagents

Christopher M. Beck, You-Jung Park and Robert H. Crabtree\*†

Yale University, Department of Chemistry, 225 Prospect Street, New Haven, CT 06511, USA

Magnesium anthracene selectively reduces  $C_6F_{12}$  or  $C_6F_6$  and  $CF_3C_6F_{11}$  or  $CF_3C_6F_5$  to  $C_6F_5MgF$  and  $CF_3C_6F_4MgF$ , respectively

Magnesium anthracene<sup>1</sup>  $MgC_{14}H_{10}$  **1**, has found a wealth of applications in organic chemistry.<sup>2</sup> This compound is believed to act as a soluble, activated form of magnesium metal,<sup>2a,b</sup> and is often the compound of choice for the preparation of Grignard reagents that are difficult or impossible to obtain directly from magnesium metal.<sup>2</sup> Here, we describe the use of **1** in new synthetic routes to perfluoroaromatic Grignard reagents from both perfluoroaromatic compounds as well as from the less costly analogous saturated fluorocarbons.

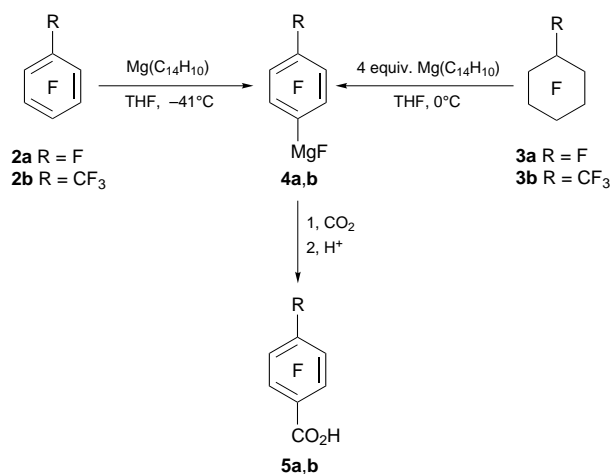
Rare cases are known in which perfluoro Grignard reagents have been synthesized from perfluoroaromatic compounds (but not from perfluoroalkanes) and magnesium by entrainment with a more reactive organic bromide, with<sup>3</sup> or without<sup>4</sup> transition metal catalysis. Important work by Richmond and Pez and their coworkers has shown that transition metal compounds<sup>5</sup> and arene anions<sup>6</sup> can reduce saturated perfluorocarbons in solution but never previously to give such useful species as Grignard reagents.

We now find that hexafluorobenzene **2a** reacts cleanly with 1 equiv. of the orange species **1** in THF solution at  $-41$  °C to afford a solution, the blue color of which is believed to be associated with the anthracene monoanion. Treatment of this solution with  $CO_2$  followed by acid work-up, yielded pentafluorobenzoic acid **5a** in moderate yield (34%), along with unreacted **2a**. The reaction appears to proceed *via* net insertion of a Mg atom into the aromatic C–F bond, forming a Grignard reagent which subsequently reacts with  $CO_2$  to form the carboxylic acid (Scheme 1). Since **1** exists in a temperature dependent equilibrium with anthracene and magnesium metal,<sup>1b</sup> it is unclear if the formation of the Grignard reagent occurs directly or by prior production of a highly active form of magnesium metal.

The reaction of perfluorotoluene **2b** with 1 equiv. of **1** at  $-41$  °C produced perfluorotoluic acid **5b**‡ exclusively as the *para* isomer but in low yield (8.5%). The yields did not change significantly between  $-78$  and  $0$  °C or in the presence of an excess of **1**. Perfluoronaphthalene gave no identifiable organic products in the presence of **1** at  $-78$  °C. For comparison, Mg powder (Aldrich Co., 50 mesh) was exposed to **2a** or **2b** under analogous conditions. In this case, no reaction was observed between the perfluoroarene and magnesium, further illustrating the necessity for using **1** in Grignard synthesis.

Our success with these perfluoroarenes led us to look at the corresponding perfluoroalkanes. When a THF solution of 4 equiv. of **1** at  $0$  °C was treated with perfluorocyclohexane **3a**, the initial orange solution rapidly turned dark brown. Subsequent work-up with  $CO_2$ , then acid, followed by extraction with dilute base afforded dark brown solids after removal of the solvent. Direct sublimation of these solids at  $115$  °C *in vacuo* afforded white crystals which proved to be an inseparable mixture of  $C_6F_5CO_2H$  and 2,3,5,6- $C_6HF_4CO_2H$ § by  $^{19}F$  NMR spectroscopy in 14 and 4% overall chemical yield based on fluorocarbon. This result is consistent with initial reduction of perfluorocyclohexane to hexafluorobenzene which would then be expected to react with an additional equivalent of **1** to yield the corresponding Grignard reagent. Similarly, perfluoromethylcyclohexane **3b** upon treatment with 4 equiv. of **1** yielded **5b** in 5.7% yield, exclusively as the *para* isomer. As in the case of the perfluoroarenes, no products were observed when commercial Mg powder was treated with **3a** or **3b** in an analogous manner. These transformations constitute, to our knowledge, the only known conversions of perfluoroalkanes directly to Grignard reagents. **CAUTION:** Fluorinated Grignards can spontaneously explode;<sup>8</sup> appropriate care must therefore be exercised.

The authors are grateful to the Department of Energy and the 3M corporation for financial support.



Scheme 1

Table 1 Yields of **5** and reaction temperature for the reactions of **2** and **3** with **1**<sup>a</sup>

Fluorocarbon	$T/^\circ C$	Yield (%)
<b>2a</b>	$-41$	34.3
<b>2b</b>	$-41$	8.5
<b>3a</b>	$0$	14.0 <sup>b</sup>
<b>3b</b>	$0$	5.7

<sup>a</sup> Fluorocarbon was added to a pre-cooled THF solution of **1** and allowed to stir for 15–40 min. Dry  $CO_2$  was introduced for *ca.* 40 min at the reaction temperature and allowed to warm to room temperature under a  $CO_2$  flow. The mixture was then quenched with dilute  $H_2SO_4$  and the THF removed *in vacuo*. The product was then extracted with  $Et_2O$ , and then extracted by shaking with 1 M (aq) KOH. The basic extracts were acidified with dilute  $H_2SO_4$  and extracted with  $Et_2O$  to yield the product. Yields reported here are for the doubly sublimed, analytically pure solids. <sup>b</sup> Isolated as a mixture which also contained 2,3,5,6- $C_6HF_4CO_2H$  in 4% yield based on fluorocarbon.

## Notes and References

† E-mail: robert.crabtree@yale.edu

‡ Data for **5b**:  $^{19}\text{F}$  NMR (461 MHz,  $[\text{D}_6]\text{acetone}$ , 20 °C,  $\text{CFCl}_3$ );  $\delta$  -56.5 (t, 3F,  $^4J_{\text{FF}}$  22 Hz), -138.9 (m, 2 F), -140.7 (m, 2 F); mp 109–112 °C, lit.<sup>7</sup> 110–111.5 °C. Anal. Calc. for  $\text{C}_8\text{HF}_7\text{O}_2$ : C, 36.64; H, 0.38; F, 50.76. Found: C, 36.62; H, 0.36; F, 50.74%.

§ This compound was identified by  $^{19}\text{F}$  NMR in comparison with an authentic sample. Occasionally, traces of this species could be distinguished in the crude solids obtained from the reaction of **2a** with **1**, but was absent after purification.

- (a) B. Bogdanovic, N. Janke, H. Kinzelmann, K. Seevogel and J. Treber, *Chem. Ber.*, 1990, **123**, 1529; (b) B. Bagdanovic, S. Liao, R. Mynott, K. Schlichte and U. Westeppe, *Chem. Ber.*, 1984, **117**, 1378.
- (a) M. Gallagher, S. Harvey, C. Raton and R. Sue, *J. Chem. Soc., Chem. Commun.*, 1988, 289; (b) B. Bogdanovic, *Acc. Chem. Res.*, 1988, **21**, 261;

(c) S. Harvey and C. Raston, *J. Chem. Soc., Chem. Commun.*, 1988, 652

(d) T. Hudlicky, M. Natchus and G. Sinai-Zingde, *J. Org. Chem.*, 1987, **52**, 4644.

- W. Respass and C. Tamborski, *J. Organomet. Chem.*, 1969, **18**, 263.
- W. Respass, J. Ward and C. Tamborski, *J. Organomet. Chem.*, 1969, **19**, 191.
- J. Kiplinger, T. Richmond and C. Osterberg, *Chem. Rev.*, 1994, **94**, 373, and references within; B. Bennett, R. Harrison and T. Richmond, *J. Am. Chem. Soc.*, 1994, **116**, 11 165; J. Kiplinger and T. Richmond, *J. Am. Chem. Soc.*, 1996, **118**, 1805; *Chem. Commun.*, 1996, 1115.
- J. Marsella, A. Gilicinski, A. Coughlin and G. Pez, *J. Org. Chem.*, 1992, **57**, 2856; A. Oku., J. Nishimura, S. Nakagawa and K. Yamada, *Nippon Kagaku Kaishi*, 1985, **10**, 1985; *Chem. Abstr.*, 1986, **105**, 97074z.
- C. Tamborski and E. Soloski, *J. Org. Chem.*, 1966, **31**, 746.
- E. C. Ashby and D. Al-Fekri, *J. Organomet. Chem.*, 1990, **390**, 275.

Received in Bloomington, IN, USA, 25th November 1997; 7/08515J