

## Large Scale Preparation of $\text{Fe}_2(\text{adt})(\text{CO})_6$

From the Supporting Information in R. Zaffaroni, T. B. Rauchfuss, D. L. Gray, L. De Gioia, G. Zampella "Terminal vs Bridging Hydrides of Diiron Dithiolates: Protonation of  $\text{Fe}_2(\text{dithiolate})(\text{CO})_2(\text{PMe}_3)_4$ " *J. Am. Chem. Soc.* **2012**, *134*, 19260.

The following procedure is a modification of the published procedure (Li, H.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2002**, *124*, 726.). A 500-mL Schlenk flask equipped with a dropping funnel was dissolved 3.00 g (8.72 mmol) of  $\text{Fe}_2\text{S}_2(\text{CO})_6$  in 100 mL of THF. This red-orange homogeneous solution was cooled to  $-78\text{ }^\circ\text{C}$ . The dropping funnel was charged with 20 mL of THF followed by 17.88 mL (17.87 mmol, 2.05 equiv) of 1M solution of  $\text{LiBHET}_3$  in THF. The hydride solution was added to the reaction over the course of 20 min to afford a dark green solution. After the addition was complete, the reaction mixture was stirred for an additional 20 min. The reaction temperature was allowed to slowly rise to  $-30\text{ }^\circ\text{C}$ , which caused the color to change from deep green to deep red (note) After 10 min. of stirring at  $-30\text{ }^\circ\text{C}$ , the reaction mixture was cooled again to  $-78\text{ }^\circ\text{C}$ . The addition funnel was charged with 15 mL of THF and 1.4 mL (18.31 mmol, 2.10 equiv) of  $\text{CF}_3\text{CO}_2\text{H}$ . This solution was added to the reaction flask over 20 min. During this addition the color changed from deep red to deep green, then to deep red again and finally to a red-orange clear solution. To this solution was added 1.223 g (8.72 mmol) of hexamethylenetetramine, which had been finely ground and subsequently vacuum-dried. This mixture was allowed to warm to room temperature while stirring. The reaction was stirred for 28 h before solvent was removed in vacuo to afford a dark red/black gummy residue. The residue was then extracted with ca. 100 mL of  $\text{CH}_2\text{Cl}_2$ , and this extract was passed through a plug of silica gel. Solvent was evaporated under vacuum, and the residue was extracted in minimal amount of a pentane/ $\text{CH}_2\text{Cl}_2$  mixture (8:2, ca. 20 mL is required). This extract was chromatographed on a 5 x 25 cm column of silica gel eluting with pentanes to remove two red orange undefined products. The polarity of the eluting solvent was then increased to pentane/ $\text{CH}_2\text{Cl}_2$  mixture (9:1), then increased to pentane/ $\text{CH}_2\text{Cl}_2$  mixture (7:3) to afford the product as bright red colored solid. Yield: 1.3 g (38.5%). IR (pentanes): 2075, 2035, 2007, 1990, 1980  $\text{cm}^{-1}$  (see Lawrence, J. D.; Li, H.; Rauchfuss, T. B.; Bénard, M.; Rohmer, M.-M. *Angew Chem., Int. Ed.* **2001**, *40*, 1768).

Note: About the color changes: green could be  $\text{Li}_2[\text{Fe}_4\text{S}_4(\text{CO})_{12}]$  (Bose, K. S., Sinn, E., Averill, B. A., "Synthesis and x-ray structure of the  $[\text{Fe}_4\text{S}_4(\text{CO})_{12}]^{2-}$  ion: an example of intermolecular disulfide formation by the  $(\mu\text{-S})_2\text{Fe}_2(\text{CO})_6$  unit", *Organometallics* **1984**, *3*, 1126). Red is presumably  $\text{Li}_2[\text{Fe}_2\text{S}_2(\text{CO})_6]$ .