



## Synthesis and reactivity of silylated tetrathiafulvalenes

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Résumé en anglais Novel organosilylated tetrathiafulvalenes (TTFs) possessing Si-H or Si-Si bonds have been synthesised. The crystal structures of several derivatives have been determined by X-ray diffraction, including that of dimeric  $(\text{SiMe}_2)(\text{TTF})_2$  (11) incorporating a diatomic  $\text{SiMe}_2\text{-SiMe}_2$  linker. Cyclic voltammetry measurements in all cases show two oxidation waves. DFT calculations were performed to rationalize the absence of an electronic communication between the two TTF moieties of 11 through the disilanyl spacer. The reactivity of the Si-H bond has been exploited to prepare the dinuclear complex  $[\{\text{Ru}(\text{CO})_4\}_2\{\mu\text{-(Me}_2\text{Si)}_4\text{TTF}\}]$  (14), starting from  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{TTF}(\text{SiMe}_2\text{H})_4$  (1). Treatment of 14 with 2 equiv. of  $\text{PPh}_3$  or  $\text{dppm}$  results in selective substitution of a CO ligand trans to a  $\text{SiMe}_2$  group to afford  $\text{mer-}[\{\text{Ru}(\text{PPh}_3)(\text{CO})_3\}_2\{\mu\text{-(Me}_2\text{Si)}_4\text{TTF}\}]$  (13) and  $\text{mer-}[\{\text{Ru}(\text{CO})_3\}_2(\eta^1\text{-dppm})\{\mu\text{-(Me}_2\text{Si)}_4\text{TTF}\}]$  (16). Attempts to transform the Si-H bonds of some  $\text{TTF}(\text{SiMe}_2\text{H})_n$  ( $n = 1, 2$ ) into Si-O functions using stoichiometric amounts of water in the presence of  $\text{tris}(\text{dibenzylideneacetone})\text{dipalladium}(0)$  were unsuccessful. Quantitative cleavage of the CTTF-Si bond was observed instead of formation of TTF-based-siloxanes. Essays of catalytic bis-silylation of phenylacetylene with 11 and  $\text{TTF}(\text{SiMe}_2\text{-SiMe}_3)$  (9) in the presence of  $\text{Pd}(\text{OAc})_2/1,1,3,3\text{-tetramethylbutylisocyanide}$  failed. Again, cleavage of the CTTF-Si bond was noticed.

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