

Thiophene Complexes of Early Transition Metals

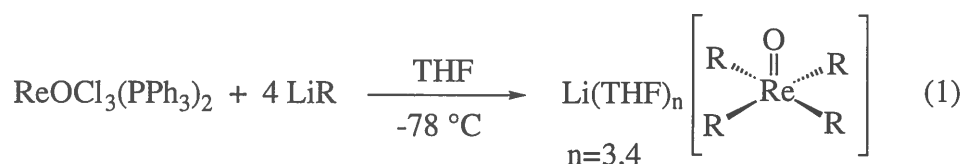
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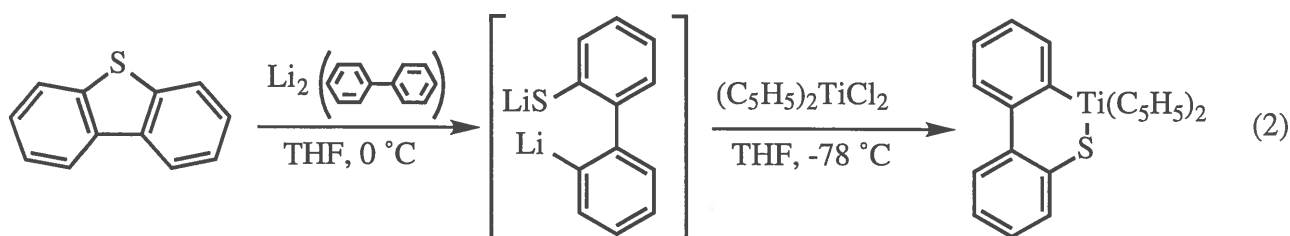
The hydrogenolysis of organosulfur compounds found in fossil fuels is of paramount importance due to the adverse environmental consequences associated with the combustion of these fuels and the detrimental effect that these compounds have on the catalysts used in the refining process. Commercially, the hydrogenolysis reactions, termed hydrodesulfurization (HDS), are typically carried out over a partially sulfided molybdenum catalyst promoted by either cobalt or nickel [1]. A plethora of organometallic studies involving later transition metals (Ru, Rh, Ir, Co, Pt, Fe) to model the HDS process have been undertaken and significant insights concerning the coordination of thiophenes to transition metals and subsequent C-S cleavage reactions have been realized [2]. The research presented today focuses on organometallic HDS modeling by probing the reactivity of thiophenes with (i) early transition metals having low d-electron counts, (ii) transition metals having oxo coligands, and (iii) C-S cleavage reactions involving condensed thiophenes.

The treatment of a THF slurry of $\text{ReOCl}_3(\text{PPh}_3)_2$ with thienyllithium reagents afforded $\text{Li}(\text{THF})_n[\text{ReO}(\text{thienyl})_4]$, where thienyl is $\text{C}_4\text{H}_3\text{S}$, 5-Me $\text{C}_4\text{H}_2\text{S}$, $\text{C}_8\text{H}_5\text{S}$ (benzothieryl), and $\text{C}_{12}\text{H}_7\text{S}$ (dibenzothieryl) (eq. 1) [3].



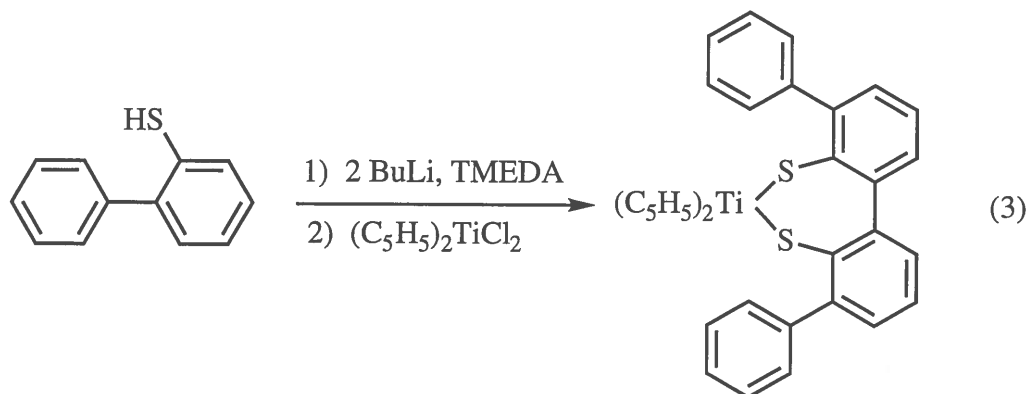
Crystallographic characterization of $\text{Li}(\text{THF})_3[\text{ReO}(\text{C}_4\text{H}_3\text{S})_4]$ and $\text{Li}(\text{THF})_4[\text{ReO}(\text{C}_8\text{H}_5\text{S})_4]$ indicate a square pyramidal Re center with the four thienyl ligands tilted in a pinwheel arrangement. In contrast to analogous Re(VI) aryl complexes [4] and Re(I) thienyl complexes, these complexes are reactive towards protic reagents to afford thiophene. Electrochemical studies demonstrate that these Re(V) complexes undergo oxidation at mild potentials; unfortunately, preparative scale oxidations generate coupled organic products.

The scission of C-S bonds in dibenzo-thiophene (DBT) has recently attracted much attention. Early investigations indicated that the C-S bond in DBT can be cleaved upon reduction with lithium [5] while more recent investigations have involved the oxidative addition of DBT to electron deficient metal centers [6]. The work here began by generating a metallacycle via metathetical routes starting from the lithium reduced intermediate (eq. 2) [7].

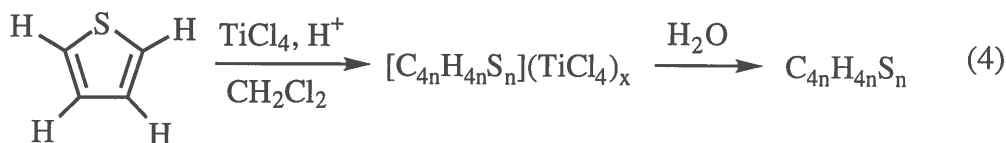


The single crystal X-ray structure of the metallacycle indicated a tetrahedral geometry about the Ti center and a cyclohexadiene-like metallacyclic ring. Dynamic NMR studies showed that the complex is stereochemically nonrigid as a result of the folding of the organosulfur chelate. The complex decomposes photolytically to afford dibenzothiophene and, in the pres-

ence of a CO atmosphere, titanocene dicarbonyl. Attempts to generate the metallacycle via the double metallation of 2-phenylbenzenethiol with two equivalents of butyllithium in the presence of TMEDA followed by $(C_5H_5)_2TiCl_2$ afforded the coupled, dimercaptobiaryl complex $(C_5H_5)_2TiS_2C_{24}H_{16}$ (eq. 3).



Previous studies have indicated that thiophene can undergo electrophilic substitution at the α -carbon and the treatment of thiophene with acids leads to insoluble material [8]. Investigations in this lab found that treatment of solutions of $TiCl_4$ and thiophene with strong acids leads to the formation of a soluble polymer as determined by size exclusion chromatographic analysis (eq. 4) [9].



Microanalytical data indicates a composition of $C_{4n}H_{4n}S_n$ and spectroscopic data suggest that the polymer contains a combination of thiophene and tetrahydrothiophene units. The polymer can coordinate to metals, can be dehydrogenated by quinones, and can be partially desulfurized by Raney-Ni.

References

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