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SYNTHESIS OF TITANOCENE COMPLEXES USING POLYAROMATIC LIGANDS CONTAINING A DISULFIDE BRIDGE

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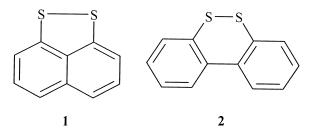
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The complexes $\operatorname{Cp_2Ti}[S_2X]$ ($\operatorname{Cp} = \operatorname{cyclopentadienyl}$), where S_2X is a polyaromatic dithiolate ligand, are readily prepared by addition of the appropriate ligand to $\operatorname{Cp_2Ti}(\operatorname{CO})_2$. The resulting complexes have the $\operatorname{Cp2Ti}$ unit inserted into the sulfur sulfur bond. A number of novel complexes have been prepared using a series of naphthalene based and biphenyl based ligands, the simplest examples in each case being naphtho[1,8- cd]-1,2-dithiole 1 and dibenzo[ce]-1,2-dithiine 2.



In the case of the complexes titanocene 1,8-dithiolato-naphthalene, titanocene 4,5-dithiolato-acephenanthrylene, titanocene 2,7-di(tert-butyl)-1,8-dithiolato-naphthalene and titanocene 1,8-dithiolato-5,6-dihydroacenaphthalene, these compounds show dynamic solution NMR behavior due to the aromatic region of the ligand being outwith the Ti-S-S plane, reducing the symmetry of the compound. This type of behavior has not been noticed with the biphenyl

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based complexes titanocene 2,2'-dithiolato biphenyl and titanocene 1,1'-dithiolato[2,2']binaphthalene as the torsion angle of the biphenyl group conferred symmetry onto the complex, resulting in the two cyclopentadienyl groups being equivalent at all times.

Wherever possible, these complexes have been characterized by single crystal x-ray analysis.