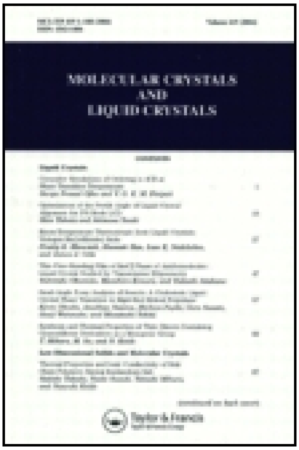

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NOVEL MATERIALS BASED ON METALLOCENE-DITHIOLENES

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ABSTRACT

Novel metallocene-dithiolene complexes with titanocene and zirconocene as the organometallic ligand have been prepared and characterised.

INTRODUCTION

In recent years, the chemistry of metallocenes and in particular ferrocene chemistry has gained renewed interest. Already extensively used as the backbone to many ligand systems, the potential of the ferrocene synthon to be used in molecular ferromagnets[1] and sensors[2] within the growing area of "new material science" seems promising. Ferrocene is a good electron donor and has great synthetic promise since the redox potential of the iron(II)/iron(III) couple is highly dependent on the cyclopentadienyl substituents. This has opened up a new area of molecular conductors based on the integration of multi-sulphur π-acceptors of transition metal bis-dithiolene complexes that contain organometallic ligands[3]. Incorporation of metallocenes and dithiolenes into a single moiety might be expected to change the unusual electrical conduction, magnetic and optical properties already shown for dithiolene systems[4]. In an approach to combining these two synthons, this present study concerns the synthesis and characterisation of novel materials based on metallocene-dithiolenes.

EXPERIMENTAL

(i) Preparation of Titanocene-dmid

To a green solution of *(TBA)$_2$[Zn(dmid)$_2$] (0.90g, 0.001 mol) in THF was added a slurry of Cp$_2$TiCl$_2$ (0.50g, 0.002 mol) in THF. The mixture was heated to reflux under N$_2$ for 3 hours. After cooling to room temperature, the solution was filtered through silica, washed with THF and concentrated *in vacuo*. Addition of hexane and subsequent cooling yielded a green/black powder in 90% yield (mpt. 174-176°C uncalibrated).

[* TBA = Tetrabutylammonium]

$C_{13}H_{10}OS_4Ti$	Calc%	C: 43.59	H: 2.79	N: 0.00
	Found%	C: 44.00	H: 3.24	N: 0.00

IR (KBr, cm^{-1}): 1651 (C=O)

(ii) Attempted Preparation of a Titanocene-dithiolene Metal Complex

To a slurry of titanocene-dmid (0.40g, 0.0012 mol) in ethanol, sodium (0.05g, 0.0024 mol) in 20 mls ethanol was added dropwise under N$_2$ and stirred for 45 minutes. Unreacted starting material was filtered off and TBABr (0.37g, 0.0012 mol) was added to the filtrate followed by NiCl$_2$.6H$_2$O (0.14g, 0.0006 mol) dropwise in ethanol and under N$_2$. The black solid was filtered, washed with ethanol and dried under suction. Characterisation revealed the product to be (TBA)[Ni(dmid)$_2$] (b) instead of a titanocene-dithiolene metal complex (a).

(a) ($C_{40}H_{56}NNiS_8Ti_2$)	Calc%	C: 49.98	H: 5.83	N: 1.46
(b) ($C_{20}H_{36}NNiO_2S_8$)	Calc%	C: 39.95	H: 5.44	N: 2.11
	Found %	C: 39.61	H: 5.56	N: 1.81

IR (KBr, cm^{-1}): 1654 (C=O)

FAB MS (m/z): 418 - consistent with the [Ni(dmid)$_2$] monoanion

NIR (nm): 1080 - consistent with TBA[Ni(dmid)$_2$]

(iii) Preparation of Zirconocene-dmit

Sodium (0.113g, 0.005 mol) in 20 mls dry ethanol was added to crushed 4,5-bis(benzoylthio)-1,3-dithiole-2-thione (1.0g, 0.0025 mol) slurried in ethanol and the reaction mixture allowed to stir for 15 minutes. Zirconocene dichloride (0,72g, 0.0025 mol) in 20 mls dry THF was added dropwise and the mixture refluxed for 20 hours. After cooling to room temperature, the brown product was filtered off, washed with water and THF and dried *in vacuo.*

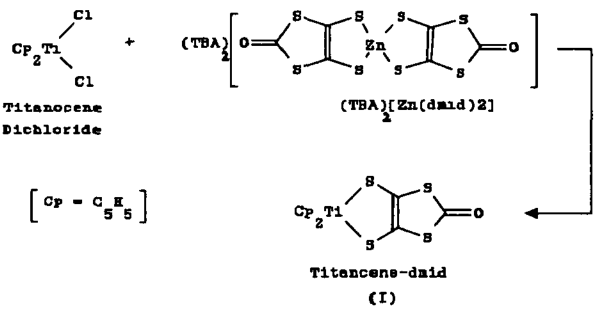
$C_{13}H_{10}S_5Zr$	Calc%	C: 37.41	H: 2.40	N: 0.00
	Found%	C: 36.03	H: 2.85	N: 0.00

IR (KBr, cm^{-1}): 1065 (C=S)

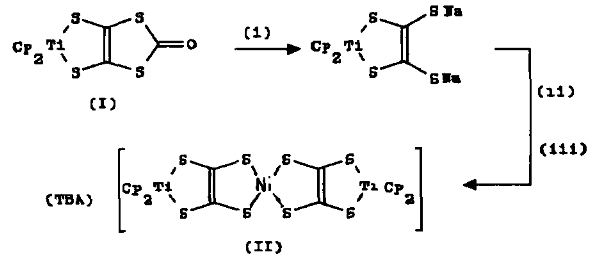
RESULTS AND DISCUSSION

The most successful work to date has concentrated on titanocene and zirconocene as the organometallic ligand. The synthesis of titanocene-dmit from titanocene dichloride and (TEA)$_2$[Zn(dmit)$_2$] has previously been published by Rauchfuss *et al.*[5] Studies at Bangor have attempted to synthesise new metal complexes (of type II) *via* the ketone derivative titanocene-dmid (I) as shown in schemes 1-3.

Scheme 1: Synthesis of Titanocene-Dmid



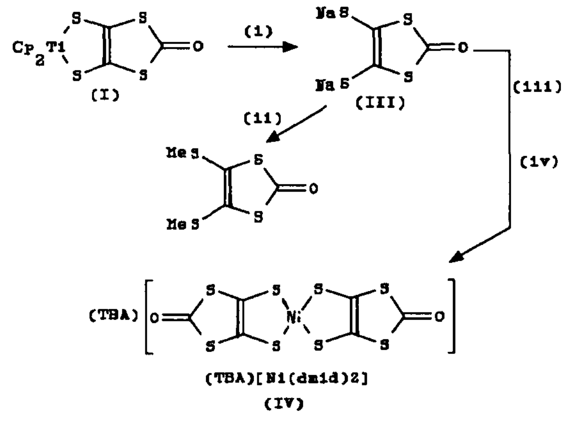
Scheme 2: Proposed Metal Complex Formation from Titanocene-Dmid



Reagents (i) NaOR where R = Me, Et
(ii) TBABr
(iii) $NiCl_2.6H_2O$

Base induced opening of the dithiole ring at the site of the ketone functionality was expected to yield the disodium salt and ultimately complex (II) upon addition of a suitable metal. However, the Cp_2TiCl_2 moiety acts as a group transfer agent[6] with the scission of the weak titanocene-sulphur bonds leaving the dithiolene unit intact as shown in the following scheme:

Scheme 3: Observed Reaction

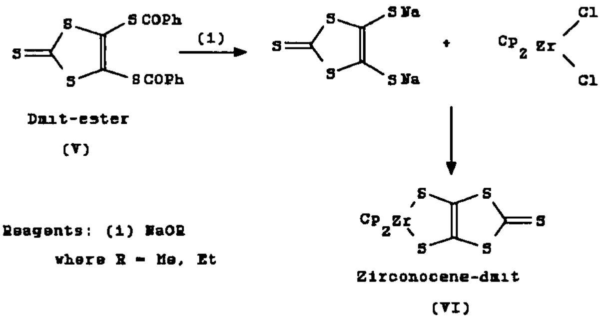


Reagents. (i) NaOR (ii) MeI (iii) TBABr
(iv) $NiCl_2.6H_2O$

The formation of the sodium-dmit salt (III) has been proven by trapping with methyl iodide (as shown above) to form methyl-dmit which has been characterised by ^{1}H-nmr and IR. The final product (IV) has been characterised by CHN analysis and FAB mass spectrometry. It exhibits an intense NIR absorption band at 1080 nm, consistent with (TBA)[Ni(dmid)$_2$]. Coupling of titanocene-dmid (I) using P(OEt)$_3$ proved unsuccessful possibly due to the harsh reaction conditions breaking up the labile titanocene-sulphur bonds.

Studies on the analogous zirconocene system have recently been commenced. Attempts to synthesise zirconocene-dmit (VI) from zirconocene dichloride and (TEA)$_2$[Zn(dmit)$_2$] were unsuccessful although more promising results were obtained by using compound (V) (as shown in scheme 4).

Scheme 4: Synthesis of Zirconocene-Dmit



Complex (VI) has been characterised by CHN analysis and IR. Synthetic studies involving metal complexation reactions with the zirconocene-dmit system are underway. However, the formation of the metal complex could be hindered as zirconocene is similar to titanocene in the ability to serve as a group transfer agent.[7]

CONCLUSIONS

In summary, this paper has outlined the synthesis and characterisation of several new dithiolene systems incorporating zirconocene and titanocene as the organometallic ligand. Although clearly in its infancy, further studies at Bangor are being undertaken to integrate dithiolenes with ferrocenes by attachment to the cyclopentadienyl rings. In this way, the coplanarity between the ligand π-system and dithiolene core can be enhanced and the donor potential of the metallocenes fully realised.

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REFERENCES

1. C. R. Kollmar, M. Couty, O. Kahn, J. Am. Chem. Soc., 113 (1991) 7994.
2. E. C. Constable, Angew. Chem. Int. Ed. Eng., 30 (1991) 407.
3. U. T. Mueller-Westerhoff, D. I. Yoon, K. Plourde, Mol. Cryst. Liq. Cryst., 183 (1990) 291.
4. A. E. Underhill, Chem. In Britain, (Aug. 1991) 708.
5. T. B. Rauchfuss, X. Yang, S. R. Wilson, J. Am. Chem. Soc., 111 (1989) 3465.
6. D. M. Giolando, M. Papavassiliou, J. Pickardt, T. B. Rauchfuss, R. Steudel, Inorg. Chem, 27 (1988) 2596.
7. P. J. Fagan, W. A. Nugent, J. Am. Chem. Soc., 110 (1988) 2310.