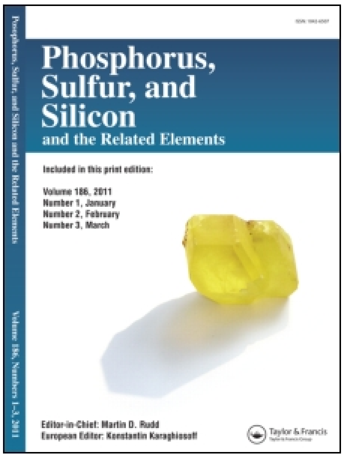


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Metalla-2,5-Dichalcogena Cyclopentenes - S, Se and Te Containing Organometal Heterocycles

Thomas M. Klapötke[a]
[a] Institut für Anorganische und Analytische Chemie, Technische Universität, Berlin, F.R.G.

To cite this Article Klapötke, Thomas M.(1989) 'Metalla-2,5-Dichalcogena Cyclopentenes - S, Se and Te Containing Organometal Heterocycles', Phosphorus, Sulfur, and Silicon and the Related Elements, 41: 1, 105 — 111
To link to this Article: DOI: 10.1080/10426508908039698
URL: http://dx.doi.org/10.1080/10426508908039698

Phosphorus, Sulfur and Silica, Vol. 41, pp. 105–111
Reprints available directly from the publisher
Photocopying permitted by license only

METALLA-2,5-DICHALCOGENA CYCLOPENTENES - S, Se AND Te CONTAINING ORGANOMETAL HETEROCYCLES

THOMAS M. KLAPÖTKE
Institut für Anorganische und Analytische Chemie,
Technische Universität Berlin, D-1000 Berlin 12, F.R.G.

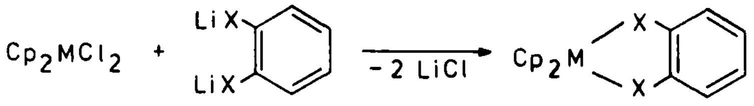
Abstract Synthesis, spectroscopic (^{1}H N.M.R., ^{77}Se N.M.R., ^{1}H D.N.M.R., MS), and structural characterization of five-membered metalla-2,5-dichalcogena heterocycles are presented. The practicable applications of these metallacycles are discussed.

INTRODUCTION

A considerable number of S,S' co-ordinated five-membered metallacycles in the metallocene system has been characterized in the past 20 years.[1] It was only in recent years that the investigation of Se and Te analogues began.[1] Also in organo Bi chemistry the dithiolene derivatives are known for a long time, whereas the Se containing heterocycle has been reported quite recently and the Te,Te' co-ordinated metallacycle is not yet known.[2] These complexes are of interest not only on account of their structures in solution and in crystals, but also in respect of their significance in bonding theory and their conformative flexibility of the folded, flexible heterocycles.[1] The biologically active compounds may well turn out to open up a novel form of chemotherapy.[3,7]

SYNTHESIS

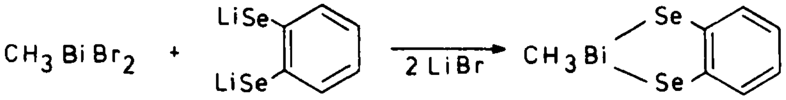
There are several ways to prepare the metallocene dichalcogenolene heterocycles. One of the most convenient methods is the salt elimination by reaction of the corresponding metallocene dichloride with one equivalent of the appropriate lithium ligand salt according to eq. 1.[1]



(1)

(Cp = η^5-C_5H_5; M = Ti, Zr, Hf, Mo, W; X = S, Se, Te)

The preparation of the first Se,Se' co-ordinated Bi metallacycle was carried out analogous according to eq. 2.[2]



(2)

STRUCTURAL CHARACTERIZATION

The structures of many metalla-2,5-dichalcogena cyclopentenes in the solid state (see Fig. 1) and in solution have been determined by X-ray structure analysis and by temperature-dependent dynamic ^1H D.N.M.R. spectroscopy.[1] All five-membered heterocycles exist in an envelope conformation folded along the X· · ·X axis.

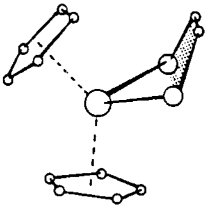


FIGURE 1 Structure of $Cp_2Ti(S_2C_2H_2)$.

In the Cp region of the temperature-dependent ^1H N.M.R. spectrum the singlet due to the Cp protons appears only at high temperatures in the case of the unsubstituted metallocene derivatives. At lower temperatures it is subject to a coalescence phenomenon and is split into two signals of equal intensity below that coalescence temperature (Fig. 2).[1]

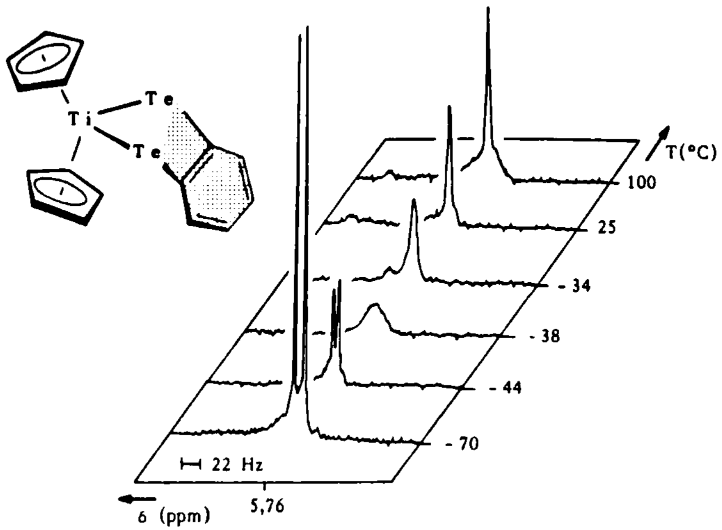
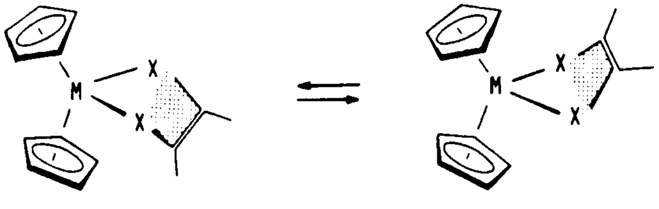


FIGURE 2 Temperature-dependent ^1H N.M.R. spectrum (Cp region) of $Cp_2Ti(Te_2C_6H_4)$.

On the basis of this result an envelope conformation of the metallacycles also in solution can be deduced. Whereas a rapid ring inversion takes place at room temperature (see eq. 3), a "freezing" of the chelate ring into a fixed envelope conformation with different surroundings of the two Cp ligands appears at low temperature.[1]



(3)

The activation parameters of the chelate ring inversion were estimated according to eq. 4 and some of them are summarized in Table I.[1]

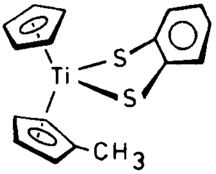
$$\Delta G_C^* = 19.13\ T_C\ (9.97 + \lg \frac{T_C}{\Delta\nu}) \qquad (4)$$

$(T_c\ /\ K;\ \Delta\nu\ /\ Hz;\ \Delta G_c^*\ /\ J\ mol^{-1})$

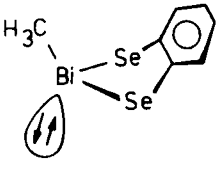
TABLE I Activation parameters of the ring inversion of $Cp_2M(X_2C_6H_4)$; ΔG^*_c values ± 10%.

M	X	ΔG^*_c / KJ mol^{-1}
Ti	S	53
Hf	S	45
Ti	Se	57
Ti	Te	51
Zr	Te	51
Hf	Te	48

While the energy barrier of the chelate ring inversion often seems to be inversely proportional to the radius (not mass (!), cf. lanthanide contraction: $r(Ti) < r(Hf) \lesssim r(Zr)$) of the central metal atom (especially in the case of the S co-ordinated species), there is no significant connection between the chelating atom and the ΔG^*_c values. This might be due to the significant influence of the (similar) re-hybridization energy of the chalcogenes at the conformation change by ring flipping (N.B. for $Cp_2Ti(SC_6H_4NH\text{-}o)$ $\Delta G^*_c > 80$ KJ mol^{-1}, for $Cp_2Hf(SC_6H_4NH\text{-}o)$ $\Delta G^*_c = 58$ KJ mol^{-1}).[1] In the case of unsymmetrically substituted derivatives like $CpCp'Ti(S_2C_6H_4)$ (A) ($Cp' = \eta^5\text{-}C_5H_4CH_3$)[1] and the pseudo tetrahedral $CH_3Bi(Se_2C_6H_4)$ (B)[2] the two conformeres (endo and exo) appear in different ratios. At -50°C both, the conformer with the exo standing Cp' ring (A) and that with the exo standing stereochemically active lone pair of electrons (B) are slightly favoured by their thermodynamics (integration of the ^1H N.M.R. spectra).



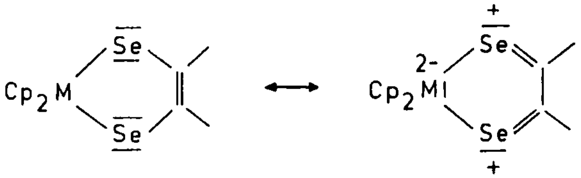
A



B

^{77}Se N.M.R.

In the ^{77}Se N.M.R. the Se co-ordinated titanocene system shows a low field shift by proceeding from the non-cyclic derivative ($Cp_2Ti(SeC_6H_5)_2$, δ = 847 ppm) to the five-membered Se,Se' co-ordinated heterocycle ($Cp_2Ti(Se_2C_6H_4)$, δ = 982 ppm).[4] This effect may be explained by a mesomerism according to eq. 5 (V.B. theory) or by M.O. theory by $(p_{Se} \rightarrow d_{Ti})_\pi$ interaction in these 16 electron complexes. (Moreover, the M.O. theory explains the folded geometry of these derivatives, too.)[5]



(5)

Surprisingly, in comparison with Ti the Zr metallacycle shows a reversed shielding effect.[4] But in case of Zr the 18 electron configuration also can be realized by intermolecular interaction (co-ordination number = 5). This may also explain the unusual behaviour of zirconocene metallacycles in the ^{1}H D.N.M.R. spectra (repeated no coalescence above -80°C).[1]

MASS SPECTRA

Fragmentation patterns of the above discussed metallacycles have been studied intensively and the ion genesis often was elucidated by purchasing metastable transitions.[1,6] Surprisingly, after cleavage of one Cp ring the unsubstituted ethene dithiolates ($Cp_2M(S_2C_2H_2)$; M = Ti, Mo, W) show an intense peak corresponding to an elimination of acetylene as a neutral particle (see Fig. 3), which contrasts to the analogous maleonitrile derivatives.[6]

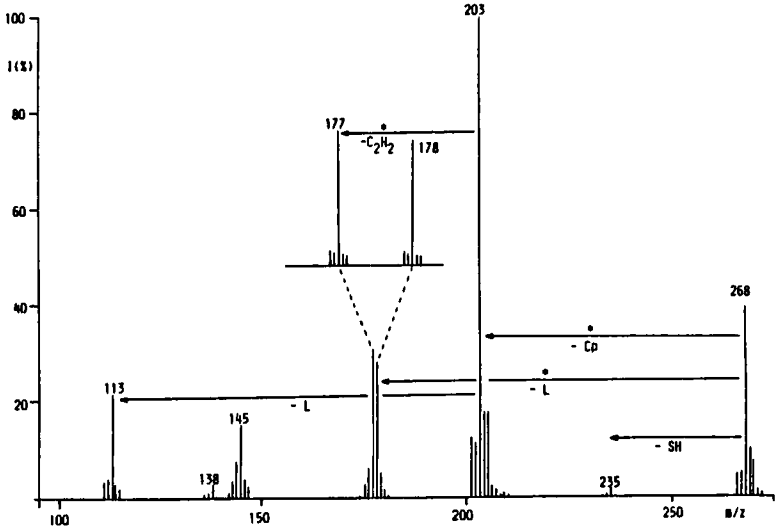


FIGURE 3 Mass spectrum (EI, 70 eV, 120°C) of $Cp_2Ti(S_2C_2H_2)$; * ion genesis proved by metastable transition.

ANTITUMOR ACTIVITY

Most of the titanocene compounds which are already known as antitumor agents are neutral complexes like Cp_2TiCl_2 and the maleonitrile heterocycle $Cp_2Ti(S_2C_2(CN)_2)$.[7]

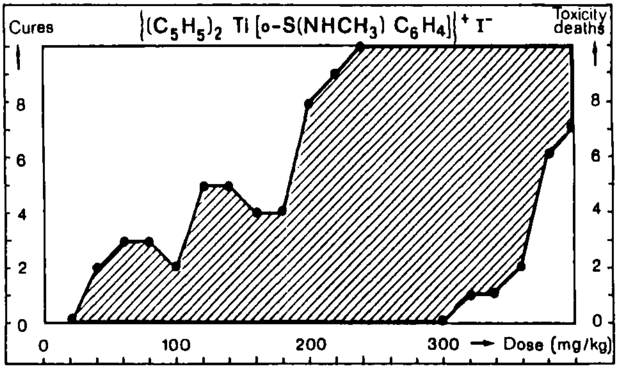


FIGURE 4 Dose response (left) and dose lethality (right) correlations of C against fluid Ehrlich ascites tumor.

Quite recently we investigated the antiproliferative properties of some new ionic titanocene mercaptoanilinium derivatives.[3] The metallacycle $(Cp_2Ti[o\text{-}S(NHCH_3)C_6H_4])^+I^-$ (C) was prepared analogously from Cp_2TiCl_2 and $o\text{-}LiSC_6H_4NHLi$ and following reaction of the neutral five-membered heterocycle with CH_3I. The dose response and the dose lethality correlations of **C** (which undoubtedly is more hydrophilic than the neutral derivatives!) against fluid Ehrlich ascites tumor are shown in Fig. 4.

REFERENCES

1. Th. Klapötke and H. Köpf, J. Organomet. Chem. Library, **Vol. 20**, 343 (1988), and references therein.
2. Th. Klapötke, Polyhedron, **Vol. 6 No. 7**, 1593 (1987).
3. H. Köpf, Th. Klapötke, and P. Köpf-Maier, Abstr. 192nd ACS Ntl. Meeting, Anaheim, California, **INOR 132** (1986).
4. Th. Klapötke, Spectrochim. Acta, **43 A No. 12** (1987).
5. J. W. Lauher and R. Hoffmann, J. Am. Chem. Soc., **98**, 1729 (1976).
6. Th. Klapötke and H. Köpf, Z. Allg. Anorg. Chem., in press.
7. P. Köpf-Maier, Th. Klapötke, and H. Köpf, Inorg. Chim. Acta, in press.