

Invited review

Optically active organometallic compounds (a personal account from the inside)

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Abstract

Results of a long experience of our group in Moscow in the area of chiral organometallic stereochemistry are described. They embrace optically active organometallic derivatives of mercury, palladium, platinum, functionalized ferrocenes, ruthenocenes, and cymantrenes as well as less common objects such as organometallic fullerenes and the cyclodextrin–metallocenes inclusion complexes.

Keywords: Mercury; Palladium; Ruthenium; Metallocenes; Manganese

1. Introduction

I welcome this opportunity of describing some of my work in organometallic stereochemistry. A large proportion of our papers have been published in Russian journals and, in spite of the availability of English translations have not become fully known to the international community.

In organometallic stereochemistry I have been able to unite my main scientific interests in molecular structures and reactivities with the optical activity connected inseparably to the mathematical basis of stereochemistry through the symmetry of molecules. This has satisfied my original passion for mathematics that had been forced to yield to chemistry when I had to chose my branch of science.

The strictness inherent in the mathematics of theoretical stereochemistry is combined with the remarkable diversity of the specific chemical structures to give special charm to practical stereochemistry. There is no other section of chemistry in which reactivity is as varied as in organometallic chemistry, in particular, that of transition metals in which each metal has its own chemistry.

I graduated from Moscow University and undertook my Ph.D work there. At that time my supervisor, Professor Oleg Reutov, began to work with optically active organomercurials, diastereomeric 1-menthyl esters of α -bromophenylacetic acid [1], as model compounds for mechanistic studies of electrophilic substitution. He was

in fact the first chemist in the Soviet Union and one of the first few in the world to recognise the importance of optically active organometallics for such studies. Thus the starting point for my entry into experimental stereochemistry was with organomercurials.

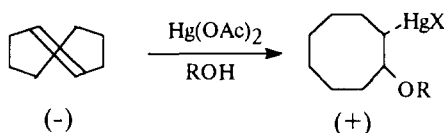
However, I had been always deeply interested in optical activity in itself, trying to understand what chirality and (absolute) configuration mean. My way of thinking in this area had been influenced by works of Prelog, Mislow and other outstanding stereochemists. My first publication in this field was the calculation of the angle of rotation of methylethylphenylphosphinoxide [2] using Brewster's approach [3] and gave results in good accordance with experiment.

In the years to follow, I tried to tackle in parallel some problems in both theoretical and experimental but always chiral stereochemistry. As a result of this dual interest two monographs have appeared [4,5]. While theoretical exercises have been my own individual job the experimental work has been done mostly by my coworkers, persons of great ability and skill. Among them Dr. Ludmila Troitskaya and Dr. Vassily Bashilov have been with me for longest time.

2. Organomercurials

My stereochemical work with organomercurials began with the calculation of the optical rotation of the very few enantiomers known at that time. It was possi-

ble to demonstrate *trans*-addition of mercuric salts to cyclohexene and to determine the conformational energy difference between the axial and equatorial positions of the HgCl group [6]. The *cis*-oxymercuration of strained *trans*-cyclooctene had been established [7], and enantiomeric organomercurials were obtained by using mercuric acetate, as expected from an optically active olefin. This steric course was in accordance with the ideas of Traylor and Baker [8] about the influence of steric strain on the stereochemistry of oxymercuration whereas the sign of the optical rotation obeyed Brewster's rule [3] for the conformational contribution. Oxymercuration of (–)-1,2-dimethylcyclopropane [9] confirmed the inversion of configuration at the site of nucleophilic attack. In the part of this extensive investigation of the reactions between mercuric salts and achiral olefins, cyclopropanes, or arenes [10] several novel reactions were observed [11].



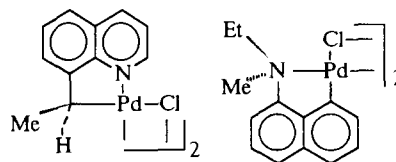
Later we have synthesized and resolved two γ -aminomercurials in order to study their reactivity towards zero-valent palladium complexes since they are ideal precursors for the stable five-membered metallochelates, namely, 8-(α -bromoethyl)quinoline [12] and 3-dimethylaminobutylmercuric bromide [13].

3. Organopalladiums and organoplatinums

The stereochemical potential of mercury in itself is negligible compared with that of carbon. It can only be part of a chiral fragment as a substituent and may supply information about the mechanism of substitution at the chiral centre when it serves as a leaving or entering group. Metals with a broader spectrum of synthetic and stereochemical possibilities looked more interesting. Palladium and platinum show a remarkable similarity to mercury in reactivity towards double bonds [14], but besides they are also able to form stable chelate metallocycles.

After the report on cyclometalation involving the alkyl group of 8-methyl-quinoline [15] we have designed a chiral analogue derived from 8-ethylquinoline, carried out cyclopalladation and separated the diastereomers by use of the α -phenylethylamine ligand, which then was replaced by triphenylphosphine. To my knowledge, this compound was the first reported optically active σ -bonded organopalladium species [16]. A re-

lated organoplatinum was obtained with low optical rotation using oxidative addition of enantiomeric 8-(α -bromoethyl)-quinoline to tris(triphenylphosphine)-platinum(0) [17].



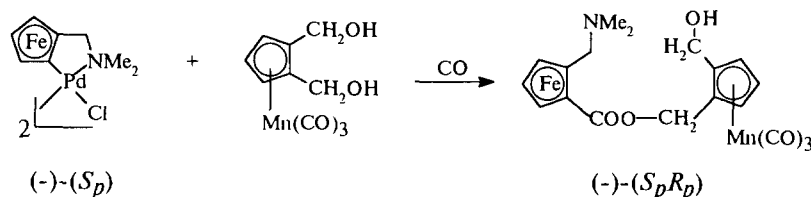
Another attempt to prepare an enantiomeric cyclopalladated compound with coordinated nitrogen as a chiral centre was unsuccessful [18]. Resolution was not achieved, but the existence of two different dimers, arising from the presence of two chiral nitrogen centres was demonstrated.

Interest in cyclometalation has led to a most fruitful discovery of an asymmetric reaction in the ferrocene series. Cyclopalladation and cycloplatination of dialkylbenzylamines had been first observed by Cope and Friedrich [19] with tertiary amine as catalyst. Later Gaunt and Shaw [20] had shown that cyclopalladation of dimethylaminomethylferrocene occurred with sodium acetate as catalyst.

The remarkable difference between these two similar organopalladium chelates is that the arene species is essentially planar and so achiral but any ferrocene derivative with two dissimilar substituents in the same Cp ring is chiral! As soon as I learnt that cyclopalladation of the ferrocene tertiary amine was catalysed by acetate anion I immediately realised that optically active carboxylate should afford an optically active product, and this was indeed the case. Use of salts of *N*-acylated α -amino acids was successful and our first note on this appeared in 1976 [21]. At first the asymmetric yield was not high, about 10%. During the detailed study the crucial role of pH value was recognised and an enantiomeric excess as high as 90% has been reached by careful pH control [22]. The absolute configuration and enantiomeric purity of this key organopalladium were determined by means of chemical correlations with two reference compounds previously investigated in detail by Reich-Rohrwig and Schlogl [23]. The absolute configuration S_p for the (–)-enantiomer of α -(dimethylamino)ethylferrocenylpalladium acetoacetate was also determined by X-ray diffraction study [24]. Interestingly, direct cycloplatination of the aminoalkylferrocenes does not occur. The chelated organoplatinum was obtained using redox-demercuration (see below) of 2-chloromercurial derivative with platinum(0) reagent [25].

4. 2-Dimethylaminomethylferrocenylpalladium chloride dimer as an asymmetric inducer in carbonylation

One of the most specific reactions of the carbon–palladium bond is carbonylation in alcohols to afford esters with elimination of palladium. It struck me that the use of prochiral diols as partners to the enantiomeric organopalladium might result in asymmetric induction on the newly formed chiral fragment. We had at our



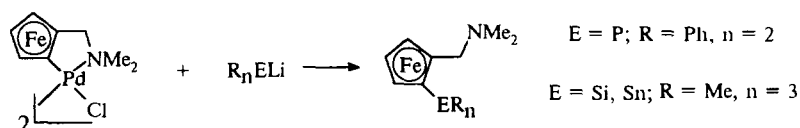
More recently, planar chirality was developed using 1,2-bis-hydroxymethylcymantrene as a prochiral partner for the same organopalladium complex and given similar value for the diastereomeric excess in the product [27].

disposal just such an organopalladium in high enantiomeric purity, and followed the plan announced in Ref. [22].

The synthetic utility of this approach was first demonstrated during work directed at finding a facile entry into a series of optically active glycerides [26]. Only one hydroxyl group of 2-O-benzylglycerol is involved in carbonylation and the new chiral centre appears at C-2. The reaction sequence shown resulted in the preparation of monoacylglycerides in 35%–40% ee.

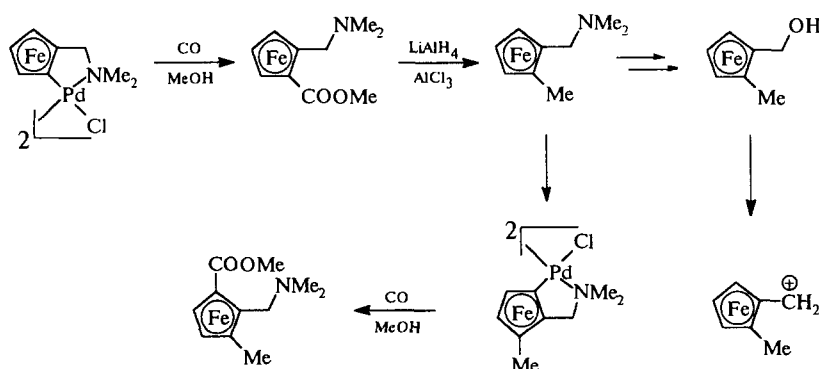
5. Ferrocenes and ruthenocenes

As could be expected, the above-mentioned organopalladium can serve as starting compound for preparation of many 1,2-disubstituted ferrocenes by either conventional reactions of the palladium–carbon bonds [28] or novel ones such as replacement of the metal by phosphorus, silicon, or tin [29].

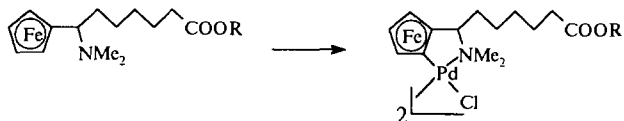


Noteworthy among those reactions was the synthesis and CD study of α -ferrocenylcarbenium ions enantiomeric as a result of the planar chirality of the whole molecule [30]. These unprecedented species were ob-

tained and investigated in solution according to the following scheme. The same paper reported the synthesis of some vicinal 1,2,3-trisubstituted ferrocenes by the same methodology involving repeated cyclopalladation.

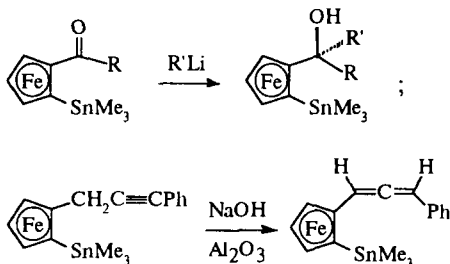


Asymmetric catalysis takes place efficiently not only with the parent achiral ferrocenyl amines but also with chiral α -alkylated amines having an additional chiral centre on the α -carbon atom. Asymmetric cyclopalladation of one particular amine played a key role in the multistep synthesis of the optically active ferrocene analogues of prostaglandins [31].

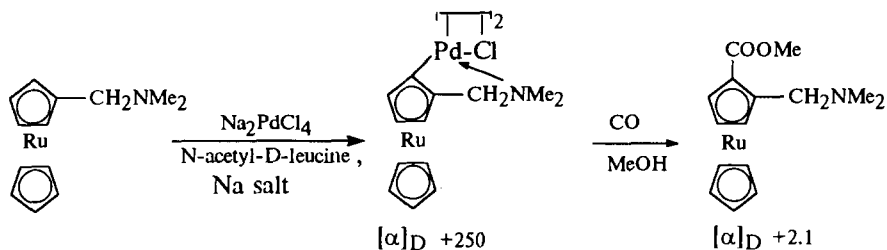


Reaction conditions have been developed for preparing nearly pure optically active diastereomers (such as R_cS_p and S_cS_p for example) from α -aminoferrocenophane, and more recently from α -(dimethylamino)-ethylferrocene [32].

Intramolecular asymmetric induction of chiral centre [33] and of chiral axis [34] by planar chirality has been studied using optically active 1,2-disubstituted ferrocenes of the following types:



These reactions provide a novel route to enantiomeric secondary and the relatively inaccessible tertiary α -fer-

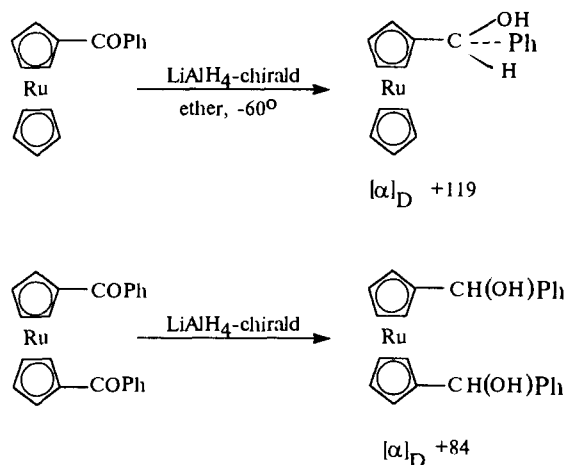


6. Ferricinium and haloruthenocenium salts

The only important difference between the chemistries of ferrocene and ruthenocene involves their oxidative behaviour. The former can lose one electron to give the cation-radical ferricinium, whereas the latter loses two electrons and loss of one charge unit is compensated by adding a halide ion to give the haloruthenocenium cation [38]. No optically active example of these two classes was known until our recent work.

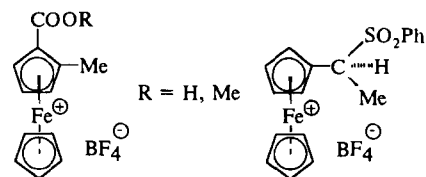
rocenyl alcohols, as well as an approach to optically active ferrocenylallenes.

A convenient synthesis of optically active mono- and bis- α -metallocenyl carbinols and of corresponding α -carbocations was performed by use of asymmetric reduction of mono- and bis-ketones with LiAlH_4 -chirald [35].



Chirality in a representative α -ferrocenylcarbenium ion, namely 1-ferrocenyl-2-methylpropyl cation, was first demonstrated (in one of our early papers [36]) by observing diastereotopism in ^1H and ^{13}C NMR spectra.

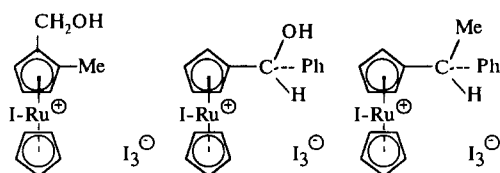
Very recently the asymmetric cyclopalladation was extended onto the ruthenocene series, and some optically active derivatives were obtained by using the approach developed for ferrocene [37]. Enantiomeric purity of the key organopalladium is not yet determined.



Several enantiomeric ferricinium salts were obtained by oxidation of enantiomerically enriched ferrocenes with planar or central chirality prepared by our method-

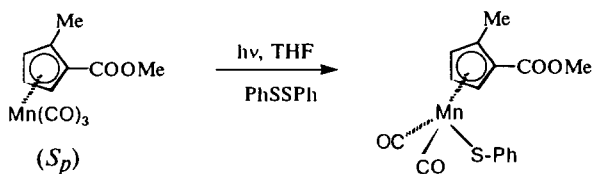
ology [39]. The circular dichroism (CD) spectra have been registered and a Cotton effect corresponding to the charge-transfer band near 620 nm ("ferricinium band") has been observed for a salt with planar chirality [40].

In the case of haloruthenocenium salts, the very deep red-brown colour of the solution prevents direct measurement of optical rotation. A crystalline salt prepared from optically active 1-hydroxymethyl-2-methylruthenocene was isolated in pure state and characterised by combustion analysis and NMR spectroscopy. It was then treated in solution with reducing agents, NaBH_4 being the best. The recovered ruthenocene had the same optical rotation as the starting material, confirming retention of the optical activity in the haloruthenocenium salt.

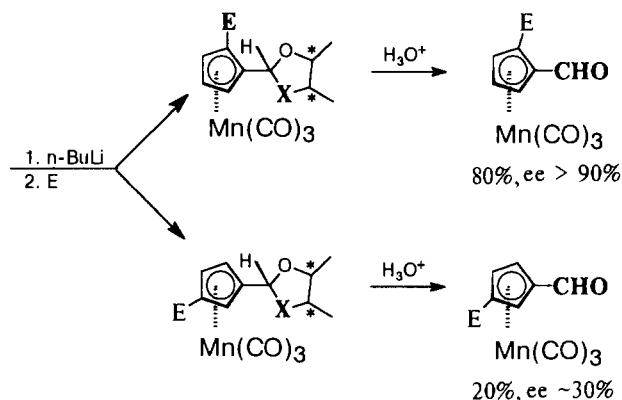
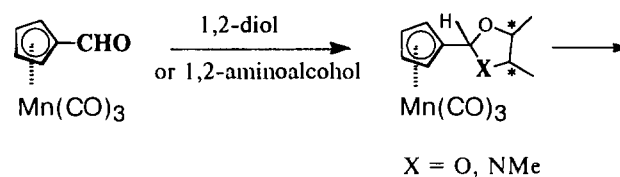


7. Cymantrenes

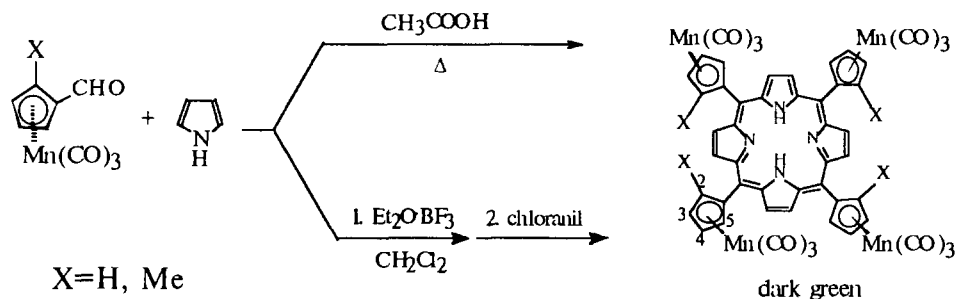
When in 1989 a new Laboratory of Organometallic Stereochemistry was established at INEOS, Dr. Allan Ginzburg and Dr. Nikolay Loim, who had much experience in the cymantrene chemistry, joined me there. So the opportunity arose to extend stereochemical studies to the models of this series. In cymantrenes, there is planar chirality, as in other metallocenes, but substitution has to be localised within a single cyclopentadienyl ligand. At the same time different ligands can be attached to the metal by the CO exchange. Among them, one type looked especially attractive, namely the free-radical thiyl ligand $\cdot\text{SR}$. Some years ago Huttner and coworkers discovered the unusual stability of such odd-electron molecules in which spin density is delocalised over the S-Mn-Cp system [41]. We found an alternative entry to these interesting complexes using thiophosphoryl compounds as a source of thiyl radicals [42] and then concentrated on the synthesis of the first optically active organometallic radical. It was obtained from the enantiomeric 1-carbomethoxy-2-methylcymantrene available from our previous studies. This radical has the planar chirality and its CD spectrum shows several Cotton effects [43].



A new methodology for enantioselective introduction of another substituent in addition to a formyl group has been developed for the case of cymantrenecarbaldehyde. The aldehyde is converted into an (amino)acetal by use of an optically active diol or aminoalcohol. Then lithiation is performed, to have two diastereomers being formed in unequal amounts, and lithium is exchanged for some group. Finally hydrolysis regenerates the aldehyde group, at the same time removing the chiral auxiliary [44]. The most interesting auxiliary was shown to be ephedrine. It turned out that the lithiation of the corresponding oxazolidine occurred predominantly at the 2-position but also to some extent at the 3-position. After hydrolysis 2-substituted aldehyde was isolated in 90% ee and the 3-isomer in ca. 30% ee [45]. The oxazolidine ring contains two sites which can direct metalation; in the ferrocene series it was demonstrated that the nitrogen atom was able to promote cyclopalladation [46].

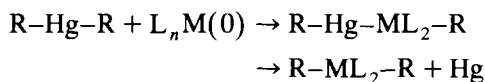


One interesting application of these enantiomeric formylmetallocenes is to provide a facile route to optically active porphyrins. As we have shown recently aldehydes of the cymantrene series react readily with pyrrole [47] under the conditions used in the classical synthesis of porphyrins. Moreover, enantiomeric 2-methylcymantrenecarbaldehyde smoothly affords optically active meso-tetrakis(2-methylcymantrenyl)porphyrin in fair yield (about 50%) [48]. Thus a new family of optically active (metallo)porphyrins has become readily available that can be expected to act as asymmetric catalysts for epoxidation, and, perhaps, of other reactions.



8. Stereochemistry of redox-demercuration

In 1976 we observed the reaction between organomercurials and zerovalent complexes of palladium and platinum, the first step of which is the insertion of L_2M into the mercury–element bond [49]. Extrusion of mercury then follows in many but not all cases, depending on the structure involved in the term redox-demercuration [50]. Several papers have described the application of this reaction to the diastereomeric optically active



M = Pt, Pd or Ni; $n = 3$ or 4.

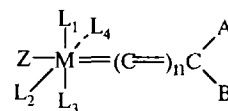
organomercurials [51]. The stereochemistry of this reaction was studied for the following examples. 8-(α -Bromomercuri)ethylquinoline was resolved via the diastereomeric camphorsulphonates and then treated with $Pd_2(dba)_3$ [12] to give the already known chelated organopalladium complex (see above). The CD spectra demonstrated that the chiral carbon centres in the starting organomercurial and the final organopalladium have opposite configurations because two curves look like almost mirror images with an additional Cotton effect due to the palladium chromophore. A similar reaction sequence was carried out with 4-dimethylamino-2-bromomercuributane [13].

9. Optical activity due to enantiomeric ligands

This is certainly the most trivial and least interesting case. Such approach is widely used in applied stereochemistry when screening of optically active ligands at the metal is carried out and the structure of catalytical centre is tuned in order to increase the ee of a particular target product. However, it can also be used to chiralize electronic transitions in an achiral chromophore by placing it into chiral environment that makes them optically active. This is exemplified by the recent synthesis of the first optically active organometallic derivatives of fullerenes in which palladium or platinum coordinated to C_{60} in η^2 -fashion bears a (+)DIOP ligand [52].

10. Supramolecular compounds exemplified by the inclusion metallocene–cyclodextrin complexes

In recent years the feeling has been growing that the classical chiral stereochemistry of individual molecules is in principle close to completion. Certainly the appearance of novel molecular species such as fullerenes [53] may bring new problems to tackle. There are a few types of chiral structures that have not yet been realised in molecular form. Chirality conditions for one such class, metallocumulenes with an octahedral metal, have been analysed [54].



However, the main interest is shifting noticeably to the aggregates formed from different molecules owing to weak, noncovalent bonds between them. This is the area of supramolecular chemistry embracing inclusion complexes, topological structures, intermolecular complexes held together by hydrogen bonds etc.

Among the most studied host molecules in inclusion complexes are cyclodextrins (CyD's), natural oligosaccharides composed of six (α), seven (β), or eight (γ) residues of α -glucose arranged in a closed fashion. The electronic transitions of the included molecule become optically active in the chiral environment of the enantiomeric host. This means that CD spectroscopy is a powerful tool for investigation of the complexes.

Solid complexes of cyclodextrins with ferrocene and its few derivatives were isolated in 1984 by Harada and Takahashi [55] who also observed their induced CD spectra in solution. We have extended the range of metallocenes included into cyclodextrins, and have determined the equilibrium constants for ruthenocene, osmocene, cymantrene and other metallocene guests [56], as well as thermodynamic parameters in some cases [57]. CD spectroscopy was shown to be a very convenient method for investigation of structural effects on the equilibria [58].

We have also observed in one case the influence of inclusion in a cyclodextrin matrix on the reactivity of ruthenocene [59]. The colourless powder of β -CyD · Cp₂Ru · 5H₂O (dried in vacuo) became dark brown after a short exposure to iodine vapour in closed desiccator. This product was satisfactorily analysed for β -CyD · Cp₂Ru · I₂ · 5H₂O but the ¹³C NMR MAS spectrum revealed the presence of unchanged ruthenocene, δ 69.9 ppm, shifted downfield from solid Cp₂Ru (73.2 ppm) due to inclusion. Longer keeping to iodine vapour caused the gradual appearance of the signal corresponding to Cp₂RuI⁺ (93.4 ppm). This means that the inclusion in β -cyclodextrin slows down the oxidation of Cp₂Ru. Organometallic derivatives of CyD with a covalent linkage to the benchrotrene moiety have been prepared by direct metallocarbonylation of perbenzoyl- α - or - β -CyD [60].

Acknowledgements

Experimental work in chiral stereochemistry requires a special attitude to chemical species, a readiness to respond to the challenge produced by the existence of optically active compounds and to have fun playing with them. I am very thankful to all my coworkers who share my love of this part of chemistry. Their names appear in the references.

References and notes

- [1] A.N. Nesmeyanov, O.A. Reutov and S.S. Poddubnaya, *Dokl. Akad. Nauk SSSR*, 88 (1953) 479. Nearly pure diastereomers have been prepared by V.I. Sokolov, O.A. Reutov, G.Z. Suleimanov, et al., *J. Organomet. Chem.*, 201 (1980) 29.
- [2] V.I. Sokolov and O.A. Reutov, *Izv. AN SSSR, Ser. Khim.* (1964) 394.
- [3] J.H. Brewster, *J. Am. Chem. Soc.*, 81 (1959) 5475, 5483, 5493.
- [4] V.I. Sokolov, *Introduction to Theoretical Stereochemistry*, Nauka, Moscow, 1979 and 1983, two Russian editions. English translation of revised and up-to-dated text appeared under the same title in 1991, Gordon & Breach, New York–London, 1991.
- [5] V.I. Sokolov, *Chirality and Optical Activity in Organometallic Compounds*, Gordon & Breach, New York–London, 1991.
- [6] V.I. Sokolov and O.A. Reutov, *Dokl. Akad. Nauk SSSR*, 148 (1963) 867.
- [7] V.I. Sokolov, L.L. Troitskaya and O.A. Reutov, *Dokl. Akad. Nauk SSSR*, 166 (1966) 136; idem. *J. Organomet. Chem.*, 17 (1969) 323.
- [8] (a) T.G. Traylor and A.W. Baker, *Tetrahedron Lett.*, (1959) 14; (b) T.G. Traylor, *J. Amer. Chem. Soc.*, 86 (1964) 244; (c) T.G. Traylor, *Acc. Chem. Res.*, 2 (1969) 152.
- [9] V.I. Sokolov, N.B. Rodina and O.A. Reutov, *Zh. Org. Khim.*, 3 (1967) 2089.
- [10] V.I. Sokolov, *D.Sc. Thesis*, INEOS, Moscow, 1971.
- [11] (a) Vinylic mercuration with exchange of a vinylic proton in 1,1-diaryl-ethylenes for mercury: V.I. Sokolov, V.V. Bashilov and O.A. Reutov, *Dokl. Akad. Nauk SSSR*, 188 (1969) 127; (b) Peroxymercuration of olefines and cyclopropanes: V.I. Sokolov and O.A. Reutov, *Zh. Org. Khim.*, 5 (1969) 174, *Izv. Akad. Nauk SSSR*, (1969) 1634; (c) Other kinds of conjugate mercuration: V.I. Sokolov and O.A. Reutov, *Izv. SSSR, Ser. Khim.*, (1967) 1632; (1968) 222; (d) Use of polyfluoroalkylmercuric salts: V.V. Bashilov, E.V. Maskaeva, V.I. Sokolov and O.A. Reutov, *Metalloorg. Khim.*, 2 (1989) 1114.
- [12] V.I. Sokolov, V.V. Bashilov, A.A. Musaev and O.A. Reutov, *J. Organomet. Chem.*, 225 (1982) 57.
- [13] V.I. Sokolov, V.V. Bashilov, E.V. Maskaeva and P.V. Petrovskii, *J. Organomet. Chem.*, 292 (1985) 89.
- [14] (a) V.I. Sokolov, *Dokl. Akad. Nauk SSSR*, 197 (1971) 362. (b) O.A. Reutov, I.P. Beletskaya and V.I. Sokolov, *Mechanisms of Reactions of Organometallic Compounds* (Russian), Moscow, Khimiya, 1972, Chap. 4.
- [15] J.E. Hartwell, R.V. Lawrence and M.J. Smas, *J. Chem. Soc., Chem. Commun.*, (1970) 912.
- [16] V.I. Sokolov, T.A. Sorokina, L.L. Troitskaya, L.I. Solovieva and O.A. Reutov, *J. Organomet. Chem.*, 36 (1972) 389. For X-ray structure see: L.G. Kuzmina, Yu. T. Struchkov, V.V. Bashilov, A.A. Musaev and V.I. Sokolov, *Koord. Khim.* 11 (1985) 1543.
- [17] V.I. Sokolov, *Inorg. Chim. Acta*, 18 (1976) L9.
- [18] V.I. Sokolov, L.L. Troitskaya and T.A. Sorokina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1971) 2611.
- [19] A.C. Cope and E.C. Friedrich, *J. Am. Chem. Soc.*, 90 (1968) 909.
- [20] J.C. Gaunt and B.L. Shaw, *J. Organomet. Chem.*, 102 (1975) 511.
- [21] V.I. Sokolov and L.L. Troitskaya, *Chimia*, 32 (1978) 122.
- [22] V.I. Sokolov, L.L. Troitskaya and O.A. Reutov, *J. Organomet. Chem.*, 182 (1979) 537.
- [23] P. Reich-Rohrwig and K. Schlogl, *Monatsh. Chem.*, 99 (1968) 1752.
- [24] V.I. Sokolov, L.L. Troitskaya, L.G. Kuzmina, Yu.T. Struchkov and O.A. Reutov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1979) 1528.
- [25] V.I. Sokolov and L.L. Troitskaya, *J. Organomet. Chem.*, 328 (1987) 169.
- [26] L.L. Troitskaya and V.I. Sokolov, *J. Organomet. Chem.*, 285 (1985) 389.
- [27] L.L. Troitskaya, L.A. Bulygina and V.I. Sokolov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1993) 1799.
- [28] V.I. Sokolov, L.L. Troitskaya, N.S. Khrushchova and O.A. Reutov, *Zh. Org. Khim.*, 18 (1982) 2606.
- [29] (a) V.I. Sokolov, L.L. Troitskaya and O.A. Reutov, *J. Organomet. Chem.*, 202 (1980) C58; (b) V.I. Sokolov, L.L. Troitskaya and L.A. Bulygina, *Metalloorg. Khim.*, 3 (1990) 1435.
- [30] V.I. Sokolov, L.L. Troitskaya, L.A. Bulygina and P.V. Petrovskii, *Metalloorg. Khim.*, 2 (1989) 356.
- [31] (a) V.I. Sokolov, L.L. Troitskaya, N.S. Khrushchova and O.A. Reutov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1987) 2387; (b) V.I. Sokolov, *Pure Appl. Chem.*, 55 (1983) 1837; (c) V.I. Sokolov, L.L. Troitskaya, N.S. Khrushchova and O.A. Reutov, *J. Organomet. Chem.*, 378 (1989) 227.
- [32] (a) V.I. Sokolov, L.L. Troitskaya, B. Gautheron and G. Tainturier, *J. Organomet. Chem.*, 235 (1982) 369; (b) L.L. Troitskaya, L.A. Bulygina and V.I. Sokolov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1994) 1315.
- [33] L.L. Troitskaya, L.A. Bulygina and V.I. Sokolov, *Metalloorg. Khim.*, 4 (1991) 653.
- [34] L.L. Troitskaya, L.A. Bulygina and V.I. Sokolov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1994) 1111.
- [35] M.N. Nefedova, I.A. Mamedyarova, P.V. Petrovskii and V.I. Sokolov, *J. Organomet. Chem.*, 425 (1992) 125.

- [36] V.I. Sokolov, P.V. Petrovskii and O.A. Reutov, *J. Organomet. Chem.*, **59** (1973) C27.
- [37] (a) I.A. Mamedyarova, *Ph.D Thesis*, INEOS, 1994; (b) M.N. Nefedova, I.A. Mamedyarova and V.I. Sokolov, *J. Organomet. Chem.*, in press.
- [38] Y.S. Sohn, D.N. Hendrickson and H.V. Gray, *J. Am. Chem. Soc.*, **93** (1971) 3603.
- [39] V.I. Sokolov, M.N. Nefedova, I.A. Mamedyarova and A. Khatami, *Metalloorg. Khim.*, **4** (1991) 191.
- [40] M.N. Nefedova, I.A. Mamedyarova, G. Snatzke and V.I. Sokolov, *J. Organometal. Chem.*, **438** (1992) C26.
- [41] (a) A. Winter, G. Huttner, M. Gottlieb and I. Jibril, *J. Organomet. Chem.*, **286** (1985) 317; (b) P. Lau, H. Braunwarth, G. Huttner et al., *Organometallics*, **10** (1991) 3861.
- [42] V.A. Milyukov, I. Yu Gorshunov, O.G. Sinyashin, V.I. Morozov, E.S. Batyeva, A.G. Ginzburg and V.I. Sokolov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1993) 614.
- [43] V.A. Milyukov, O.G. Sinyashin, A.G. Ginzburg, M.A. Kondratenko, N.M. Loim, V.P. Gubskaya, R.Z. Musin, V.I. Morozov, E.S. Batyeva and V.I. Sokolov, *J. Organomet. Chem.*, **493** (1995) 221.
- [44] N.M. Loim, M.A. Kondratenko and V.I. Sokolov, *J. Org. Chem.*, **59** (1994) 7487.
- [45] N.M. Loim, M.A. Kondratenko and V.I. Sokolov, *Dokl. Akad. Nauk SSSR*, **320** (1991) 1123.
- [46] N.M. Loim, M.A. Kondratenko, M.M. Khrapov and V.I. Sokolov, Xth FEChem Conf. Organometallic Chemistry Abstracts, p. 19.
- [47] N.I. Pyshnograeva, N.M. Loim and V.I. Sokolov, *Dokl. Akad. Nauk SSSR*, **318** (1991) 345.
- [48] N.M. Loim, M.A. Kondratenko, E.B. Grishko and V.I. Sokolov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1994) 959.
- [49] V.I. Sokolov, V.V. Bashilov, L.M. Anishchenko and O.A. Reutov, *J. Organomet. Chem.*, **71** (1974) C41.
- [50] (a) V.I. Sokolov and O.A. Reutov, *Coord. Chem. Rev.* **27** (1978) 189; (b) V.V. Bashilov, V.I. Sokolov and O.A. Reutov, *Izv. Akad. Nauk SSSR*, (1982) 2069.
- [51] G.Z. Suleimanov, V.V. Bashilov, A.A. Musaev, V.I. Sokolov and O.A. Reutov, *J. Organomet. Chem.*, **202** (1980) C61.
- [52] V.V. Bashilov, P.V. Petrovskii and V.I. Sokolov, *Izv. Akad. Nauk*, (1993) 428. Many Cotton effects corresponding to the fullerene absorption bands have been observed in CD spectrum; for the platinum complex X-ray structure has been determined (unpublished data).
- [53] It was predicted recently that C₆₀ doubly bonded to a metal in η^6 -fashion should be chiral if nonadjacent hexagons are complexed: V.I. Sokolov, *Dokl. Russ. Akad. Nauk*, **326** (1992) 647. For C₇₀ with lower symmetry chiral molecules will also result from double η^5 complexation on two pentagons or from a mixed η^5/η^6 case. Metal complexes of this kind have not been synthesised yet (unpublished data).
- [54] V.I. Sokolov, *Metalloorg. Khim.*, **1** (1988) 473.
- [55] A. Harada and S. Takahashi, *J. Chem. Soc. Chem. Commun.* (1984) 645.
- [56] V.I. Sokolov, V.L. Bondareva and I.F. Golovaneva, *Metalloorg. Khim.*, **2** (1989) 1252.
- [57] V.I. Sokolov, V.L. Bondareva and G.V. Shustov, *Metalloorg. Khim.*, **4** (1991) 697.
- [58] V.I. Sokolov, V.L. Bondareva and I.F. Golovaneva, *J. Organomet. Chem.*, **358** (1988) 401.
- [59] V.I. Sokolov, A.L. Blumenfeld, Z. Narankiewicz, M.N. Nefedova and I.A. Mamedyarova, *Izv. Akad. Nauk SSSR, Ser. Khim.* (1991) 2165.
- [60] V.I. Sokolov and V.L. Bondareva, *Metalloorg. Khim.*, **1** (1988) 1195.