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# Novel optically active organometallic derivatives of fullerenes with non-central types of chirality in addends: synthetic and CD studies

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ABSTRACT

Palladium and platinum complexes of $C_{60}$ and $C_{70}$ possessing the enantiomeric ligand (−)-Bitianp with axial chirality and a pyrrolidino[60]fullerene bearing a planar chiral organometallic π-complex group in the heterocyclic ring have been synthesized and their CD spectra recorded.

## 1. Introduction

The stereochemistry of fullerenes is one of the least investigated areas of fullerene chemistry. Only a few optically active fullerene compounds have been reported, the first type to be investigated by CD spectroscopy being double osmate esters obtained by asymmetric osmylation of $C_{60}$. Two isomeric products separated from the reaction mixture had different chiral arrangements of achiral addends on the fullerene core.[1] They cannot be considered as organometallic derivatives, however, because a direct metal–carbon bond is absent. This work was followed by the preparation of a sugar-$C_{60}$ derivative[2] and the resolution of $C_{76}$ with intrinsic chirality of the $D_3$ skeleton.[3] The first optically active palladium- and platinum-containing organometallic π-complexes of fullerenes were prepared by our research group[4,5] using the known enantiomeric ligand 2,2-dimethyl-4,5-[(diphenylphosphino)dimethyl]dioxolane [(+)-DIOP] which possesses two chiral carbon centres, and the CD spectra were recorded in two solvents,[6] polar *N,N*-dimethylformamide and non-polar toluene. This work was repeated by another group who obtained similar results using (−)-DIOP.[7] The synthesis of a molybdenum-($\eta^2$-$C_{60}$) complex with an optically active N,N-ligand, as two enantiomers, for which mirror CD curves were obtained, has been reported.[8] Chirality and optical activity in fullerenes have been described in our review,[9] and in a recent article[10] wherein, however, many papers dealing with organometallics were omitted. In general, the analysis of CD spectra in fullerenes is a very difficult subject.[11] It is only possible at present to distinguish which Cotton effects (CEs) are due to the electronic transitions within the fullerene core or within addends, or which are associated with electron transfer between these two moieties.

## 2. Results and Discussion

In this Letter, we report on the synthesis and CD spectra of (i) the palladium and platinum complexes of $C_{60}$ and $C_{70}$ possessing an enantiomeric ligand with axial chirality, and (ii) pyrrolidino[60]fullerene bearing an enantiomeric organometallic π-complex group with planar chirality at position 2 of the heterocyclic ring. Our aim was to make accessible novel types of optically active fullerene derivatives and to investigate their CD spectra.

Recently a novel class of axially chiral atropoisomeric diphosphines was reported.[12] These ligands are characterized by the presence of a σ-bond between two five-membered heteroaromatic

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rings. Rotation around the interannular bond is prevented by steric hindrance imposed by *ortho* diphenylphosphino groups. One of these ligands, (−)-2,2′,5,5′-tetramethyl-4,4′-bis(diphenylphosphino)-3,3′-bithienyl, (−)-(tetraMe-Bitiop), was used for preparing optically active palladium–fullerene complexes in our recent work.[13]

A related enantiomeric ligand, (−)-2,2′-bis(diphenylphosphino)-3,3′-dibenzo[*b*]thiophene, (−)-Bitianp, has been used in the synthesis of the novel palladium–fullerene complexes: $(\eta^2\text{-}C_{60})Pd[(-)\text{-Bitianp}]$, **1**, and $(\eta^2\text{-}C_{70})Pd[(-)\text{-Bitianp}]$, **2**, which have been prepared by direct synthesis from $C_{60}$ and $C_{70}$ fullerenes, the diphosphine ligand and $Pd_2(dba)_3{\cdot}C_6H_6$ (see synthesis of **2** for an example). Platinum–fullerene compound $(\eta^2\text{-}C_{60})Pt[(-)\text{-Bitianp}]$, **3**, was synthesized by exchange of the triphenylphosphine ligand in $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$ for (−)-Bitianp[14] (Scheme 1).

In the CD spectra of both the $C_{60}$ and $C_{70}$ palladium complexes the positions of the (+) and (−) Cotton effects (CEs) between 350 and 400 nm coincide, whereas they are different for CE at higher wavelengths such as 437 nm for **1** and 479 nm for **2**. This 42 nm shift is also observed in the isotropic UV–vis region (Fig. 1).

When an organometallic group is placed within the addend it is remote from the fullerene core, however, we know from electrochemistry and isotropic absorption spectra that electronic communication exists between them. The Prato reaction is a versatile synthetic procedure for the introduction of an organometallic moiety into a pyrrolidine ring fused to fullerene.[15–17] We chose this method to synthesize an optically active organometallic derivative starting with the planar chiral aldehyde **4** derived from dicymantrenyl $[CpMn(CO)_3]_2$. The synthesis and resolution of this aldehyde (β-isomer) has been described in our previous work[18,19] and has been slightly modified herein. The chiral moiety is retained intact during the Prato reaction, therefore the configuration of the chiral plane is the same as in aldehyde **4**, Schiff base **5** and 2-dicymantrenylpyrrolidino[60]fullerene **6** (Scheme 2). The new chiral centre at C-2 in the heterocyclic ring has no effect on the CD spectra (Figs. 2 and 3) but results in doubling of the signals in the $^1$H NMR spectrum of **6**. The short-wavelength positive Cotton effect (CE) exhib-

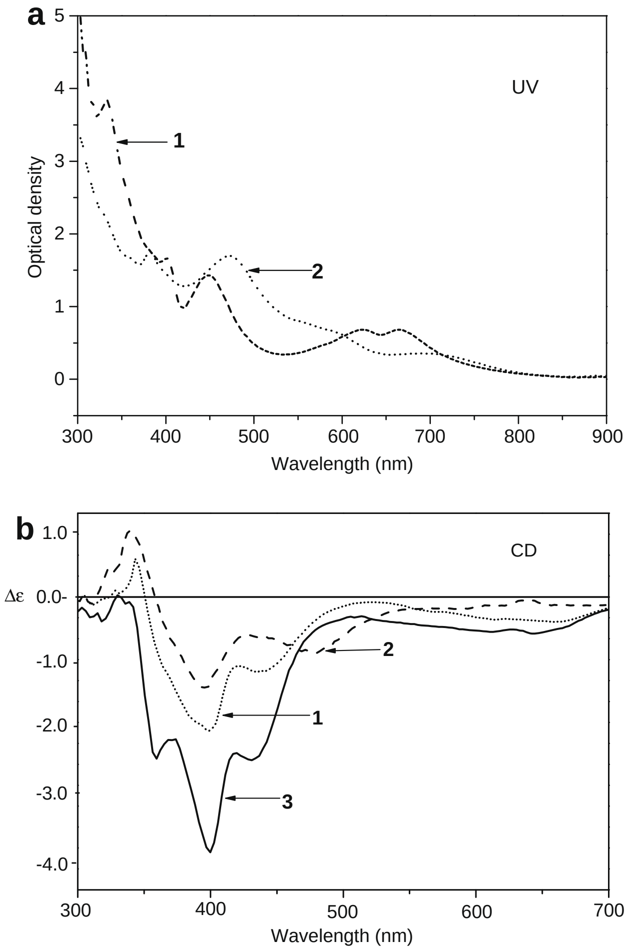
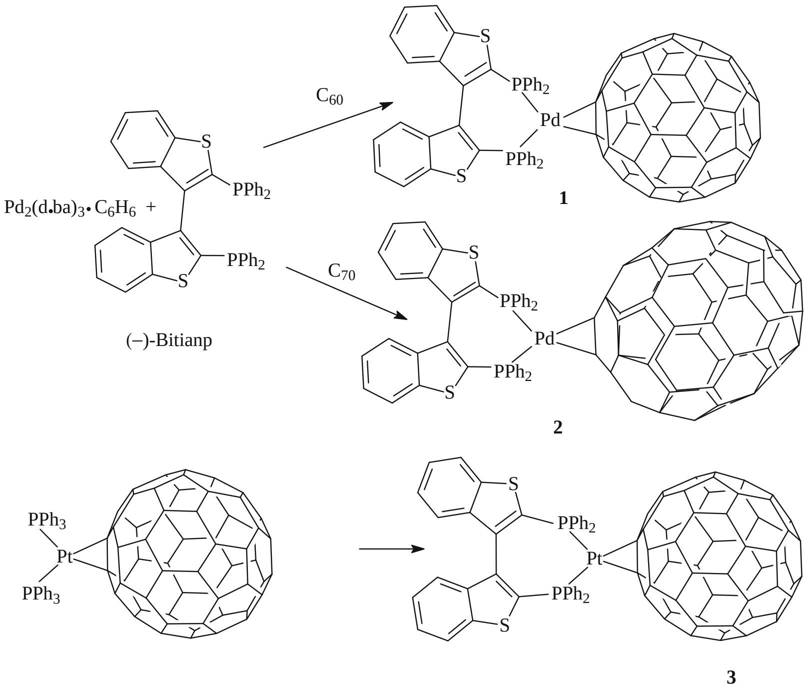
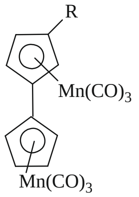


**Figure 1.** (a) UV spectra of **1** and **2**, (b) CD spectra of **1**, **2** and **3**. Solvent in all cases is 1,2-dichlorobenzene.

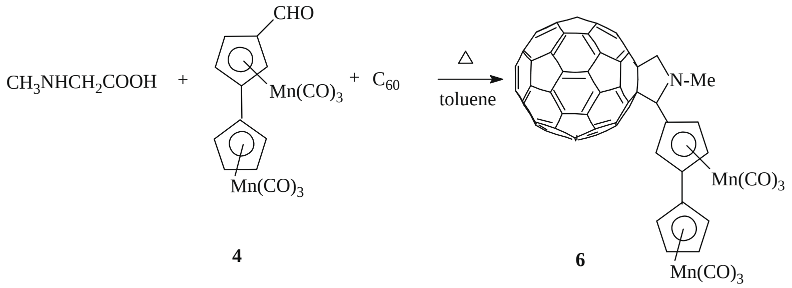


**Scheme 1.** Synthesis of the palladium and platinum complexes of $C_{60}$ and $C_{70}$ using the (−)-Bitianp ligand.



**4** R = CHO

**5** $R = CHN\text{-}\overset{*}{C}HMePh$



**Scheme 2.** Synthesis of *N*-methyl-2-β-dicymantrenyl[60]fullereno[*c*]pyrrolidine.

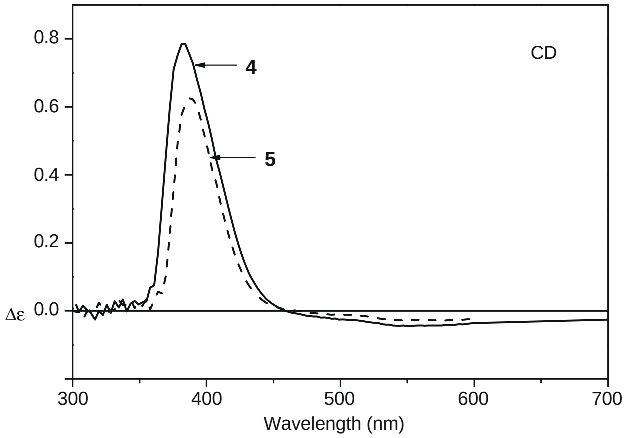


**Figure 2.** CD spectra of **4** and **5**.

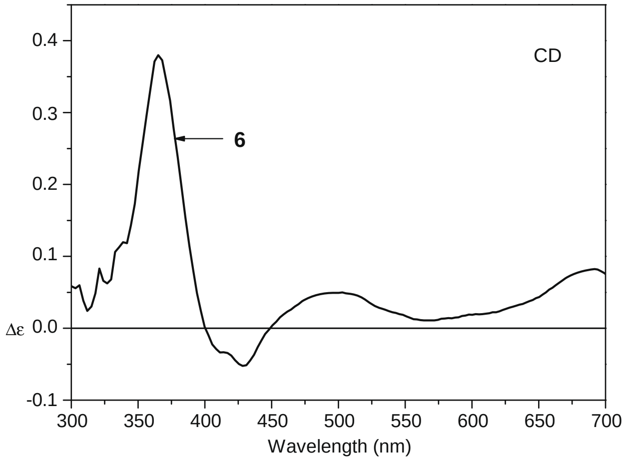


**Figure 3.** CD spectrum of **6**.

its a very small shift (384 and 387 nm) and corresponds unambiguously to the electronic transition within the dicymantrenyl chromophore. The other Cotton effects are present in the fullerene derivative only. Those in the middle wavelength region (~400–550 nm) can be attributed to the charge transfer between the metallocenyl fragment and the fullerene core, whereas the long-wavelength effects have their origin in the electronic transitions of the fullerene itself. It is appropriate to note that some years ago we synthesized the first relatively stable free radical of the cymantrene series with planar chirality and were able to record its CD spectrum[20] which contained two Cotton effects at (+) 347 and (+) 480 nm. The short-wavelength CE is due to the cymantrene chromophore and is close to those in the CD spectra of dicymantrenyl aldehyde **4** and 2-dicymantrenylpyrrolidino[60]fullerene **6**.

Thus we have shown that a chiral group, either axial or planar, when placed in the addend, can lead to asymmetric influence on the electronic transitions in fullerenes, making them optically active as indicated by the appearance of Cotton effects.

The β-isomer of dicymantrenyl aldehyde was prepared, separated by column chromatography and resolved by crystallization of the azomethine derivative with (−)-α-phenylethylamine via slightly modified procedures.[18] The CD intensity was calibrated with an aqueous solution of D-10-camphorsulfonic acid assuming $\Delta\varepsilon = 2.2\ M^{-1}\ cm^{-1}$ at 291 nm.[21] All CD measurements were performed at a resolution of 3 nm and with scanning at 35 nm/min. The results are expressed in terms of molar circular dichroism Δε (in $M^{-1}\ cm^{-1}$). Measurements were carried out in a 1 cm quartz cell between 300 and 750 nm, at 23 °C in toluene. The CD spectra of the investigated compounds were recorded at concentrations between 1.0 and $3.0 \times 10^{-3}$ mol/l.

## 3. Synthesis of ($\eta^2$-$C_{70}$)Pd[(−)-Bitianp], 2

(−)-Bitianp[12] (63.5 mg, 0.1 mM), $Pd_2(dba)_3{\cdot}C_6H_6$ (49.6 mg, 0.0499 mM) and fullerene $C_{70}$ (84.0 mg, 0.1 mM) were dissolved in toluene (14 ml) in a Schlenk tube with a magnetic stirrer and argon inlet. The formation of the novel Pd complex with two non-equivalent phosphorus atoms was evident from $^{31}P$ NMR spectroscopy: $\delta(P_A) = 19.0$ ppm and $\delta(P_B) = 18.0$ ppm. For isolation of the fullerene–palladium complex, dry $Et_2O$ was layered over the reaction mixture and then left at room temperature to crystallize. The crystals were separated from the mother liquor, washed with $Et_2O$ and pentane and dried in vacuo. Analytically pure ($\eta^2$-$C_{70}$)Pd[(−)-Bitianp] was isolated as very dark red-brown crystals, yield 118.3 mg (75%). Calcd for $C_{110}H_{28}P_2PdS_2$: C, 83.52; H, 1.78; P, 3.92. Found: C, 83.57; H, 1.82; P, 3.46.

## 4. Preparation and hydrolysis of the Schiff base 3-[(1-phenylethyl)-iminomethyl]-dicymantrenyl, 5

Schiff base **5** was obtained by reaction of 5 mmol of aldehyde **4** with 5% excess (*S*)-(−)-α-phenylethylamine in benzene (8 ml). The mixture was carefully heated at reflux and then left overnight to crystallize slowly. The resulting brown solution was decanted and the remaining yellow precipitate (usually no more than 25–30% of the theoretical amount) was washed 3–4 times with hexane (0.5 ml portions) and dried in vacuo. If no precipitate formed, the solvent was slowly removed in vacuo until crystallization began. The product **5** was recrystallized from hexane–benzene (4:1) to afford yellow crystals, mp 109–110 °C. Calcd for $C_{25}H_{17}NMn_2O_6$: C, 55.87; H, 3.17; N, 2.61. Found: C, 55.94; H, 3.18; N, 2.54. MS: *m/z* 537 [$M^+$], 453 [M−3CO], 369 [M−6CO].

For decomposition to the aldehyde, 0.3–0.4 g of Schiff base **5** was heated at reflux in MeOH (15 ml) containing 6–8 drops of 20% aqueous $H_3PO_4$ for 15–20 min (with monitoring of the IR-spectra for the disappearance of $\nu$(C=N) at 1650 $cm^{-1}$, and the appearance of an aldehyde $\nu$(C=O) at 1690–1710 $cm^{-1}$). The solution was cooled, poured into water, and aldehyde **4** was extracted with ether.

## 5. Enantiomeric *N*-methyl-2-β-dicymantrenyl[60]fullereno[*c*]-pyrrolidine, 6

Fullerene $C_{60}$ (0.1 g, 0.138 mM), aldehyde **4** (0.120 g, 0.278 mM) and *N*-methylglycine (0.0245 g, 0.275 mM) were heated at reflux in toluene (100 ml) under a slow stream of argon for 4 h. Evaporation of the solvent followed by column chromatography on $SiO_2$ (eluent: hexane–toluene, 1:1) gave product **6** (13% yield) as two diastereomers due to the formation of a new chiral carbon centre. Calcd for $C_{79}H_{13}NO_6Mn_2$: H, 1.11; C, 80.29; N, 1.19. Found: H, 1.09; C, 80.21; N, 1.24. $^1$H NMR ($CDCl_3$), $\delta$, ppm: 3.14, 3.20 (2s, 6H, N-Me), 4.29, 4.31 (d, $J$ = 8.4 Hz, 2H, $CH_2$), 4.53 (m, 1H, Cp), 4.71–4.79 (m, 5H, CH and Cp), 4.88–4.98 (m, 7H, Cp and $CH_2$), 5.08 (m, 1H, Cp), 5.18 (m, 1H, Cp), 5.21 (m, 1H, Cp), 5.54 (m, 1H, Cp), 5.76 (m, 1H, Cp). $^{13}$C NMR ($CDCl_3$), $\delta$, ppm: 41.3, 41.5 (N-Me); 71.2 ($CH_2$); 75.4 (CH), 78.4, 78.6, 80.4, 80.5, 81.2, 81.5, 82.7, 83.7, 83.8, 85.1 (Cp), 135.5-153.5 ($C_{60}$), 224.3 (CO).

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14. Pure complexes were isolated as crystalline solids by slow crystallization from toluene and characterized by elemental analysis and NMR spectroscopy. ($\eta^2$-$C_{60}$)Pd[(−)-Bitianp], **1**, $^{31}$P NMR (161.98 MHz, *o*-dichlorobenzene–$C_6D_6$): singlet, $\delta$(P) 17.25 ppm. ($\eta^2$-$C_{70}$)Pd[(−)-Bitianp], **2**, $^{31}$P NMR (161.98 MHz, *o*-dichlorobenzene–$C_6D_6$): AB system, $\delta(P_A)$ 19.4 ppm, $\delta(P_B)$ 18.4 ppm, $J(P_A,P_B)$ = 18.8 Hz. Single crystals of **1** were grown and analyzed by X-ray crystallography. Preliminary X-ray data were presented at an International meeting: Bashilov, V. V., Dolgushin, F. M., Petrovskii, P. V., Babievsky, K. K., Sokolov, V. I. Book of Abstracts, 8th Biennial International Workshop on Fullerenes and Atomic Clusters, July 2–6, 2007, St Petersburg, Russia. Full crystallographic details will be published elsewhere.
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