

## THE ORIENTATION OF SUBSTITUTION IN METALLATION OF DIMETHYLAMINOMETHYL-, HYDROXYMETHYL- AND DIPHENYLPHOSPHINO-CYMANTRENES

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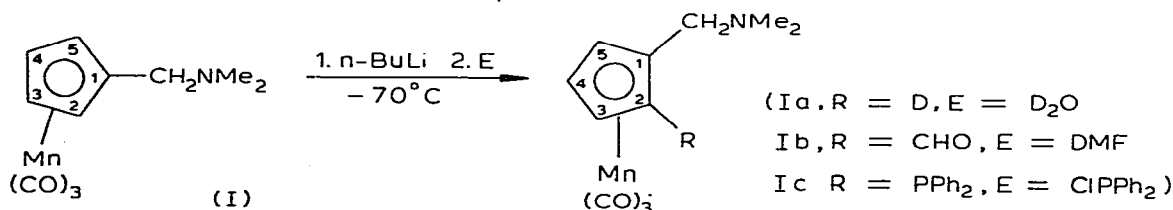
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### Summary

Dimethylaminomethyl- and hydroxymethyl-cymantrenes, when treated with n-butyllithium, are selectively metallated in the 2(5) position of the Cp ring and are converted into 1,2-disubstituted derivatives of cymantrene by subsequent treatment with electrophilic reagents. Similar reactions in the case of diphenylphosphinocymantrene result in a selective preparation of 1,3-disubstituted derivatives. The metallation orientation is established by chemical methods and NMR-LIS (lanthanide-induced shift) techniques. A full assignment of signals in the PMR and  $^{13}\text{C}$  NMR spectra of the studied monosubstituted cymantrene derivatives has been effected.

### Introduction

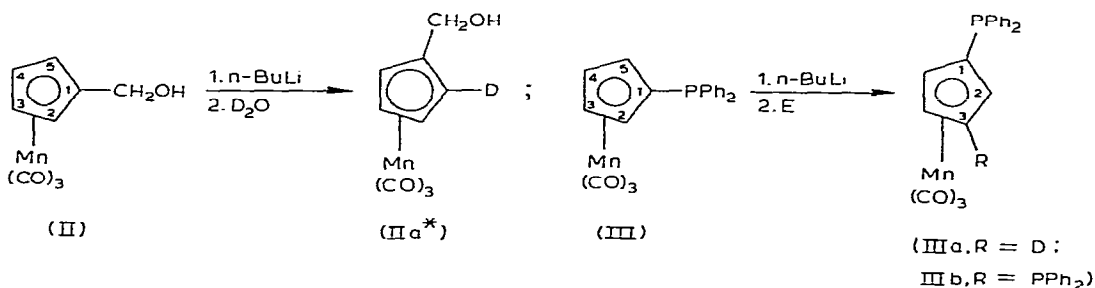
We have shown earlier that metallation of dimethylaminomethylcymantrene (I) with n-butyllithium proceeds predominantly (about 97%) in the 2(5) position of the cyclopentadienyl ring (Cp ring), thus resulting, after a subsequent introduction of an electrophilic agent (E) into the reaction mixture, in the formation of 1,2-disubstituted derivatives of cymantrene [1]. The substitution orientation was established by analysis of PMR spectra of the reaction products Ia and Ib and was supported by an X-ray study of one of the Ib enantiomers [2].



Continuing our study of the effect of the substituent nature on the metallation orientation of monosubstituted cymantrene derivatives, the present paper deals with the determination of the structure of the reaction products of hydroxymethylcymantrene (II) and diphenylphosphinocymantrene (III) with *n*-BuLi.

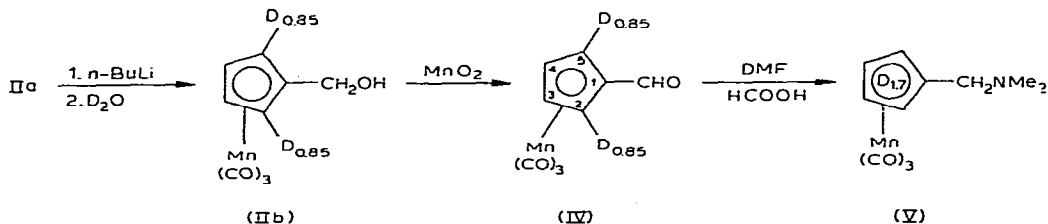
## Results and discussion

The reaction of *n*-butyllithium with II and III under the conditions of metallation of amine I results in the formation of organolithium compounds which, after treatment with deuterium oxide, give corresponding deuterated derivatives IIa and IIIa. PMR spectra of these derivatives, obtained on an instrument with a working frequency of 60 MHz using  $\text{Eu}(\text{fod})_3$  or  $\text{Dy}(\text{fod})_3$  and on an instrument with a working frequency of 100 MHz, show that metallation of II and III proceeds, within the experiment accuracy limits, fully into one of two non-equivalent positions relative to the substituent: either 2(5) or 3(4). No substitution of hydrogen with lithium in the  $\text{CH}_2$  group (for II) and in the phenyl radicals (for III) is observed.



For the determination of the direction of attack of the metallation agent in the metallation of II, we have carried out the series of transformations shown in Scheme 1. The alcohol IIb, containing 1.7 D atoms in the same positions of the Cp ring as in IIa, is obtained by a repeated metallation of IIa, followed by treating the reaction mixture with deuterium oxide. Oxidation of IIb with "active"  $\text{MnO}_2$  gives deuterated formylcymantrene (IV) which is treated with dimethylformamide in formic acid to form amine V, fully retaining the initial amount of deuterium.

SCHEME 1



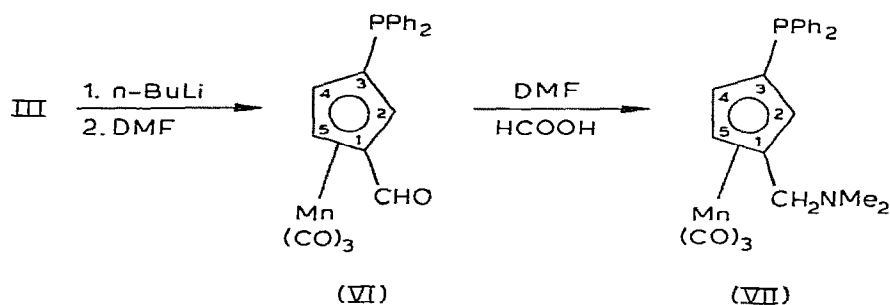
\* Metallation of II and IIIa is effected with excess of *n*-BuLi for the reaction of *n*-BuLi with a proton of the OH group of the alcohol; however, in the isolation of the deuterated product a complete exchange of deuterium for hydrogen occurs in the OD groups.

Comparison of PMR spectra of amines V and Ia in  $\text{CF}_3\text{COOH}$  or  $\text{CDCl}_3$  shows that in both amines the signal of the ring protons (with its intensity lowered due to a partial substitution of protons in this position of the Cp ring with deuterium) has the same chemical shift (4.83 and 4.69 ppm, respectively). Consequently, metallation of alcohol II, as well as amine I, occurs in the 2(5) position of the Cp ring, i.e. the hydroxymethyl group possesses a clearly pronounced *ortho*-orientation effect in the metallation of alcohol II.

It should be noted that an attempt to carry out a counter synthesis of II from I by alkaline decomposition of amine I iodomethylate proved to be unsuccessful. In contrast to a similar quaternary derivative of ferrocene, which readily transforms into ferrocenylmethanol [3] under these conditions, refluxing a solution of  $(\text{CO})_3\text{MnC}_5\text{H}_4\text{CH}_2\text{N}(\text{CH}_3)_3\text{I}$  in 2 N NaOH does not result in the formation of II.

The determination of the deuterium position in phosphine IIIa by a method similar to that employed in the case of IIa turned to be difficult due to the absence of simple methods for the conversion of phosphine III into amine I or vice versa. For this reason, the metallation orientation for III was determined by comparing the characteristics of 1-dimethylaminomethyl-2-diphenylphosphinocymantrene (Ic) with the aminophosphine derivative of cymantrene (VII) which was prepared according to Scheme 2, involving metallation of III.

SCHEME 2



Analysis of the PMR and  $^{13}\text{C}$  NMR spectra of aminophosphines Ic and VII (Tables 1 and 2) indicates that compound VII is 1-dimethylamino-3-diphenylphosphinocymantrene. It should be noted that in the PMR spectra of isomeric aminophosphines Ic and VII a characteristic difference in the signals of the  $\text{CH}_2$  groups is observed, in addition to a difference in the Cp ring proton signals. Thus, though in both cases the presence of diastereotopic hydrogen atoms in the  $\text{CH}_2$  group results in an AB quartet, the difference between the values of  $\delta(\text{H(A)})$  and  $\delta(\text{H(B)})$  for the 1,2-isomer (Ic) is 35.23 Hz greater than for the 1,3-isomer (VII). Moreover, the doublet of one of diastereotopic protons of the  $\text{CH}_2$  group in Ic with the values of  $\delta = 3.47$  ppm is additionally split by the  $^{31}\text{P}$  nucleus of the diphenylphosphino group with  $J(\text{PH})$  of 1.7 Hz (Fig. 1). The selective fission of one of the two diastereotopic methylene protons and its relationship with the conformation of the substituents in Ic is the subject of our current studies. We should merely like to note here that the spin-spin interaction of  $^{31}\text{P}$  with H of the methylene group disappears both upon the displacement of the PPh<sub>2</sub> substituent from the 2 position of the Cp ring to the

TABLE I  
PMR AND <sup>31</sup>P-NMR SPECTRA OF THE MONO- AND DISUBSTITUTED DERIVATIVES OF CYMANTRENE <sup>a</sup>

| Compound        | H(2)   | H(5)   | H(3)   | H(4)  | Other signals   | <sup>31</sup> P |
|-----------------|--|--|--|---|---|-----------------|
| I               | 4.69m  | 4.65m  |  |   | 3.04s, CH <sub>2</sub> ; 2.23s, N(CH <sub>3</sub> ) <sub>2</sub> .  |                 |
| I <sup>b</sup>  | 4.83s  | 4.65s  |  |   | 3.78d( <sup>3</sup> J(HH <sup>+</sup> ) 5.6), CH <sub>2</sub> ; 2.74d( <sup>3</sup> J(HH <sup>+</sup> ) 5.0), $\ddagger$ N(CH <sub>3</sub> ) <sub>2</sub> H;<br>7.4 bd.m, NH <sup>+</sup> .     |                 |
| II              | 4.77ps.t<br>3J(HH) + <sup>4</sup> J(HH) 4      | 4.66ps.t   |  |   | 4.27bd.s, CH <sub>2</sub> ; 2.42bd.s, OH.   |                 |
| III             |  | 4.69m  |  |   | 7.22m, PPh <sub>2</sub>   | 20.97           |
| IV              | 5.45ps.t<br><sup>4</sup> J(H,CHO) $\approx$ 0  | 4.93ps.t<br><sup>5</sup> J(H,CHO) 0.4<br>3J(HH) + <sup>4</sup> J(HH) 4.5 |  |   | 9.60bd.s, CHO   |                 |
| Ic              | 5.1-4.9m(1 H) and 4.7-4.4m(2 H)                |  |  |   | 3.47d( <sup>2</sup> J(HH) 13.6, <sup>4</sup> J(HP) 1.7) HA and 2.97 d( <sup>2</sup> J(HH) 13.6)<br>HB, CH <sub>2</sub> ; 2.03s, N(CH <sub>3</sub> ) <sub>2</sub> ; 7.2-7.5m, PPh <sub>2</sub> . | 27.61           |
| IIb             | 4.62tt<br><sup>4</sup> J(HH) 1.6<br>3J(HP) 1.3 | 4.86m<br><sup>4</sup> J(HH) 1.6<br>3J(HP)                                |  | 4.86m<br><sup>4</sup> J(HH) 1.6<br>+ <sup>4</sup> J(HP) 2.2 | 71-7.7m, PPh <sub>2</sub>   | 23.05           |
| VI <sup>c</sup> | 5.06m  | 5.89m  |  | 4.96m   | 9.29s, CHO; 7.2-7.3m, PPh <sub>2</sub> .  |                 |
| VII             | 4.8-4.7m                                       | 4.67m  |  | 4.8-4.7m  | 3.11d( <sup>2</sup> J(HH) 13.1) HA and 2.96d( <sup>2</sup> J(HH) 13.1) HB, CH <sub>2</sub> ;<br>2.25s, N(CH <sub>3</sub> ) <sub>2</sub> ; 7.3-7.4m, PPh <sub>2</sub> .                          |                 |
| VIII            | -  | 4.69dd<br><sup>3</sup> J(HH) +<br><sup>4</sup> J(HH) 5.5                 | 4.98dd<br><sup>3</sup> J(HH) +<br><sup>4</sup> J(HH) 7.9 | 4.61t<br><sup>3</sup> J(HH) 2.6                             | 3.44d( <sup>2</sup> J(HH) 14.2) HA and 2.98d( <sup>2</sup> J(HH) 14.2) HB, CH <sub>2</sub> ;<br>2.03s, N(CH <sub>3</sub> ) <sub>2</sub> ; 7.3-7.9, PPh <sub>2</sub> .                           | -20.51          |

<sup>a</sup> PMR in CDCl<sub>3</sub>;  $\delta$  (ppm) relative to internal TMS, J(Hz), ps.t = pseudotriplet, bd. = broadened; <sup>31</sup>P NMR (36.43 MHz) in CCl<sub>4</sub>,  $\delta$  (ppm) relative to external 80% H<sub>3</sub>PO<sub>4</sub>. <sup>b</sup> In CF<sub>3</sub>COOH, ext. TMS, 60 MHz (Perkin-Elmer R-12). <sup>c</sup> In CCl<sub>4</sub>, ext. TMS, 60 MHz.

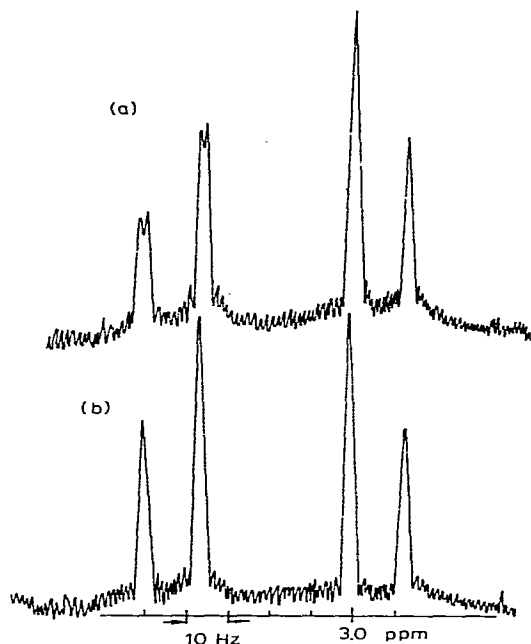


Fig. 1. Methylene pattern of the PMR spectra (90 MHz) of aminophosphine Ic: (a)  $^1\text{H}$  spectrum and (b)  $^1\text{H}\text{-}\{^3\text{1P}\}$  double-resonance spectrum.

3 position (i.e. on conversion of Ic to VII) and in the conversion from Ic to its P-oxide (VIII) (see Table 1).

Therefore, in contrast to amine I and alcohol II, metallation of phosphine III is effected into the remote, from the substituent, 3(4) position of the cyclopentadienyl ligand. It can be assumed that the 3(4)-orientation effect of the diphenylphosphine group in the metallation of III is associated with a low coordinating ability of the phosphorus atom towards the metallation agent (which is obviously the reason for the 2(5)-attack in the reaction of I and II with *n*-BuLi). This low coordinating ability of the phosphorus atom can be explained by either the low basicity of phosphine or steric hindrance.

The above data show that metallation of dimethylaminomethyl- and hydroxymethylcymantrene is a convenient method for the selective synthesis of 1,2-disubstituted cymantrene derivatives, whereas the reaction of *n*-butyllithium with diphenylphosphinocymantrene provides an opportunity for a selective preparation of 1,3-disubstituted cymantrene derivatives.

In addition to chemical methods for the determination of the orientation of substitution in the metallation of II and III, we have carried out a direct determination of the position of deuterium in IIa and IIIa by NMR techniques with the use of paramagnetic lanthanide shift reagents (NMR-LIS [4]). Table 3 shows relative values of LIS for the Cp ring protons in the PMR spectra of II and III as well as amine I and aldehyde IV, obtained from the graph of the chemical shifts of these protons vs. the value of  $[\text{LSR}]/[\text{substance}]$ , wherein LSR = lanthanide shift reagent =  $\text{Eu}(\text{fod})_3$  in the case of I and IV or  $\text{Dy}(\text{fod})_3$  for II and III. Since the centre of coordination of atoms Eu and Dy in the LSR-

TABLE 2  
<sup>13</sup>C NMR SPECTRA OF THE MONO- AND DISUBSTITUTED DERIVATIVES OF CYMANTRENE <sup>a</sup>

| Compound | Cp ring signals       |                      |                                     |                      |                      |        | (CO) <sub>3</sub>  | CH <sub>2</sub> N | (CH <sub>3</sub> ) <sub>2</sub> N |
|----------|-----------------------|----------------------|-------------------------------------|----------------------|----------------------|--------|--------------------|-------------------|-----------------------------------|
|          | C(1)                  | C(2)                 | C(3)                                | C(4)                 | C(5)                 | C(6)   |                    |                   |                                   |
| I        | 100.9                 | 83.58<br>1J(CD) 27.2 | 81.31                               | see C(3)             | see C(2)             | 223.99 | 56.55              | 44.66             |                                   |
| Ic       | 110.01<br>2J(CP) 22.8 | 93.22<br>1J(CP) 18.4 | 91.56<br>2J(CP) 5.2                 | 78.26                | 88.33<br>3J(CP) 2.9  | 224.45 | 55.98<br>J(CP) 8.1 | 45.15             |                                   |
| II       | 104.5                 | 81.82<br>1J(CD) 27.2 | 81.56<br>1J(CH) 179.4<br>2J(CD) 7.5 | see C(3)             | see C(2)             | 223.06 |                    |                   |                                   |
| III      | 92.94<br>1J(CP) 17.7  | 90.14<br>2J(CP) 13.2 | 83.01<br>3J(CP) 2.2                 | see C(3)             | see C(2)             | 223.31 |                    |                   |                                   |
| IIIb     | 95.41<br>1J(CP) 19.1  | 96.55<br>2J(CP) 8.8  | 95.41<br>1J(CP) 19.1                | 91.58<br>2J(CP) 16.2 | see C(4)<br>3J(CP) 3 | 223.67 |                    |                   |                                   |
| IV       | 91.79                 | 87.13<br>1J(CD) 29.3 | 84.70                               | see C(3)             | see C(2)             | 222.39 |                    |                   |                                   |
| VI       | 91.61                 | 83.01<br>2J(CP) 7.4  | 97.06<br>1J(CP) 20.6                | 92.76<br>2J(CP) 9.6  | 87.37<br>3J(CP) 3.7  | 222.05 |                    |                   |                                   |
| VII      | 101.79<br>3J(CP) 2.2  | 91.33<br>2J(CP) 13.9 | 91.77<br>1J(CP) 17.6                | 89.43<br>2J(CP) 11.8 | 84.44<br>3J(CP) 2.2  | 223.37 | 56.42              | 44.66             |                                   |

| Compound | CH <sub>2</sub> OH    | CHO                    | Ph ring signals <sup>b</sup>          |                                     |                                   | C(4)                     |
|----------|-----------------------|------------------------|---------------------------------------|-------------------------------------|-----------------------------------|--------------------------|
|          |                       |                        | C(1)                                  | C(2,6)                              | C(3,5)                            |                          |
| VIII     | 110.44<br>2J(CP) 9.6  | 87.05<br>1J(CP) 105.1  | 92.67<br>2J(CP) 12.5                  | 79.59<br>3J(CP) 10.3                | 87.75<br>3J(CP) 8.8               | 223.41<br>55.46<br>45.12 |
| Ic       |                       |                        | 136.11; 136.82<br>1J(CP) 8.1; 9.6     | 134.78; 132.87<br>2J(CP) 20.6; 19.1 | 128.68; 128.39<br>3J(CP) 7.4; 5.9 | 129.55; 128.52           |
| II       | 58.24<br>1J(CH) 144.1 |                        |                                       |                                     |                                   |                          |
| III      |                       |                        | 136.76<br>1J(CP) 11.8                 | 133.11<br>2J(CP) 19.9               | 128.23<br>3J(CP) 6.6              | 128.80                   |
| IIIb     |                       |                        | 137.03<br>1J(CP) 10.3                 | 133.53<br>2J(CP) 19.9               | 128.75<br>3J(CP) 6.6              | 129.42                   |
| IV       |                       | 186.98                 |                                       |                                     |                                   |                          |
| VI       |                       | 186.75<br>1J(CH) 180.9 | 136.38; 135.94<br>1J(CP) 10.3; 9.6    | 133.79; 133.46<br>2J(CP) 19.9; 19.9 | 128.95<br>3J(CP) 6.6              | 129.88; 129.59           |
| VII      |                       |                        | 137.03; 136.78<br>1J(CP) 11; 11       | 133.14; 133.04<br>2J(CP) 19.9; 19.9 | 128.25<br>3J(CP) 7.4              | 128.74                   |
| VIII     |                       |                        | 133.63; 133.22<br>1J(CP) 108.1; 107.4 | 128.54; 128.45<br>2J(CP) 12.5; 12.5 | 131.86<br>3J(CP) 10.3             | 132.09                   |

<sup>a</sup>  $\delta$  values in ppm relative to TMS (internal standard, solvent; CCl<sub>4</sub>,  $\delta$  95.9898 ppm, for I–III, VII and CH<sub>2</sub>Cl<sub>2</sub>,  $\delta$  54.0203 ppm, for Ic, IIIb, IV, VI, VIII) and J in Hz. The assignment of the signals of C atoms in the Cp ring of compounds Ic, IIIc, VI–VIII and in the Ph<sub>2</sub>P groups was effected on the basis of their intensities and J(CP) values and it should be regarded as tentative. <sup>b</sup> In the case of Ic, VI–VIII the phenyl radical in the Ph<sub>2</sub>P group are diastereotopic.

TABLE 3

RELATIVE VALUES OF INDUCED PARAMAGNETIC SHIFT (LIS) OF Cp RING PROTONS IN I-IV <sup>a</sup>

| Compound         | LSR                  | Proton | $\delta$ (ppm) | Intensity (au) <sup>b</sup> | LTS (%) |
|------------------|----------------------|--------|----------------|-----------------------------|---------|
| I                | Eu(fod) <sub>3</sub> | 2(5)   | 4.69           | 0.3                         | 100     |
|                  |                      | 3(4)   | 4.65           | 2                           | 11      |
| II               | Dy(Fod) <sub>3</sub> | 2(5)   | 4.77           | 0.3                         | 100     |
|                  |                      | 3(4)   | 4.66           | 2                           | 44      |
| III <sup>c</sup> | Dy(fod) <sub>3</sub> | 2(5)   | 4.69           | 2                           | 100     |
|                  |                      | 3(4)   | 4.67           | 1                           | 22      |
| IV               | Eu(fod) <sub>3</sub> | 1(5)   | 5.45           | 0.3                         | 100     |
|                  |                      | 3(4)   | 4.93           | 2                           | 35      |

<sup>a</sup> Spectra recorded on a Perkin-Elmer R-12 spectrometer (60 MHz) in CCl<sub>4</sub>: TMS internal standard, <sup>b</sup> For the deuterated derivatives of compounds I-IV, <sup>c</sup> Values of  $\delta$  for the 2(5)- and 3(4)-positions were obtained by extrapolation from a graph of  $\delta$  vs. [Dy(fod)<sub>3</sub>]/[III].

substance complex is obviously the heteroatom in the substituent \* (N, O or P), in accordance with ref. 4b, the signal with a higher LIS value (assumed as 100%) should be attributed in each case to the protons of the 2(5)-positions of the ring which are closer to the coordination centre. The intensity of this signal in the PMR spectra of deuterated compounds Ia, IIa and IV is below 2 H which corresponds to the presence of deuterium atoms in the 2(5)-position of these compounds (see above). On the contrary, in the case of IIIa the intensity of this signal (i.e. the signal of the 2(5)-protons of the Cp ring) is equal to 2 H, whereas the intensity of the signal with lowest LIS value, corresponding to the protons of the 3(4)-position, is 1.1 H. This conclusion is in agreement with the above conclusion on the 3(4)-orientation of metallation of phosphine III.

The consistences of the results on the distribution of the deuterio-label in the Cp ring in deuterated derivatives of compounds I-IV obtained by the NMR-LIS technique with the data from chemical studies infers the following. The use of paramagnetic shifting reagents makes it possible to effect an unambiguous assignment of the signals of the cyclopentadienyl protons in PMR spectra of achiral monosubstituted cymantrene derivatives directly from a graph of the change  $\delta$  vs. [LSR]/[substance].

The monosubstituted cymantrene derivatives with a known deuterium position in the Cp ring described in this paper enable an unambiguous assignment of the signals of the ring H and C atoms in PMR and <sup>13</sup>C NMR spectra of these compounds (Tables 1 and 2). As a result, it was in particular established that the proton of the CHO group in the aldehyde IV was coupled via spin-spin interaction to those Cp ring protons in the most remote position, 3(4), from the substituent. The coupling constant <sup>4</sup>J(HH) between H(2(5)) and the proton of the CHO group is too small to be observed in the spectrum. However, it apparently differs from zero since the signal of the formyl proton appeared to be a broadened singlet and not a doublet. It should be also noted that the central lines of the pseudo-triplets from the protons of both the 2(5)- and 3(4)-

\* The use of Eu(fod)<sub>3</sub> and Dy(fod)<sub>3</sub> in the case of cymantrene and methylcymantrene results only in a slight broadening of the signal of the Cp ring protons without significantly changing its chemical shift.



positions in the PMR spectrum of IV, with spin-decoupling of the formyl proton are noticeably broadened. That means that the constants  $^3J(\text{HH})$  and  $^4J(\text{HH})$  for the magnetically inequivalent protons of the Cp ring are close, but not equal.

## Experimental

The synthesis of amines I and Ia and non-deuterated aldehyde IV was effected by the method given in ref. 1. PMR spectra were obtained on Varian XL-100 (100.1 MHz) and RYa-2309 (90 MHz) spectrometers;  $^{13}\text{C}$  NMR spectra on a Bruker HX-90 (22.635 MHz) instrument.

### *I. General procedure for metallation and synthesis of Ic, IIa, b, III, IIIa, b and IV*

The reaction of n-BuLi with I, II, III and cymantrene was conducted as in ref. 1 for 1–2 hours at a molar ratio of the substrate to n-BuLi of 1 : 1.5 (in the case of cymantrene, I and III) or 1 : 3 (for alcohols II and IIa). The resulting corresponding organolithium compounds were treated with an appropriate electrophilic agent ( $\text{D}_2\text{O}$ , DMF,  $\text{ClPPh}_2$ ) at  $-70^\circ\text{C}$  and the reaction mixture temperature allowed to rise to  $10-20^\circ\text{C}$ . Further treatment of the reaction mixture was carried out as described below.

A) The reaction mixture produced from 10.2 g (0.05 mol) of cymantrene and 33 g (0.15 mol) of  $\text{Ph}_2\text{PCl}$  was kept at room temperature for 2 hours and decomposed by 2 N HCl with cooling. Then the pH of the aqueous layer was brought to 8 by adding 2 N KOH, extracted with ether or  $\text{CH}_2\text{Cl}_2$  and the organic extracts were washed with water. The dried solution was evaporated and the residue was crystallized from hexane or ethanol to give 16.9 g (87.4%) of phosphine III, m.p.  $111-112^\circ\text{C}$ . Analysis: Found: C, 61.95, 61.93; H, 3.62, 3.59; P, 7.76, 7.82; Mn, 13.80, 14.24.  $\text{C}_{20}\text{H}_{14}\text{O}_3\text{MnP}$ . Calcd.: C, 61.87; H, 3.63; P, 7.97; Mn, 14.14%.

B) In a similar manner, from 5 g (0.0125 mol) of III and 8.25 g (0.0375 mol) of  $\text{Ph}_2\text{PCl}$  there were obtained 4.5 g (62.9%) of diphosphine IIIb, m.p.  $108-109^\circ\text{C}$  (ethanol). Analysis: Found, C, 66.85; 66.97; H, 4.00; 4.22; P, 10.83, 10.87; Mn, 9.18, 9.26.  $\text{C}_{32}\text{H}_{23}\text{O}_3\text{MnP}_2$ . Calcd.: C, 67.15; H, 4.02; P, 10.83; Mn, 9.61%.

C) In a similar manner, from 5 g of III and 2.5 g (0.0375 mol) of DMF there were obtained 3.9 g (74.2%) of phosphinoaldehyde VI, m.p.  $112-113^\circ\text{C}$  (hexane). Analysis: Found: C, 60.97, 60.87; H, 3.59, 3.66; P, 7.40, 7.52; Mn, 13.12, 13.13.  $\text{C}_{21}\text{H}_{14}\text{O}_4\text{MnP}$ . Calcd.: C, 60.60; H, 3.36; P, 7.44; Mn, 13.20%.

D) The acidic aqueous solution of the reaction products of metallation (see (A)) obtained from 13.2 g (0.05 mol) amine I and 33 g (0.15 mol) of  $\text{Ph}_2\text{PCl}$  was extracted with ether or benzene and brought to pH 9–10 by adding 2 N KOH. The extraction with ether or benzene, followed by washing the combined organic extracts with water, drying over anhydrous  $\text{Na}_2\text{SO}_4$  and removal of the solvent resulted in 16.2 g (72.8%) of 1,2-aminophosphine Ic, m.p.  $92-93^\circ\text{C}$  (ethanol). Analysis: Found: C, 61.86, 61.90; H, 4.69, 4.91; N, 3.08, 3.09; P, 6.81, 7.06; Mn, 12.17, 12.33.  $\text{C}_{23}\text{H}_{21}\text{NO}_3\text{MnP}$ . Calcd.: C, 62.03; H, 4.75; N, 3.14; P, 6.96; Mn, 12.34%.

E) The reaction mixture prepared from 12 g (0.055 mol) of alcohol II and 7 g (0.35 mol) of  $D_2O$  was maintained at room temperature for 2 hours and poured into 500 ml of water: the pH of the solution was brought to 7–8 and the solution was then extracted with ether or benzene, the organic extracts were washed with water, dried with anhydrous  $Na_2SO_4$  and the solvent was evaporated. Crystallization of the residue from hexane gives 9.1 g (76%) of IIa, m.p. 40–41°C, containing about 1D according to the PMR data.

The repeated metallation of IIa and subsequent treatment of the reaction mixture with deuterium oxide resulted in the formation of alcohol IIb containing 1.7 D atoms, m.p. 41–42°C (pentane).

F) In a manner similar to that of (E), from 5 g (0.0125 m) of III and 3.5 g (0.18 mol) of deuterium oxide there were obtained 3.95 g (79%) of deuterated phosphine IIIa (about 1D), m.p. 112–113°C.

### II. Preparation of 1-dimethylaminomethyl-3-diphenylphosphinocymantrene

A mixture of 1.46 g (0.02 mol) of DMF, 1.15 g (0.025 mol) of HCOOH and 2.1 g (0.005 mol) of aminoaldehyde VI was refluxed for 3 hours at 150°C under argon. Then the mixture was acidified with 2 N HCl, poured into water; the latter was extracted with benzene. The acidic solution was brought to pH 9–10 by adding 2 N KOH and extracted with benzene. The extract was washed with water until the washings were neutral, and dried over  $Na_2SO_4$ . After the removal of the solvent the residue was purified by column chromatography on  $Al_2O_3$  benzene eluent. The yield of VII was 0.84 g (38%); an oil slowly crystallizing when allowed to stand for a long time. Analysis: Found: C, 61.85, 61.88; H, 4.82, 4.97; N, 2.96, 3.21; P, 6.70, 6.71; Mn, 11.90.  $C_{23}H_{21}NO_3MnP$ . Calcd.: C, 62.03; H, 4.75; N, 3.14; P, 6.96; Mn, 12.34%.

### III. Preparation of hydroxymethylcymantrene II from IV

To a solution of 46.2 g (0.2 mol) of IV in 500 ml of abs. ethanol there were added portion-wise 16 g (0.42 mol) of  $NaBH_4$  for 2 hours with stirring at 20°C. The mixture was kept for 1 hour under these conditions, and then into 1 l of water and extracted with methylene chloride. The organic layer was washed with water and dried over  $Na_2SO_4$ . After removal of the solvent, distillation of the residue gave 35.1 g (74.7%) of alcohol II, b.p. 92°C ( $6 \times 10^{-2}$  mmHg), m.p. 40–41°C (hexane). M.p. from literature 41–42°C [5].

### IV. Oxidation of alcohol II to formylcymantrene IV

A suspension of 21 g (0.24 mol) of active  $MnO_2$  in 170 ml of benzene was refluxed for 4 hours with Dean-Stark packing and on addition of 11.2 g (0.05 mol) of II heated further for 20 hours. After cooling, the benzene solution was twice filtered from the residue which was washed with benzene. The benzene solution was evaporated to dryness and 5.5 g (50%) of IV, m.p. 80–81°C (pentane), were isolated from the residue by crystallization from hexane.

### V. Preparation of the P-oxide of 1-dimethylaminomethyl-2-diphenylphosphinocymantrene (VIII)

To a solution of 1.33 g (0.0029 mol) of Ic in abs. acetone 1 ml of 30%  $H_2O_2$  was added drop-wise at 10°C with stirring. The mixture was kept for additional

1 hour at 10° C, and then poured into 200 ml of water, extracted with benzene and the extract was dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed and the residue was crystallized from hexane to give 1.07 g (80%) of the P-oxide, VIII, m.p. 110–111° C. Analysis: Found: C, 59.97, 59.77; H, 4.66, 4.70; Mn, 11.98, 12.10. C<sub>23</sub>H<sub>21</sub>NO<sub>4</sub>MnP. Calcd.: C, 59.87; H, 4.59; Mn, 11.91%.

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