Metallation of bicymantrenyl and synthesis of polycymantrenyls [1,2]

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Abstract

Bicymantrenyl, η^5,η^5-$C_{10}H_8[Mn(CO)_3]_2$ (1), may be metallated at the Cp-ring with BuLi (THF, $-60\,°C$) to give monolithium (2) and polylithium derivatives. Metallation of 1 proceeds concurrently on both α- and β- positions, the β-substitution product being predominant. A number of derivatives of 1 with substituents R = D, COOH, CHO, PPh_2 have been synthesized in the reactions of monolithium derivative 2 with different electrophiles (D_2O, CO_2, DMFA, Ph_2PCl respectively). Under the action of $CuCl_2$ the oxidative coupling of 2 proceeds to give tetracymantrenyl (11a). Oxidative coupling of a mixture of 2 with cymantrenyllithium affords two isomers of tricymantrenyl (12a, 12b). The structures of 11a, 12a, 12b were established by an X-ray study. © 1997 Elsevier Science S.A.
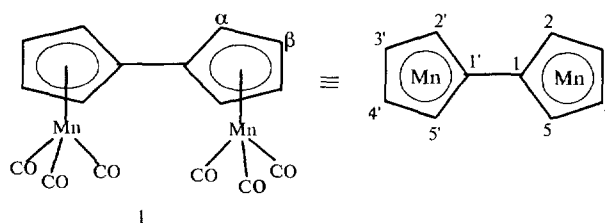
1. Introduction

The chemistry of bicymantrenyl (1), in contrast to that of cymantrene, has received little attention [3,4]. Complex 1 was synthesized more than 20 years ago [5,6], but until the present time only the acylation reaction [7] and CO substitution [8] have been studied.

Recently, we started an investigation of bicymantrenyl chemistry. It was shown that, in contrast to the results reported in earlier work [7], acetylation and benzoylation of 1 under the Friedel–Crafts conditions proceeds on both unequivalent positions (α- and β-) [9]. Acylation of 1 leads to mixtures of two ketones, β-ketones being predominant in both cases (β/α ratio approximately 5–6).

In this work, we studied the metallation of 1 with BuLi as well as some reactions of lithium derivatives.

2. Results and discussion

Like cymantrene, 1 can be metallated with BuLi into η^5,η^5-difulvalene ligand (in THF at $-60\,°C$). Depending on the amount of BuLi, the monolithium derivative 2 or a mixture of 2 with polylithium derivatives may be obtained. If the ratio BuLi/1 is equal to 4–5 then, after D_2O quenching, the mixture of isotopomers of 1 containing 1–4 deuterium atoms per molecule (mass spectral data) was obtained.

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Metallation of 1 is non-selective, as in the case of methylcymantrene [10]. Lithium enters in both the α- and the β-position, β-substitution being predominant
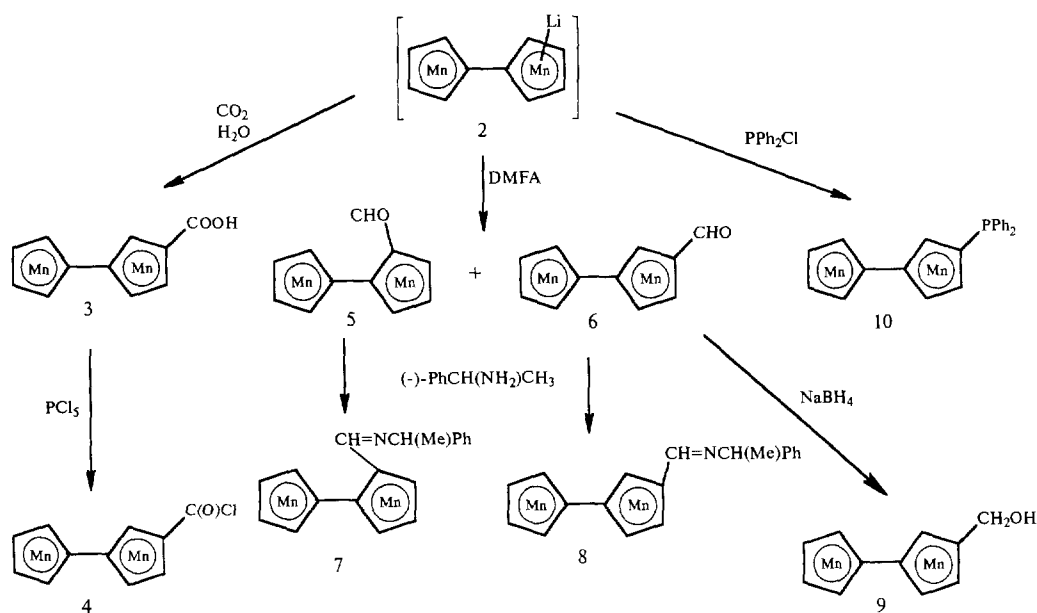
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[1] Dedicated to the memory of Professor Yuri T. Struchkov in recognition of his great contribution to the structural chemistry of organometallic compounds.

[2] Preliminary communication, see Refs. [1,2].

Scheme 1.

(β/α ratio of deuterium after D_2O quenching for un-substituted 1 equal to 3–4). When β-ethylbicymantrenyl [1] was metallated with BuLi the reaction was also non-selective, with all seven non-equivalent positions of the $C_5H_4C_5H_3$ fragment being involved.

The reaction of lithium derivatives 2 with electrophilic reagents is a simple way to a number of new monosubstituted derivatives of 1 (Scheme 1).

Carboxylation of 2 with CO_2 gives rise to a mono-carboxylic acid (3), from which acylchloride (4) was obtained. Reaction of 2 with DMFA gives a mixture of two isomeric monoaldehydes (5 and 6), the ratio β/α in this case is equal to 10–15. Aldehydes 5 and 6 have practically identical mass spectra, but rather different ^1H NMR spectra. Reactions of aldehydes 5 and 6 with

(−)-(α)-phenylethylamine lead to the corresponding Schiff bases (7, 8). Reduction of 6 with $NaBH_4$ in EtOH or ether gives carbinol (9) and quenching of 2 with Ph_2PCl affords phosphine (10).

Some of the monosubstituted cymantrenes may be metallated regio- and enantioselectively [11–15]. In particular, such substituents as SO_2NMe_2 [11], CH_2OH and CH_2NMe_2 [12] and also dioxolanes and their analogs [13–15] which have a heteroatom (O, N) with lone electron pair direct metallation solely or largely in the neighboring position. For comparison with cy-mantrene we studied metallation of carbinol 9, in the ^1H NMR spectra of which signals of all seven protons $C_5H_4C_5H_3$ are well resolved. After metallation of 9 with 3–5 equivalents of BuLi and quenching with D_2O,

Scheme 2.

α–β–isomer (11b)   α–α–isomer (11c)
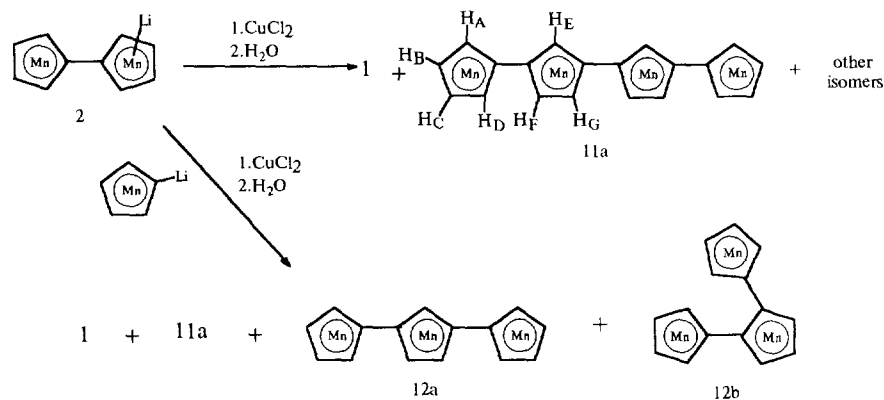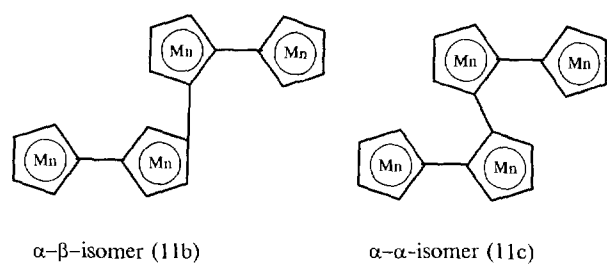
Scheme 3.

deuterium in the C_5H_3 ring inserts exclusively into the 3-position so the orienting effect of the CH_2OH group in the C_5H_3 fragment is the same as in cymantrene. However, it follows from ^{1}H NMR data that, in the case of 9, deuterium inserts not only in the C_5H_3 ring but also in two β-positions of the C_5H_4 ring.

A preparative method of synthesis of 1 is oxidative coupling of cymantrenyllithium by anhydrous $CuCl_2$ [8]. With the aim of synthesizing compounds which have more than two cymantrenyl fragments, we performed the oxidative coupling of 2 and prepared first a complex having a chain of four cymantrenyl units (11a) (Scheme 2). So far as metallation of 1 is non-selective, three different dimers can be formed (11a–c) where two $C_5H_4C_5H_3$ fragments are linked in the β–β (11a), α–β (11b) or α–α mode (11c) (see Scheme 3). Statistically, the formation of 11a is most favorable. It follows from ^{1}H NMR data that coupling of 2 with $CuCl_2$ results in a mixture which contains more than 95% 11a and 3–5% of another isomer (probably 11b).

Metallation of an equimolar mixture of 1 and cymantrene with subsequent oxidative coupling (2 + 1 reaction) after hydrolysis results in a mixture of two isomers of tricymantrenyl (12a and 12b) with 11a (a product of 2 + 2 reaction) and some of the parent 1 (Scheme 2).

All new compounds were characterized by analytical and spectral data (IR, NMR, MS).

IR spectra. All bicymantrenyl derivatives exhibit two intensive CO stretching frequences at around 2025(sh 2035) and 1945–1950 cm^{-1}, which may be attributed to the symmetrical and degenerate CO vibrations in the $Mn(CO)_3$ moiety with C_{3v} local symmetry (A_1 and E symmetry classes respectively). In the spectra of com-

pounds 3–6 there are also characteristic bands belonging to substituents with a carbonyl group (Table 1). In the spectra of acyl chloride 4 there are two sets of $Mn(CO)_3$ stretching frequencies. The $(CO)_3MnC_5H_3C(O)Cl$ moiety gives bands at 2041, 1964/1972 cm^{-1}, which coincides exactly with the corresponding frequencies for $(CO)_3MnC_5H_4C(O)Cl$. At the same time the $(CO)_3MnC_5H_4$ moiety, which has no strong electron-withdrawing substituent, gives three other bands at 2029, 1950(sh)/1954 cm^{-1}.

^{1}H NMR spectra. The parent compound 1 is prochiral. Any bicymantrenyl derivatives with non-hydrogen substituents in either the 2- or 3-position will have planar chirality. Owing to the diastereotopic non-equivalence, all seven protons in the $C_5H_4C_5H_3$ fragment must give seven separate signals in the ^{1}H NMR spectra (Table 2). Four protons in the C_5H_4 fragment form an ABCD system and four separate multiplets are observed in the spectrum. Each of the two α-protons forms a doublet of triplets (six lines) in low field but, owing to partial overlapping, the resulting multiplet has five lines. Each of the two β-protons forms a triplet of doublets (six lines) in high field, the constants of spin–spin coupling being as follows: [1]J(H,H) 2.6–3.0 Hz and [2]J(H,H) 1.6–1.8 Hz.

Three protons in the C_5H_3 ring give rise to three separate multiplets (ABC system) with the same constants but different multiplicity. For compounds 4, 6, 8–10, which have an acceptor substituent in the β-position, proton H(2) gives a low field triplet and each of the protons H(4) and H(5) gives a doublet of doublets with constants [1]J(4,5) 2.9–3.0 Hz and [2]J(2,4) ≅ [2]J(2,5) approximately 1.7–1.8 Hz.

In the ^{1}H NMR spectra of carbinol 9 the resonances of three C_5H_3 protons appear as a triplet at δ 4.96 and two doublet doublets at 4.82 and 4.72 ppm. After metallation with BuLi and quenching with D_2O, deuterium in the C_5H_3 ring inserts regioselectively and practically only in the β-position adjacent to the CH_2OH substituent (4-position). After deuteration, the intensity of the H(4) resonance at 4.72 decreases strongly. At the same time the triplet of H(2) at 4.96 and the doublet doublets of H(5) at 4.82 transform to a new AX system as two doublets with [2]J(2,5) 1.7 Hz.

Complexes 11a, 12a and 12b may be considered as

Table 1
IR spectra of compounds 3–6

Compound	Solvent	ν(CO), $Mn(CO)_3$ (cm^{-1})	ν(C=O) (cm^{-1})
$(CO)_3MnC_5H_4COOH$	CH_2Cl_2	1955br, 2035	1695, 1740
Acid 3	CH_2Cl_2	1955br, 2025, 2035sh	1695, 1740
$(CO)_3MnC_5H_4C(O)Cl$	hexane	1966, 1972, 2043	1775
Acid chloride 4	hexane		
$(CO)_3MnC_5H_3C(O)Cl$		1964, 1972, 2041	1754, 1769sh, 1780
$(CO)_3MnC_5H_4^-$		1950sh, 1954, 2029	
Aldehydes 5 and 6	CH_2Cl_2	1950br, 2025, 2038	1689, 1705

Table 2
^{1}H NMR data for compounds 1–9

Compound	Chemical shifts δ (ppm)		
	C_5H_4 ring	C_5H_3 ring	Substituent
1	4.96 t (4H, J 2.1 Hz Γ_μ) 4.75 t (4H, J 2.1 Hz Γ_μ)	—	—
3	5.55 m (2H), 4.82 m (2H)	6.62 (1H), 5.69 (1H), 5.65 (1H)	—
4	5.03 m (2H), 4.81 m (2H)	5.71 t (1H, J 1.7 Hz), H(2) 5.63 dd (1H, J 1.7 and 3.0 Hz) 5.09 dd (1H, J 1.7 and 3.0 Hz), H(4,5)	
5	5.57 (1H, 5 lines, J 1.7 and 3.0 Hz) 5.06 (1H, 5 lines, J 1.7 and 3.0 Hz), H(2',5') 4.81 m (2H, 10 lines), H(3',4')	5.46 dd (1H, J 1.7 and 3.0 Hz) 5.15 dd (1H, J 1.7 and 3.0 Hz), H(3,5) 4.88 t (1H, J 3.0 Hz), H(4)	9.77 c (CHO)
6	5.03 m (2H, 10 lines), H(2',5') 4.81 m (2H, 10 lines), H(3',4')	5.62 t (1H, J 1.8 Hz), H(2) 5.49 dd (1H, J 1.8 and 2.9 Hz) 5.09 dd (1H, J 1.8 and 2.9 Hz), H(4,5)	9.60 c (CHO)
7 [*]	5.39 dd (1H); 4.94 dd (1H); 4.84 t (1H)	5.10 (1H, 5 lines); 5.02 (1H, 5 lines) 4.77 (1H, 6 lines); 4.71 (1H, 6 lines)	8.20 s (1H), CH=N 4.51 k (1H, J 6.2 Hz), C–H 1.55 d (1H, J 6.2 Hz), CH$_3$ 7.33 m (5H), C$_6$H$_5$
8 [*]	5.53 t (1H); 5.25 dd (1H); 4.92 m (1H)	5.02 (1H, 5 lines); 4.92 m (1H) 4.77 (1H, 6 lines); 4.72 (1H, 6 lines)	7.92 s (1H), CH=N 4.46 k (1H, J 6.2 Hz), C–H 1.53 d (1H, J 6.2 Hz), CH$_3$ 7.37 m (5H), C$_6$H$_5$
9	4.86 (1H, 5 lines, J 1.7 and 2.9 Hz) 4.85 (1H, 5 lines, J 1.7 and 2.9 Hz), H(2',5') 4.66 (1H, 6 lines, J 1.7 and 2.9 Hz) 4.64 (1H, 6 lines, J 1.7 and 2.9 Hz), H(3',4')	4.96 t (1H, J 1.8 Hz), H(2) 4.82 dd (1H, J 1.8 and 2.9 Hz) 4.72 dd (1H, J 1.8 and 2.9 Hz), H(4,5)	4.25 d (2H, J 6.0 Hz), CH$_2$ 1.71 t (1H, J 6.0 Hz), OH
10	4.831 m (1H), 4.809 m (1H) 4.809 m (1H), 4.730 m (1H)	4.986 m (3H)	7.385 m (10H), C$_6$H$_5$

[*] Data for one diastereoisomer.

Table 3
^{1}H and ^{13}C NMR data for polycymantrenyls

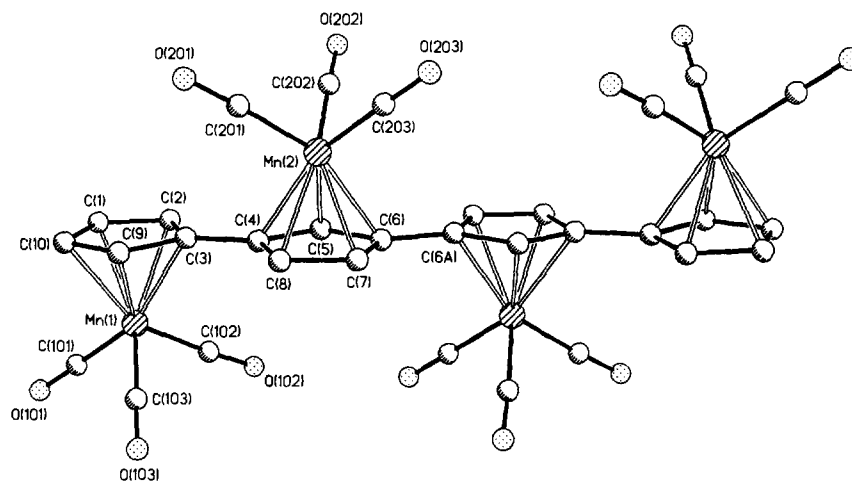| Compound	^{1}H NMR δ (ppm) (intensity, multiplicity)				^{13}C NMR δ (ppm) (quantity of carbon atoms)			
	C_5H_4 rings		C_5H_3 rings		C–H carbons		ipso-Carbons	$Mn(CO)_3$
	H_A, H_D	H_B, H_C	H_E	H_F, H_G				
11a	5.01 (2H, 5)	4.80 (2H, 6)	5.17 t (2H, 3)	4.93 d (4H, 2)	82.53 (2C)	80.14 (2C)	95.27	223.98
	4.95 (2H, 5)	4.76 (2H, 6)			82.01 (2C)	79.76 (2C)	94.45	223.53
					81.02 (2C)	78.64 (2C)	94.16	(1:1)
					80.73 (2C)			
12a	5.00 (2H, 5)	4.79 (2H, 6)	5.15 t (1H, 3)	4.95 d (2H, 2)	82.46 (2C)	80.83 (2C)	94.83	224.00
	4.96 (2H, 5)	4.75 (2H, 6)			81.91 (2C)	80.74 (2C)	94.54	223.80
					81.13 (2C)			(2:1)
					78.99 (1C)			
12b	5.02 (2H, 5)	4.78 (2H, 6)	4.60 t (1H, 3)	4.99 d (2H, 2)	86.52 (2C)	81.82 (2C)	95.46	223.85
	4.93 (2H, 5)	4.71 (2H, 6)			86.27 (4C)	81.43 (2C)	93.82	223.63
					77.74 (1C)			(2:1)

Fig. 1. Molecular structure of 11a.

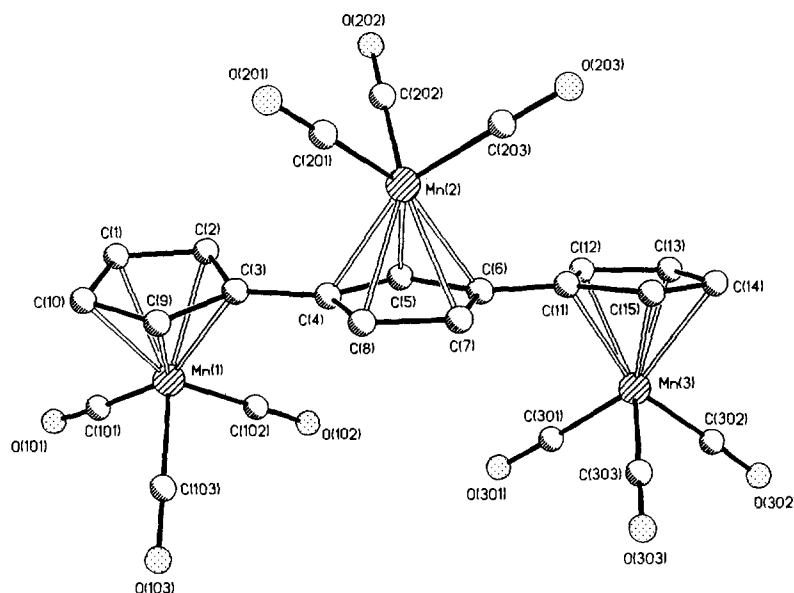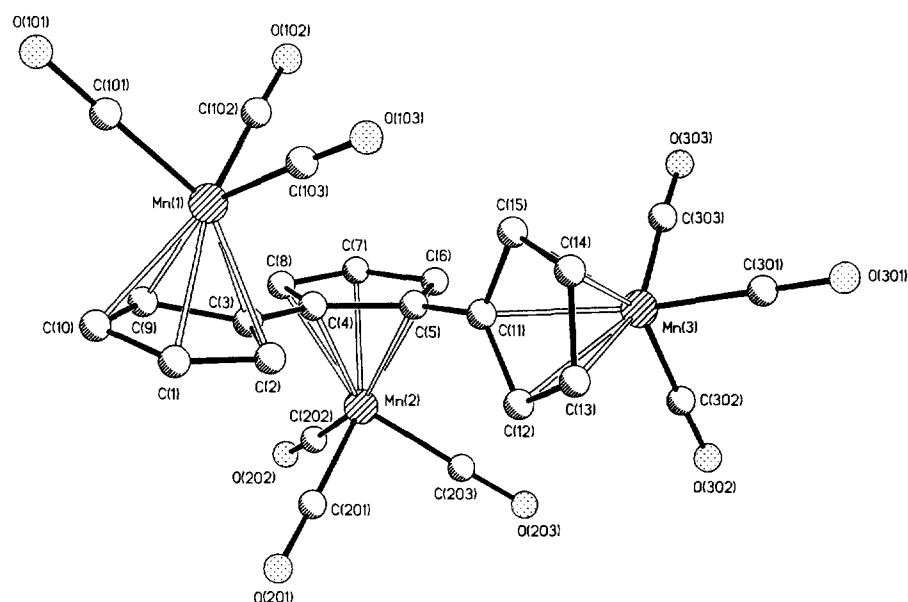

Fig. 2. Molecular structure of 12a.

Fig. 3. Molecular structure of **12b**.

bicymantrenyls which have some substituent (β-bi-cymantrenyl in **11a**, β- or α-cymantrenyl in **12a,b** respectively). As any substituted derivatives of bicy-mantrenyl, all these complexes have planar chirality. So far as four CH– groups in each of the two C_5H_4 rings are diastereotopic, they must give separate resonances. In ^{1}H NMR spectra the protons H_A–H_D appear as four one-proton multiplets of five or six lines (Table 3). Three protons of C_5H_3 rings (H_E and $H_{F,G}$ for **11a** and corresponding protons in **12a**, **12b**) form an A_2B system and give a doublet and triplet with constants ^2J(H,H) 1.7–1.8 Hz for **11a** and **12a**, or ^1J(H,H) 2.8 Hz for **12b**.

^{13}C *NMR spectra.* Complex **11a** has 14 H-bonded carbons which give seven separate resonances at 78–83 ppm owing to their pairwise equivalence. Six *ipso*-carbon atoms give three resonances at around 95 ppm (Table 3). Similarly, 11 carbons in **12a,b** exhibit five and four resonances (for **12b** two of five resonances coincide) with intensity corresponding to 2C and also one resonance with intensity corresponding to one car-bon (C–H_E). Four *ipso*-carbon atoms give two reso-nances at around 95 ppm. 12 or nine carbons of CO groups give two resonances at around 224 ppm with intensity ratio 1:1 (**11a**) or 2:1 (**12a,b**) which corre-spond to 'central' and 'peripheral' Mn(CO)$_3$ units.

2.1. Crystal structure of polycymantrenyls

Molecular structures of the first representatives of the new homological series of polycymantrenyl complexes **11a**, **12a** and **12b** were established by X-ray study (see Figs. 1–3). Bond lengths are presented in Table 4.

Molecules **11a** and **12a** have similar structures, which can be considered as a bicymantrenyl framework with

Table 4
Selected bond lengths (Å) for **11a**, **12a** and **12b**

Bond	11a	12a	12b
Mn(1)–C(1)	2.144(2)	2.142(4)	2.131(4)
Mn(1)–C(2)	2.141(2)	2.149(3)	2.134(3)
Mn(1)–C(3)	2.148(2)	2.168(3)	2.146(3)
Mn(1)–C(9)	2.141(2)	2.147(4)	2.136(3)
Mn(1)–C(10)	2.139(3)	2.135(4)	2.138(4)
Mn(2)–C(4)	2.153(2)	2.148(3)	2.166(3)
Mn(2)–C(5)	2.142(2)	2.141(3)	2.147(3)
Mn(2)–C(6)	2.150(2)	2.166(3)	2.126(3)
Mn(2)–C(7)	2.135(2)	2.151(3)	2.128(3)
Mn(2)–C(8)	2.141(2)	2.141(3)	2.135(3)
Mn(3)–C(11)		2.146(3)	2.155(3)
Mn(3)–C(12)		2.147(4)	2.129(3)
Mn(3)–C(13)		2.136(4)	2.126(4)
Mn(3)–C(14)		2.143(4)	2.144(4)
Mn(3)–C(15)		2.139(4)	2.143(3)
C(1)–C(2)	1.408(3)	1.411(5)	1.416(5)
C(1)–C(10)	1.412(4)	1.419(7)	1.402(5)
C(2)–C(3)	1.430(3)	1.434(5)	1.417(4)
C(3)–C(9)	1.425(3)	1.417(5)	1.439(4)
C(4)–C(5)	1.423(3)	1.424(5)	1.415(4)
C(4)–C(8)	1.431(3)	1.427(4)	1.440(4)
C(5)–C(6)	1.421(3)	1.414(4)	1.427(4)
C(6)–C(7)	1.427(3)	1.444(5)	1.402(5)
C(7)–C(8)	1.408(3)	1.411(5)	1.410(5)
C(9)–C(10)	1.418(3)	1.426(6)	1.410(5)
C(11)–C(12)		1.429(5)	1.419(4)
C(11)–C(15)		1.427(5)	1.431(4)
C(12)–C(13)		1.425(5)	1.401(5)
C(13)–C(14)		1.418(7)	1.407(6)
C(14)–C(15)		1.420(5)	1.401(5)
C(3)–C(4)	1.465(3)	1.467(4)	1.471(4)
C(6)–C(6)#1	1.465(4)		
C(6)–C(11)		1.464(5)	
C(5)–C(11)			1.477(4)
Mean Mn–C(0)	1.796	1.796	1.793

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y+1, -z+1$.

β-bicymantrenyl (**11a**) or β-cymantrenyl (**12a**) substituent. The Cp-rings are nearly coplanar in both complexes, the carbon atoms of all Cp-ligands being planar within 0.002 and 0.003 Å in **11a** respectively. The $Mn(CO)_3$ moieties occupy in turn positions on the opposite sides of the mean plane of the Cp-rings. Molecule **11a** is located on a crystallographic inversion center; the dihedral angle between the mean planes of the C(1)C(2)C(3)C(9)C(10) and C(4)C(5)C(6)C(7)C(8) rings is equal to 2.0°. In the molecule of **12a** the planes of the two peripheral rings C(1)C(2)C(3)C(9)C(10) and C(11)C(12)C(13)C(14)C(15) form dihedral angles of 12.0° and 7.8° respectively with the plane of the central Cp-ligand C(4)C(5)C(6)C(7)C(8).

The conformation of molecule **12b** differs significantly from that of its isomer **12a**. The central Cp-ring in **12b** is nearly coplanar with one of the peripheral Cp-ligands only (dihedral angle C(1)C(2)C(3)-C(9)C(10)/C(4)C(5)C(6)C(7)C(8) 11.1°), whereas the Cp-ring plane of the other peripheral cymantrenyl group is almost orthogonal to the plane of the central Cp-ring (relevant dihedral angle 88.3°). Such a conformation is caused by the steric hindrances arising from the presence of two bulky cymantrene substituents in the neighboring position in the central ring. A similar effect has been found earlier in the molecules of bis(cymantrenyl)carbinols [16]. Bond lengths and bond angles in **11a**, **12a** and **12b** do not show any noticeable differences. They are close to the corresponding values in cymantrene [17] and coincide with standard values [18,19] and with parent **1** [20].

3. Experimental

All reactions were carried out in argon atmosphere. The parent complex **1** was obtained as described in Ref. [8]. THF was distilled over benzophenoneketyl prior to use. ^1H and ^{13}C NMR spectra were obtained on Bruker WP-200SY and Bruker AMX-400 instruments, IR-spectra on a UR-20 spectrometer, mass spectra on a Kratos MS-890 mass spectrometer (electron impact).

3.1. X-ray diffraction studies of 11a, 12a and 12b

The structures were solved by direct methods and refined on F^2 by full-matrix least-squares in the anisotropic approximation for all non-hydrogen atoms. H-atoms were located in the difference Fourier synthesis and included in the final refinment with isotropic thermal parameters. All calculations were carried out using the SHELXTL PLUS 5 (gamma version) program. Final atomic coordinates of **11a**, **12a** and **12b** structures are presented in Tables 5–7. Details of crystal data and data collection for all three structures are summarized in Table 8.

Table 5
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **11a**

Atom	x	y	z	U_{eq}
Mn(1)	1147(1)	8176(1)	2982(1)	39(1)
Mn(2)	4443(1)	7305(1)	5435(1)	35(1)
O(101)	−171(3)	8933(3)	1566(1)	87(1)
O(102)	2919(3)	5930(2)	2483(1)	83(1)
O(103)	−2093(3)	6862(2)	3290(1)	87(1)
O(201)	3108(3)	9779(2)	5822(1)	81(1)
O(202)	8036(2)	8147(2)	5244(1)	73(1)
O(203)	5428(4)	6583(3)	6893(1)	93(1)
C(1)	2768(4)	9803(2)	3117(1)	55(1)
C(2)	3625(3)	8769(2)	3435(1)	45(1)
C(3)	2567(3)	8308(2)	3979(1)	39(1)
C(4)	2969(2)	7244(2)	4444(1)	37(1)
C(5)	4467(2)	6458(2)	4415(1)	36(1)
C(6)	4367(2)	5505(2)	4932(1)	37(1)
C(7)	2788(3)	5710(2)	5287(1)	42(1)
C(8)	1933(3)	6764(2)	4991(1)	42(1)
C(9)	1045(3)	9078(2)	3984(1)	46(1)
C(10)	1177(4)	9994(2)	3451(1)	57(1)
C(101)	337(3)	8631(3)	2116(1)	56(1)
C(102)	2196(3)	6793(2)	2667(1)	54(1)
C(103)	−832(3)	7374(3)	3159(1)	57(1)
C(201)	3660(3)	8827(2)	5683(1)	50(1)
C(202)	6627(3)	7848(2)	5324(1)	49(1)
C(203)	5029(4)	6872(3)	6330(1)	56(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

3.2. Synthetic studies

3.2.1. Metallation of 1

To a solution of 0.406 g (1 mmol) of **1** in 15–20 ml of THF at −60 to 65 °C was added 0.8 ml of 1.6 N BuLi in hexane with magnet stirring. After 0% of D in each position (α- and β) mixtures were prepared by weighting on analytical 0.5–1.0 h at −60 °C, the mixture was quenched by D_2O and the solution was slowly heated to room temperature. The mixture was poured into 5% HCl and the product extracted by CH_2Cl_2. After washing, drying and evaporation of solvent, the residue was chromatographed on a column with Al_2O_3 (elution with petroleum ether–benzene 2:1). More than 90% of **1** enriched by deuterium was isolated. In the mass spectra of this sample there is a set of molecular ions with m/z ratio 406 (d_0) and 407–410 that corresponds to 1–4 atoms of D per molecule. To determine a balance of known samples of isolated **1** and an internal standard – hexamethylbenzene (singlet at δ 2.23 ppm) – the proportion of hydrogen and deuterium in each position was determined from integral intensity in the ^1H NMR spectra.

3.2.2. 3-Bicymantrenylcarboxylic acid (3)

To a solution of **2** (from 1.01 g (2.5 mmol) of **1** and 1.8 ml of 1.6 N BuLi) was added an excess of crushed

Table 6
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **12a**

Atom	x	y	z	U_{eq}
Mn(1)	3588(1)	5264(1)	6813(1)	29(1)
Mn(2)	1705(1)	9509(1)	6632(1)	25(1)
Mn(3)	7313(1)	12040(1)	9245(1)	32(1)
O(101)	4952(5)	2948(3)	6229(2)	55(1)
O(102)	7196(4)	6855(4)	7572(3)	66(1)
O(103)	2863(5)	4842(3)	8722(2)	61(1)
O(201)	−2029(4)	8189(3)	5835(3)	56(1)
O(202)	2855(6)	9342(4)	4681(2)	74(1)
O(203)	981(5)	12027(3)	6820(3)	62(1)
O(301)	8560(5)	9704(4)	9112(3)	67(1)
O(302)	10453(6)	13643(4)	10588(4)	95(2)
O(303)	5203(5)	11721(4)	10854(3)	66(1)
C(1)	2436(6)	4918(4)	5336(3)	44(1)
C(2)	3217(6)	6225(3)	5716(3)	35(1)
C(3)	2313(4)	6715(3)	6531(3)	29(1)
C(4)	2640(4)	8047(3)	7096(2)	26(1)
C(5)	4139(4)	9041(3)	7082(2)	26(1)
C(6)	3990(4)	10175(3)	7752(2)	26(1)
C(7)	2344(5)	9885(3)	8183(2)	30(1)
C(8)	1539(5)	8586(3)	7778(2)	30(1)
C(9)	992(5)	5687(3)	6649(3)	36(1)
C(10)	1063(6)	4575(3)	5911(3)	45(1)
C(11)	5286(4)	11403(3)	8008(2)	30(1)
C(12)	7027(5)	11653(4)	7683(3)	36(1)
C(13)	7846(6)	12960(4)	8116(3)	44(1)
C(14)	6636(6)	13521(4)	8700(3)	44(1)
C(15)	5058(5)	12561(3)	8633(3)	36(1)
C(101)	4450(5)	3856(4)	6475(3)	37(1)
C(102)	5786(5)	6239(4)	7285(3)	41(1)
C(103)	3173(5)	5011(4)	7983(3)	38(1)
C(201)	−578(5)	8708(3)	6143(3)	37(1)
C(202)	2397(6)	9402(4)	5436(3)	42(1)
C(203)	1260(5)	11038(3)	6729(3)	36(1)
C(301)	8083(5)	10619(4)	9177(3)	43(1)
C(302)	9252(7)	13017(5)	10060(4)	57(1)
C(303)	6057(5)	11838(4)	10239(3)	39(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

dry ice. After 30 min the cooling was removed. The solution was allowed to warm to room temperature and then poured into a mixture of 30 ml benzene and 50 ml 2% aqueous solution of KOH or NaOH. The microcrystalline residue of potassium salt precipitated from the water layer if KOH was used. Sodium salt is more soluble. From the benzene layer 15–20% of starting **1** was isolated. From an alkaline solution after acidification with HCl free acid, **3** was collected as a bright-yellow precipitate. After washing with ice-water and drying, 0.35 g (approximately 35%) of acid **3** was obtained as a yellow powder, which above 250 °C decomposed without melting. Analytical and mass spectral data for **3** and other new compounds are given in Table 9.

3.2.3. 3-Bicymantrenylcarboxylic acid chloride (4)

0.49 g (1.1 mmol) of acid **3** was stirred with 0.27 g (1.3 mmol) of PCl_5 in 10 ml of dry benzene. After 6 h the solvents were evaporated in vacuo and the residue

recrystallised from ligroin (b.p. 90–100 °C). Yellow crystals of **4** were obtained (0.13 g, 25%). M.p. 116–120 °C.

3.2.4. 2-, 3-Bicymantrenylcarbaldehydes (5, 6)

To a solution of **2**, obtained from 4.06 g (10 mmol) of **1** and 4.7 ml of 2.2 N BuLi in 100 ml THF, was added 2 ml of DMFA (excess) −60 °C. After 1 h the cooling was removed and the mixture acidified with 20% H_3PO_4 and, after heating to room temperature, poured into water. After extraction with CH_2Cl_2 and drying and evaporation of the solvent, 4.10 g of residue was obtained which was chromatographed on silica (elution with petroleum ether–benzene mixtures). The following fractions were isolated: unreacted **1** (0.73 g, 17%), aldehyde **5** (0.14 g, 3%), aldehyde **6** (1.78 g, 50%). After recrystallisation from petroleum ether, yellow crystals with m.p. 94–95 °C (aldehyde **5**) and 137–138 °C (aldehyde **6**) were obtained. The mass spectra of **5** and **6**

Table 7
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **12b**

Atom	x	y	z	U_{eq}
Mn(1)	2848(1)	8347(1)	6126(1)	42(1)
Mn(2)	1995(1)	7653(1)	9606(1)	35(1)
Mn(3)	2004(1)	3954(1)	7485(1)	40(1)
O(101)	2313(6)	9551(3)	4570(2)	102(1)
O(102)	−1351(5)	7320(4)	5845(3)	100(1)
O(103)	3410(6)	6336(3)	4778(2)	93(1)
O(201)	6145(4)	8910(2)	10070(2)	67(1)
O(202)	1000(5)	9070(3)	11300(2)	89(1)
O(203)	2712(5)	5944(3)	10684(2)	79(1)
O(301)	2379(6)	1671(3)	6542(3)	119(2)
O(302)	2734(5)	3525(3)	9443(2)	89(1)
O(303)	−2221(4)	3009(3)	7204(2)	76(1)
C(1)	5780(5)	9007(3)	6949(3)	52(1)
C(2)	4797(5)	8113(3)	7316(2)	45(1)
C(3)	3200(4)	8432(2)	7666(2)	38(1)
C(4)	1736(4)	7796(2)	8105(2)	34(1)
C(5)	1356(4)	6604(2)	8124(2)	33(1)
C(6)	−298(4)	6371(3)	8560(2)	40(1)
C(7)	−906(5)	7384(3)	8814(2)	43(1)
C(8)	349(5)	8263(3)	8545(2)	41(1)
C(9)	3232(5)	9553(3)	7509(2)	46(1)
C(10)	4821(6)	9891(3)	7072(3)	54(1)
C(11)	2340(4)	5772(2)	7642(2)	34(1)
C(12)	4147(4)	5564(3)	8013(3)	40(1)
C(13)	4694(5)	4852(3)	7249(3)	52(1)
C(14)	3250(6)	4632(3)	6390(3)	54(1)
C(15)	1787(5)	5169(3)	6622(2)	43(1)
C(101)	2525(6)	9079(4)	5179(3)	63(1)
C(102)	297(6)	7726(4)	5937(3)	61(1)
C(103)	3179(6)	7123(4)	5292(3)	60(1)
C(201)	4531(5)	8417(3)	9902(2)	44(1)
C(202)	1450(5)	8527(3)	10657(3)	55(1)
C(203)	2457(5)	6615(3)	10266(2)	49(1)
C(301)	2231(6)	2557(3)	6918(3)	68(1)
C(302)	2409(5)	3695(3)	8682(3)	59(1)
C(303)	−591(5)	3393(3)	7310(3)	50(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

are identical (see Table 9). Aldehydes **5** and **6** give essentially different ^{1}H NMR spectra (Table 2). Three protons of the C_5H_3 ring give three separate multiplets in the low field in both cases (triplet for H(2) or H(4) and two doublet of doublets for the other two protons). In aldehyde **6** four protons of the C_5H_4 ring give two two-proton multiplets each of 10 lines (δ 5.03 and 4.81 ppm, α- and β-position). At the same time in the spectra of aldehyde **5** these four protons give three rather than two separate signals. Two β-protons give one two-proton multiplet of 10 lines at 4.82 ppm. Two α-protons, one of which is more close to the –CHO substituent than the other owing to diastereotopic unequivalence, give two separate resonances at 5.57 and 5.06 ppm ($\Delta\delta$ 0.5 ppm) which appear as one-proton multiplets each consisting of five lines.

3.2.5. Schiff bases (7, 8)

From 0.5 g of aldehydes **5** or **6** and 0.15 g (excess) of (–)-α-phenylethylamine in 5 ml of benzene after slight heating, 0.61 g of **7** or **8** was obtained (the yield is close to quantitative). Brown crystals with m.p. 81–94 °C for **7** (mixture of two diastereoisomers, from hexane); 109–110 °C for **8** (one diastereoisomer, from benzene).

3.2.6. 3-Bicymantrenylcarbinol (9)

A mixture of 1.39 g (3.2 mmol) of aldehyde **6** and 0.12 g (3 mmol) of $NaBH_4$ in 30 ml of ether was stirred for 1 h at 20 °C and then hydrolyzed. From the ether layer 1.27 g (91%) of carbinol **9** was obtained as light-yellow crystals, m.p. 73.5–75.5 °C (from toluene–hexane mixture).

3.2.7. 3-Bicymantrenyldiphenylphosphine (10)

To a solution of **2** (from 1.03 g (2.5 mmol) **1** and 1.2 ml 2.2 N BuLi in 30 ml of THF) was added around 0.5 ml (excess) of Ph_2PCl at -60 °C. The mixture was stirred for 0.5 h, then the cooling was removed and after heating to room temperature the mixture was hydrolyzed. The products were extracted with CH_2Cl_2. From the organic layer 1.49 g of solid residue was isolated. After chromatography on silica (elution with benzene–petroleum ether 1:3) two fractions were collected: nonreacted **1** (0.24 g, 23%) and phosphine **10** (0.54 g, 36%). Yellow crystals, m.p. 162–165 °C (after recrystallisation from benzene–petroleum ether mixture). In the ^{31}P NMR spectra one singlet at -19.75 ppm (from 85% H_3PO_4) was found.

Table 8
Details of the crystal data and data collection and structure refinement parameters for **11a**, **12a** and **12b**

Compound	11a	12a	12b
Formula	$C_{32}H_{14}Mn_4O_{12}$	$C_{24}H_{11}Mn_3O_9$	$C_{24}H_{11}Mn_3O_9$
Formula weight	810.19	608.15	608.15
Temperature (K)	293(2)	193(2)	293(2)
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	7.642(2)	7.641(3)	7.179(1)
b (Å)	10.695(3)	11.206(3)	12.298(3)
c (Å)	19.022(6)	14.264(5)	14.246(3)
α (°)	—	104.68(3)	102.32(3)
β (°)	92.57(3)	93.33(3)	98.99(3)
γ (°)	—	102.02(3)	102.54(3)
V (Å^3)	1553.1(8)	1147.6(6)	1172.1(4)
Z	2	2	2
d_{calc} (g cm^{-3})	1.733	1.760	1.723
μ(Mo K) (cm^{-1})	16.54	16.79	16.44
$F(000)$	804	604	604
Diffractometer	Siemens P3/PC	Syntex P2$_1$	CAD4
Scan type	θ–2θ	θ–2θ	θ–5/3θ
θ_{max} (°)	30.07	30.05	24.96
Reflections collected	4856	7195	4459
Independent reflections	4547	6722	4099
R_{int}	0.0175	0.0457	0.0213
Observed reflections ($I > 2\sigma(I)$)	3610	4825	2981
No. of parameters	245	369	369
Goodness-of-fit	1.047	1.034	1.010
R_1 (for observed reflections)	0.0367	0.0591	0.0313
wR_2 (all data)	0.0947	0.1604	0.0937
Weighting scheme: $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = (F_o^2 + 2F_c^2)/3$			
a	0.0499	0.0973	0.0608
b	0.5109	0.4104	0.0674

Table 9
Analytical and mass spectral data

Compound	Anal. Found (Calc.)				Molecular formula	M^+	Mass spectral data, others
	C	H	others				
3	46.30 (45.33)	1.83 (1.79)			$C_{17}H_8Mn_2O_8$		—
4	44.07 (43.54)	1.74 (1.79)	(Cl)	7.33 (7.58)	$C_{17}H_7ClMn_2O_7$	468 470	433 (M − Cl); 384/386 (M − 3CO); 300/302 (M − 6CO) 349 (M − 3CO − Cl)
5	47.26 (47.00)	1.76 (1.84)			$C_{17}H_8Mn_2O_7$	434	350/266/238 (M − nCO), n = 3, 6, 7 211/156 (M − 6CO − nMn), n = 1, 2
6	46.99 (47.00)	1.79 (1.84)			$C_{17}H_8Mn_2O_7$	434	350/266/238 (M − nCO), n = 3, 6, 7 211/156 (M − 6CO − nMn), n = 1, 2
7	55.74 (55.87)	3.14 (3.17)	(N)	2.44 (2.61)	$C_{25}H_{17}NMn_2O_6$	537	453/369 (M − nCO), n = 3, 6 314/259 (M − 6CO − nMn), n = 1, 2
8	55.94 (55.87)	3.18 (3.17)	(N)	2.58 (2.61)	$C_{25}H_{17}NMn_2O_6$	537	453/369 (M − nCO), n = 3, 6 314/369 (M − 6CO − nMn), n = 1, 2
9	47.05 (46.79)	2.20 (2.29)			$C_{17}H_{10}Mn_2O_7$	436	434 (M − 2H); 352/268 (M − nCO), n = 3, 6 213 (M − 6CO − Mn); 196 (M − 6CO − Mn − OH) 141 (M − 6CO − 2Mn − OH)
10	57.16 (56.94)	2.82 (2.88)	(P)	5.26 (5.25)	$C_{28}H_{17}Mn_2O_6P$	590	506/422 (M − nCO), n = 3, 6
11a	47.56 (47.41)	1.73 (1.73)			$C_{32}H_{14}Mn_4O_{12}$	810	726/614/558/530/474 (M − nCO), n = 3, 7, 9, 10, 12 419/364/309/254 (M − 12CO − nMn), n = 1–4
12a	47.62 (47.37)	1.80 (1.81)			$C_{24}H_{11}Mn_3O_9$	608	524/440/412/356 (M − nCO), n = 3, 6, 7, 9 301/246/191 (M − 9CO − nMn), n = 1–3
12b	47.55 (47.37)	1.71 (1.81)			$C_{24}H_{11}Mn_3O_9$	608	524/440/412/356 (M − nCO), n = 3, 6, 7, 9 301/246/191 (M − 9CO − nMn), n = 1–3

3.2.8. Tetracymantrenyl (11a)

To a solution of **2** obtained from 2.04 g (5 mmol) **1** and 2.5 ml 2.2 N BuLi in 40 ml THF) was added 2.6 g (19 mmol) of anhydrous $CuCl_2$ at $-60\,°C$. The mixture was stirred for 3 h and then the cooling was removed. After hydrolysis by 5% HCl, extraction with CH_2Cl_2, drying and evaporation of the solvent, the solid residue was chromatographed on alumina (elution with benzene–petroleum ether mixture). The following fractions were collected: unreacted **1** (0.30 g, 15%), a mixture of **1** with some **11a**, complex **11a** (0.57 g, 29%), another isomer (or isomers) of **1** mixed with unidentified products (0.15 g). Crude complex **11a**: yellow crystals with m.p. 211–218 °C (from toluene–ligroin mixture). According to ^1H NMR data this fraction contains approximately 95% **11a** and 3–5% of another isomer (probably **11b**). The analytical sample of **11a** after three recrystallisations had m.p. 217–219 °C.

3.2.9. Tricymantrenyls (12a and 12b)

To a mixture of 2.03 g (5 mmol) and 3.06 g (15 mmol) of cymantrene in 80 ml of THF was added dropwise 9.4 ml of 2.2 N BuLi at $-60\,°C$. After 40 min 10.1 g (75 mmol) of anhydrous $CuCl_2$ was added and the mixture was stirred for 3 h at $-60\,°C$, then the cooling was removed. After heating to room temperature the mixture was hydrolyzed with 5% HCl and the products were extracted with CH_2Cl_2. A solid residue after drying and evaporation of the solvent was chromatographed on alumina. The following fractions were collected: excess of cymantrene (0.52 g), **1** (1.35 g), complex **12b** (0.09 g, 3%), a mixture of **12b** and **12a** (0.20 g), complex **12a** (0.77 g, 25%). Complexes **12a** and **12b**: yellow crystals with m.p. 136–142 °C and 156–158 °C respectively (after recrystallisation from toluene–heptane mixture 1:3). The mass spectra of **12a** and **12b** are identical (see Table 9).

4. Supplementary material

Tables of hydrogen atom coordinates and thermal parameters, a complete list of bond lengths and angles and observed and calculated structure factors for crystal structures of **11a**, **12a** and **12b** can be obtained from the authors upon request.

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