Reaction of dicymantrenylketone with mesitylmagnesium bromide

N. M. Loim,* A. G. Ginzburg, A. S. Batsanov, Yu. T. Struchkov, M. V. Galakhov, and E. V. Vorontzov

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 117813 Moscow, Russian Federation.

Fax: +7 (095) 135 5085

The reaction of dicymantrenyl ketone with the Grignard reagent 2,4,6-Me₃C₆H₂MgBr in THF occurs as the insertion of the mesityl substituent in the α -position of one of the cyclopentadienyl rings to give (2-mesitylcymantrenyl) cymantrenyl ketone (4), rather than as addition at the C=O group. Reduction of 4 by NaBH₄ in a THF-EtOH mixture affords (2-mesitylcymantrenyl)cymantrenylmethanol (5). Ionic hydrogenation of 5 with the HSiEt₃/CF₃COOH system gives (2-mesitylcymantrenyl)cymantrenylmethane (7). The structure of alcohol 5 has been established by X-ray diffraction analysis.

Key words: η -complexes, cyclopentadienyl manganese, manganese carbonyls, ketones, Grignard reagents, planar chirality, X-ray diffraction analysis.

To continue the study of the properties of diastereotopic CH groups in the Cp rings of achiral dicymantrenylcarbinols,^{1,2} we undertook an attempt to synthesize mesityldicymantrenylcarbinol (1)



For this purpose we used three different approaches, which normally result in the formation of tertiary dicymantrenylcarbinols: the reaction of cymantrenyllithium with mesitylcymantrenylketone, the reaction of MesC(O)Cl (Mes is mesityl) with cymantrenyllithium at the 1:2 ratio, and treatment of dicymantrenylketone (2) with the Grignard reagent MesMgBr. However, none of these methods afforded alcohol 1. In the first-named approach the reaction did not occur, and the starting compounds were recovered unchanged. In the second-named method a complex mixture of products was formed in which only the starting ketone 2 could be identified. The reaction of ketone 2 with the Grignard reagent MesMgBr occured more selectively. Along with the starting ketone, dicymantrenylcarbinol (3), a new carbonyl compound of the cymantrene series having a somewhat higher $R_{\rm f}$ than the starting ketone 2 was isolated from the reaction mixture. Based on the combined spectroscopic data, the structure of (2-mesitylcymantrenyl)-cymantrenylketone (4) was ascribed to the latter product. The structure of 4

was confirmed by a number of transformations and by an X-ray structural study of the product of the reduction of compound 4, *i.e.*, (2-mesitylcymantrenyl)cymantrenylcarbinol (5) (see below).

Thus, the reaction of sterically hindered Grignard reagent, MesMgBr, with dicymantrenylketone occurs as arylation of the Cp ring, rather than the expected addition at the carbonyl group. Previously this reaction route was observed in the interaction of sterically hindered diarylketones with arylmagnesium halides.³⁻⁵ Unfortunately there is no information in the literature on the mechanism of this type of reaction. However, the highly regioselective insertion of the Cp ring of ketone 2 and the formation of nearly equimolar amounts of alcohol 3 and ketone 4 make it possible to propose the following scheme of this reaction (Scheme 1).

The coordination of the Grignard reagent by the oxygen atom of the C=O group apparently results in the initial formation of complex **A**, which is converted into intermediate **B**, a Mesenheimer type complex, as a result of the intramoleculatr migration of mesityl to the nearest α -position of the Cp ring. Complex **B** acts as the source of the hydride-type hydrogen necessary to reduce some of ketone **2** to alcohol **3**.

Since one of the Cp rings in the molecule of ketone 4 contains two different substituents, this compound is planar-chiral. Therefore, the H atoms of the monosubstituted Cp ring are diastereotopic and the ¹H NMR spectrum of ketone 4 in toluene exhibits 7 separate signals for the 7 H atoms of both Cp rings (Table 1).

Reduction of ketone 4 with sodium hydroborate in a THF-EtOH mixture affords a mixture of two diastere-



Scheme 1

omers of (2-mesitylcymantrenyl)cymantrenylcarbinol (5). The reduction is accompanied by substantial asymmetric induction: the ratio of alcohols 5a and 5b is ~10:1, according to the ¹H NMR spectrum (see Scheme 1).

The stereochemistry of the prevailing isomer 5a and the location of the mesityl substituent in the disubstituted Cp ring of alcohol 5 and, thus, of ketone 4 were established by the X-ray structural investigation of a single crystal of 5a (Fig. 1, Tables 2 and 3).

The Mn(1) atom in molecule **5a** is located at a distance of 1.777 Å from the plane of Cp ring **D**, and the Mn(2) atom is 1.783 Å away from the plane of ring **E**. The dihedral angles between rings **D** and **E** and the plane of the C(8)C(7)C(13) bridging fragment (plane C) are 75.0 and 80.8°, respectively, and these rings are turned in such a way that the Mn(1) and Mn(2) atoms are located on different sides of this plane at distances of 0.45 and 0.16 Å, respectively. The mesityl radical occu-

pies the α -position of Cp ring **E** and the plane of its benzene ring is nearly perpendicular to the plane of ring **E**: the dihedral angle between them is 81.4°.

Notice that the molecules of methyl-, trifluoromethyl-, and phenyldicymantrenylcarbinols (having no substituents in the Cp rings), whose structures we studied previously, have an essentially different conformation: one of the Cp rings (ring **D**) is slightly tilted with respect to plane **C**, and the other ring (**E**) is nearly perpendicular to it.²

Molecules connected by a symmetry center (0 1/2 1/2 for the basis molecule) in a crystal of **5a** are united in a dimer by a pair of rather weak⁶ $O(7)-H(O) \cdot \cdot \cdot O(1')$ hydrogen bonds between the hydroxyl and CO groups: the O(7)-O(1) distance is 2.963(5), O(7)-H(O) is 1.02, and H(O)...O(1') is 2.35 (Å), the C(7)O(7)H(O) angle is 104°, O(7)H(O)O(1)is 118°. No $OH \cdot \cdot \cdot Mn$ agostic interactions are ob-

Compound	Solvent	δ, from TMS							
		Cyclopentadienyl	Mes					Other	
	(<i>T</i> /°C)			CH ₃		m-	<i>m</i> '-		
Ketone 4	Toluene-d ₈	5.11, 5.01, 4.87, 4.41, 4.20, 4.06, 3.94	2.82	2.26	2.17	6.92	6.88		
	CDCl ₃	5.36(2H), 5.28, 4.99, 4.84, 4.79, 4.71	2.55	2.24	2.04	6.91	6.83		
	CD ₃ CN	5.59(2H), 5.47, 5.20, 5.10, 4.93(2H)	2.56	2.25	2.16	6.95	6.86		
Alcohol 5	Toluene-d ₈	4.62, 4.50, 4.25, 4.18 - 4.10 (m), 4.05	2.90	2.32	1.94	6.93	6.89	4.87 d (C—H)	1.92 d (O-H) J = 4.4 Hz
	CDCl ₃	4.85, 4.72(2H), 4.64 4.57, 4.45	2.66	2.28	1.94	6.96	6.88	4.88 d (CH)	1.91 d (O-H) J = 4.3 Hz
	(CD ₃) ₂ CO		2.78	2.32	1.94	7.13	7.05	. ,	
Carbenium ion 6	CF ₃ COOD	6.46, 6.39, 6.08, 5.80, 5.73, 5.64, 5.51	2.65	2.48	2.47	7.27	7.23	7.31 (⁺ C–	H)
Dicyman- trenyl-	CDCl ₃ (25)	4.72, 4.65, 4.59(2H), 4.51, 4.44, 3.83	2.57	2.26	1.86	6.98	6.89	2.92, 2.84	$(CH_2(AB-system))$ J = 15.1 Hz
methane 7	Toluene-d ₈ (25)	4.80, 4.25(3H), 4.09(2H), 3.62	2.83	2.31	1.93	6.90(2	2H)	3.01, 2.95	$(CH_2(AB-system))$ J = 15.0 Hz
	Toluene-d ₈ (60)	4.25(3H), 4.12, 4.06, 3.98, 3.68	2.72	2.21	1.87	6.85	6.83	2.94 s (2H)

Table 1. ¹H NMR spectra for compounds 4-7

served (the non-bonding $Mn(1) \cdots H(O)$ distance is 3.32 Å).

It can be seen from the molecular structure of 5a that the hydroxyl and mesityl groups in the conformation presented in Fig. 1 are located on the same side of the plane passing through the C(8)C(7)C(13) atoms. Therefore, when ketone 4 is reduced with sodium hydroborate, an (*R*)- or (*S*)-configuration of the chiral plane of the disubstituted Cp ring induces predominant formation of alcohol 5 having an (*R*)- or (*S*)-configuration of the chiral center.

Ionic hydrogenation of compound 5 with the CF₃COOH/HSiEt₃ system affords (2-mesitylcyman-



Fig. 1. The molecular structure of alcohol 5a. The numbering of atoms corresponds to that accepted in Ref. 2.

trenyl)cymantrenylmethane (7) via the intermediate carbenium ion (6), which proved to be sufficiently stable in solution and is quantitatively generated when alcohol 5 is dissolved in CF₃COOH or in mixtures of it with CH₂Cl₂ (see Table 1):



It should be noted that an attempt to prepare compound 7 by ionic hydrogenation of ketone 4 turned out to be unsuccessful, though under the conditions of ionic hydrogenation the carbonyl group in sterically unhindered cymantrenylketones is reduced to give CH_2 . This is apparently caused by steric factors, since the mesityl substituent in ketone 4 prevents triethylsilane, which is more bulky than the BH_4^- anion, from approaching the carbonyl group.

The parameters of the ¹H NMR spectra of cymantrene derivatives 4, 5, and 7 prepared for the first time and containing mesityl in the α -position of one of the Cp rings, are listed in Table 1. These data indicate that the

Bond	d/Å	Bond	d/Å	Bond	d/Å
$\overline{Mn(1)}-C(1)$	1.776(4)	Mn(2)-C(17)	2.204(4)		1.417(5)
Mn(1) - C(2)	1.775(4)	O(1) - C(1)	1.152(6)	C(13) - C(17)	1.429(4)
Mn(1) - C(3)	1.784(5)	O(2) - C(2)	1.155(5)	C(14) - C(15)	1.430(5)
Mn(1) - C(8)	2.147(4)	O(3) - C(3)	1.149(7)	C(15) - C(16)	1.408(5)
Mn(1) - C(9)	2.134(4)	O(4) - C(4)	1.147(5)	C(16) - C(17)	1.434(5)
Mn(1) - C(10)	2.136(3)	O(5) - C(5)	1.145(7)	C(17) - C(21)	1.492(5)
Mn(1) - C(11)	2.142(3)	O(6)-C(6)	1.145(5)	C(21) - C(22)	1.404(4)
Mn(1) - C(12)	2.148(3)	O(7) - C(7)	1.405(4)	C(21) - C(26)	1.413(5)
Mn(2) - C(4)	1.793(4)	C(7) - C(8)	1.513(6)	C(22) - C(23)	1.402(6)
Mn(2) - C(5)	1.783(6)	C(7) - C(13)	1.511(5)	C(22) - C(27)	1.506(6)
Mn(2) - C(6)	1.796(4)	C(8) - C(9)	1.421(4)	C(23) - C(24)	1.383(6)
Mn(2) - C(13)	2.161(4)	C(8) - C(12)	1.419(5)	C(24) - C(25)	1.382(5)
Mn(2) - C(14)	2.126(4)	C(9) - C(10)	1.403(6)	C(24) - C(28)	1.511(7)
Mn(2) - C(15)	2.137(3)	C(10) - C(11)	1.414(5)	C(25) - C(26)	1.387(5)
Mn(2) - C(16)	2.151(3)	C(11) - C(12)	1.417(6)	C(26) - C(29)	1.510(4)

Table 2. Bond lengths (Å) in alcohol 5a

Table 3. Bond angles (ω /degrees) in alcohol 5a

Angle	ω	Angle	ω	Angle	ω
$\overline{C(1)-Mn(1)-C(2)}$	91.9(2)	$-\frac{1}{C(7)-C(8)-C(9)}$	126.2(3)	C(16)-C(17)-C(21)	123.8(3)
C(1) - Mn(1) - C(3)	92.0(2)	C(7) - C(8) - C(12)	126.6(3)	C(17) - C(21) - C(22)	126.8(3)
C(2) - Mn(1) - C(3)	91.2(2)	C(9) - C(8) - C(12)	126.6(3)	C(17) - C(21) - C(26)	114.3(4)
C(4) - Mn(2) - C(5)	91.2(2)	C(8) - C(9) - C(10)	108.5(3)	C(22) - C(21) - C(26)	118.9(3)
C(4) - Mn(2) - C(6)	90.2(2)	C(9) - C(10) - C(11)	108.4(3)	C(21) - C(22) - C(23)	118.5(3)
C(5) - Mn(2) - C(6)	91.9(2)	C(10) - C(11) - C(12)	107.6(4)	C(21)-C(22)-C(27)	123.0(2)
Mn(1) - C(1) - O(1)	178.2(5)	C(8) - C(12) - C(11)	108.4(3)	C(23) - C(22) - C(27)	118.5(3)
Mn(1) - C(2) - O(2)	179.3(5)	C(7) - C(13) - C(14)	123.3(3)	C(22) - C(23) - C(24)	123.2(3)
Mn(1) - C(3) - O(3)	177.9(3)	C(7) - C(13) - C(17)	127.6(3)	C(23) - C(24) - C(25)	117.3(3)
Mn(2) - C(4) - O(4)	178.2(5)	C(14) - C(13) - C(17)	108.8(3)	C(23) - C(24) - C(28)	121.2(3)
Mn(2) - C(5) - O(5)	176.5(4)	C(13) - C(14) - C(15)	108.0(3)	C(25) - C(24) - C(28)	121.4(3)
Mn(2) - C(6) - O(6)	179.2(3)	C(14) - C(15) - C(16)	107.4(3)	C(24) - C(25) - C(26)	122.1(3)
O(7) - C(7) - C(8)	110.9(4)	C(15) - C(16) - C(17)	109.6(3)	C(21) - C(26) - C(25)	120.0(3)
O(7) - C(7) - C(13)	109.8(3)	C(13) - C(17) - C(16)	106.1(3)	C(21) - C(26) - C(29)	121.8(3)
C(8) - C(7) - C(13)	109.5(2)	C(13) - C(17) - C(21)	127.0(3)	C(25)-C(26)-C(29)	118.2(3)

o-methyl groups of the mesityl substituent are exhibited as two separate singlets in all cases; the chemical shifts of the two *meta*-protons of the benzene ring are also different. This spectral pattern apparently occurs when the rotation of mesityl about the C—C bond with the Cp ring is slow in the NMR time scale or when there is no rotation at all. Consequently, chemically identical groups of the mesityl substituent in the molecules of chiral compounds **4**—7 become spatially nonequivalent (diastereotopic) and manifest themselves as separate signals in the spectrum. In the case of free rotation of mesityl, the o-methyl groups and m-protons of the benzene ring would be equivalent due to the fast exchange and would have identical chemical shifts.

To determine the energetic parameters of the internal rotation of the mesityl group in molecules 4, 5, and 7, we studied the temperature dependence of the ¹H NMR spectra of these compounds in the region of the signals for *m*-protons. For solutions of neutral compounds 4, 5, and 7 in toluene-d₈ the temperature interval studied was 183 °C (190-373 K), while for carbenium ion 6 (a solution of compound 5 in CF₃COOD) the temperature range that can be experimentally achieved is no more than 50 °C (270–320 K). Varying the temperature has a substantial effect on the difference between the chemical shifts of the mesityl *m*-protons and the width and position of the resonance signals. However, coalescence of these signals associated with the beginning of free rotation of mesityl about the C–C bond with the Cp ring was only observed in the case of ketone **4** (Fig. 2). Analysis of the line profiles in a toluene-d₈ solution gave the activation energy of the rotation around this bond (ΔG^{\pm}) equal to 16.3±1 kcal mol⁻¹. A similar temperature dependence with the coalescence of the signals was observed in MeCN (ΔG^{\pm} 18.8±1 kcal mol⁻¹).

For compounds 5 and 7 the signals for nonequivalent m-protons also coalesce, as the temperature changes (Fig. 3, a, b), however, no broadening of the signals is observed, and as the temperature is further increased, two resonance lines can again be recorded. It is obvious that this type of temperature dependence of the spectral patterns results from different effects of the temperature on the chemical shifts of the two mesityl m-protons in compounds 5 and 7. These protons remain nonequivalent over the whole temperature range studied, nevertheless,



Fig. 2. Temperature dependence of the signals for *m*- and *m'*-protons of the mesityl substituent in the ¹H NMR spectrum of ketone **4** in toluene-d₈: 193 K (1); 253 K (2); 351 K (3); 363 K (4).

at -20 °C their chemical shifts are identical. Thus, the change of the molecular structure on going from the substituted dicymantrenylketone 4 to dicymantrenylcarbinol 5 and dicymantrenylmethane 7 results in an increase in the steric hindrance to free rotation of mesityl bound with the Cp ring.

Unfortunately, the narrow temperature interval accessible to measurements in the case of carbenium ion $\mathbf{6}$ makes it possible to record only small changes in the spectral pattern. Nevertheless, the tendency of these change (slight broadening and convergence of the signals as the temperature increases) allows one to suggest that the barriers to mesityl rotation in cation $\mathbf{6}$ and ketone $\mathbf{4}$, which possess similar geometry of the fragment connecting two cymantrenyl radicals, have similar magnitudes.

Experimental

¹H NMR spectra were recorded on a Bruker WP-200-SY spectrometer operating at 200 MHz. The temperature of the sample was maintained with an accuracy of 0.5°. The forms of



Fig. 3. Temperature dependence of the signals for m- and m'-protons of the mesityl substituent in the ¹H NMR spectrum (recorded in toluene-d₈): a, alcohol 5 240 K (1); 270 K (2); 300 K (3); 350 K (4), 370 K (5); b, (2-mesitylcymantrenyl) cymantrenylmethane 7: 233 K (1), 303 K (2); 333 K (3); 373 K (4).

the lines of the ¹H NMR signals that undergo position exchange were calculated with an IBM PC AT using the NMR-5 program, in order to determine the life time (τ) of the magnetically nonequivalent states of the compounds under study. The accuracy of the determination of τ was \pm 5%. The rate constant of conformational transitions was postulated to be equal to $1/\tau$ as for normal monomolecular processes.

(2-Mesitylcymantrenyl)cymantrenylketone (4). 1 mL (6.5 mmol) of mesityl bromide in 10 mL of abs. THF was added to 0.15 g (6.25 mmol) of magnesium activated with iodine in 15 mL of THF. The mixture was heated with stirring until the magnesium entirely dissolved (1.5 h). A solution of 2.1 g (4.84 mmol) of ketone 2 in 10 mL of abs. THF was added dropwise to the resulting Grignard reagent cooled to -10 °C. The dark-red reaction mixture was boiled with stirring for 1.5 h, cooled, and treated with 20 % aqueous H₃PO₄. The reaction products were extracted with ether, washed with water, and dried with Na2SO4-MgSO4. After removal of ether, the residue was chromatographed on a column with SiO₂ (porous quartz, 50–150 μ , benzene). The second and the fourth fractions with R_r of 0.8 and 0.4 were collected, and they were ketone 4 (0.8 g) and alcohol 3 (0.6 g), respectively. Recrystallization of compound 4 from a hexane-benzene (5:1) mixture afforded gold-colored crystals, m.p. 179 °C. Found (%): C, 56.61; H, 3.28; Mn, 19.21. C₂₆H₁₈Mn₂O₇.

Calculated (%): C, 56.65; H, 3.28; Mn, 19.89. MS: 522 [M]⁺, 468 [M-3CO], 384 [M-6CO]. IR: 1650 cm⁻¹ (C=O, hexane).

(2-Mesitylcymantrenyl)cymantrenylcarbinol (5). 0.4 g of NaBH₄ was added in small portions to a stirred water-cooled solution of 0.7 g (1.3 mmol) of compound 4 in a mixture of 20 mL of THF and 20 mL of abs. EtOH. After 2 h the mixture was quenched with a 20 % aqueous solution of H₃PO₄ and the products were extracted with ether. After workup and removal of ether the residue was recrystallized from a hexane—benzene (5:1) mixture to give 0.55 g (78 %) of compound 5, m.p. 153—154 °C. Found (%): C, 56.09; H, 3.87; Mn, 19.60. $C_{26}H_{20}Mn_2O_7$. Calculated (%): C, 56.33; H, 3.64; Mn, 19.82.

(2-Mesitylcymantrenyl)cymantrenylmethane (7). 8 mL of CF₂COOH was added to a cooled and stirred solution of 0.27 g (6.5 mmol) of compound 5 in 2 mL of dry CH₂Cl₂. 0.3 mL (1.2 mmol) of triethylsilane was introduced into the resulting dark crimson-colored solution of cation 6, and the reaction mixture was heated at 30-40 °C for 30 min until the color disappeared. As this took place, pale-yellow compound 7 gradually precipitated from the solution. The reaction mixture was diluted with 50 mL of water and extracted with CHCl₂. The combined extracts were washed with water, dried with Na₂SO₄-MgSO₄, and concentrated. The residue was boiled with hexane. Cooling afforded 0.21 g (82 %) of compound 7, m.p. 154 °C. Found (%): C, 57.81; H, 3.66; Mn, 20.31. $C_{26}H_{20}Mn_2O_7$. Calculated (%): C, 58.01; H, 3.74; Mn, 20.41. MŠ: ²⁰538² ⁽[M]⁺, 454 [M-3CO], 370 [M-6CO], 315 [M-6CO-Mn] etc.

The X-ray structural study was carried out on a Siemens P3/PC four-circle automatic diffractometer (~20 °C, Mo-K α radiation, graphite monochromator) and calculations were carried out with PC using SHELXTL PLUS programs. The crystals are triclinic, a = 10.371(2), b = 11.168(2), c = 12.120(2) Å, $\alpha = 77.58(1)^\circ$, $\beta = 71.61(1)^\circ$, $\gamma = 67.05(1)^\circ$, V = 1219.8(3) Å³, space group P1, Z=2, C₂₆H₂₀Mn₂O₇,

 $\rho 1.52 \text{ g cm}^{-3}$. Intensities of 3303 independent reflections with $I > 2\sigma$ were measured by $\theta/2\theta$ -scanning ($2 \le \theta \le 50^\circ$). The structure was solved by the heavy atom method. All of the nonhydrogen atoms were taken into account by the least-squares method in the anisotropic approximation with due regard for the fixed contributions of hydrogen atoms (the position of the H(O) atom was determined by differential synthesis, the positions of other atoms were calculated) to R = 0.037 ($R_w = 0.048$). The atomic coordinates were deposited in the Cambridge Crystallographic Data Centre.*

* Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lengsfield Road, Cambridge CB2 1EW, England.

References

- N. M. Loim, A. G. Ginzburg, and M. V. Galakhov, Metalloorg. Khim., 1991, 4, 969 [Organomet. Chem. USSR, 1991, 4 (Engl. Transl.)].
- A. S. Batsanov, T. V. Timofeeva, M. Kh. Dzhafarov, Yu. T. Struchkov, N. M. Loim, A. G. Ginzburg, and M. V. Galakhov, *Metalloorg. Khim.*, 1991, 4, 976 [Organomet. Chem. USSR, 1991, 4 (Engl. Transl.)].
- Metody elementoorganicheskoi khimii. Magnii, berillii, kal'tsii, strontsii, barii. [Methods of Organometallic Chemistry. Magnesium, Berillium, Calcium, Strontium, Barium.], AN SSSR Publ., Moscow, 1963, 153–158 (in Russian).
- R. C. Fuson, M. D. Armstrong, and S. B. Speck, J. Org. Chem., 1942, 7, 297.
- 5. R. C. Fuson, Adv. Organometal. Chem., Acad. Press, New-York, London, 1964, 1, 221.
- L. N. Kuleshova and P. M. Zorky, *Acta Crystallogr.*, 1981, B37, 1363.

Received April 6, 1993; in revised form December 28, 1993