Chemistry of bicymantrenyl 6.* Synthesis and properties of quatercymantrenyls with phosphine ligands

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Oxidative coupling of lithium derivatives of the $(CO)_2PPh_3MnC_5H_4-C_5H_4Mn(CO)_3$ complex with CuCl₂ results in the formation of four isomeric quatercymantrenyls containing two phosphine ligands. The compounds isolated were characterized by the ¹H and ³¹P NMR spectra.

Key words: bicymantrenyl, butyllithium, metallation, oxidative coupling, quatercymantrenyl.

In continuation of our study of the chemistry of bicymantrenyl,¹⁻⁵ we have synthesized the first representatives of a new homological series of polycymantrenyls containing three or more cymantrenyl fragments.⁴

Considering only the complexes in which the polycymantrenyl chain contains two "external" $(CO)_3MnC_5H_4$ fragments and "internal" $(CO)_3MnC_5H_3$ fragments (one or more), two types of polycymantrenyls can be distinguished:

1) compounds with a "pseudo-linear" type of linkage in which all C—C bonds linking the rings are separated by one CH fragment and arranged at the β -positions to each other;

2) compounds in which two cyclopentadienyl substituents are at the α -position in at least one internal ring.

The simplest complexes of the first type are compounds 1 (n = 3) and 2 (n = 4), where n is the total number of Cp rings). All complexes of this type have one symmetry element. When n is odd, this element is a plane that crosses the carbon atom of the internal C₅H₃ ring and the middle of the opposite bond. When n is even, this element is a symmetry center coinciding with the middle of the bond linking the central rings. The simplest complex of the second type is compound 3 (n = 3) that also has a symmetry plane (Scheme 1). Compounds 1-3 were characterized by X-ray diffraction analysis,⁶ and their Mn(CO)₃ fragments are directed alternately in opposite directions from the plane of the Cp rings. Compounds 1 and 3 are achiral, but when any substituent, including cyclopentadienyl, is introduced into one of the external or internal cycles, the complexes formed would be planar-chiral. Complex 2 and its analogs with even n can have isomers with different types of combination of the rings (see below).

Scheme 1



Note. The $Mn(CO)_3$ fragments denoted as solid and dashed circles are directed alternately in opposite directions from the plane of the Cp rings.

In complexes 1–3, four CH groups in each of the external rings are diastereotopic, and the corresponding four protons form the ABCD system and appear as four individual signals in the ¹H NMR spectrum. Two external $C_{5}H_{4}$ rings are equivalent due to symmetry. Therefore, eight protons of two external rings are equivalent in pairs and form four individual multiplets, the intensity of each of them being 2 H. By contrast, when the external $C_{5}H_{4}$ rings are nonequivalent (if symmetry elements are absent), in the general case, all eight protons should give individual signals.

We have recently reported on some substitution reactions in the Cp rings of the monophosphine $(CO)_2PPh_3MnC_5H_4-C_5H_4Mn(CO)_3$ complex (4).¹ Unlike bicymantrenyl, complex 4 is metallated selectively by butyllithium only to two positions of the $C_5H_4Mn(CO)_3$ ring. The existence of the donating phosphine ligand results in the situation that the cyclopenta-

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Note. The $Mn(CO)_3$ and $Mn(CO)_2PPh_3$ fragments denoted as solid and dashed circles are directed in opposite directions from the plane of the Cp rings.

dienyl ring coordinated with the $Mn(CO)_2PPh_3$ fragment is not metallated under these conditions (THF, -60 °C).

For the purpose of synthesizing phosphine derivatives of quatercymantrenyl, complex 4 was metallated followed by the oxidative coupling of lithium derivatives with CuCl₂. The reaction products were chromatographed on an alumina column. Four isomeric complexes 5-8were isolated (Scheme 2). Their structure were established from the ¹H and ³¹P NMR spectra.

The compounds obtained differ sharply in the number of the signals in the ${}^{1}H$ NMR spectra and can be

divided into two groups. In complexes 5 and 6, eight protons of two external $C_5H_4Mn(CO)_2PPh_3$ fragments are equivalent in pairs and form four individual multiplets in the spectrum. Six protons of two internal $C_5H_3Mn(CO)_3$ rings form the ABC system and appear as three individual signals with the characteristic multiplicity. Thus, due to the paired equivalence, 14 protons of two $C_5H_4C_5H_3$ fragments form seven individual multiplets (Table 1), as for compounds 1-3 described previously.

By contrast, in the ${}^{1}H$ NMR spectra of compounds 7 and 8, all 14 protons of four Cp rings are nonequivalent

Com- pound	Protons of C_5H_3 rings		Protons of C ₅ H ₄ rings		Total number
	β-β-Type substitution	α-β- Type substitution	α-position	β-position	of signals
5	5.11 (t, 2 H, $J = 1.8$), 4.94 and 4.78 (both dd, J = 1.8 and 2.8)		4.53 (m, 2 H), 4.47 (m, 2 H)	4.15 (m, 2 H), 4.02 (m, 2 H)	7
6	5.21 (t, 2 H, $J = 1.7$). 4.91 and 4.80 (both dd. J = 1.9 and 2.9)	2×2 H.	4.62 (m, 2 H). 4.51 (m, 2 H)	4.20 (m, 2 H), 4.06 (m, 2 H)	7
7	5.25 (t. 1 H, $J = 1.7$), 5.03 and 4.76 (both dd, 2×1 H, J = 1.8 and 2.8)	5.11 and 4.96 (both dd, 2×1 H, <i>J</i> = 1.8 and 2.8), 4.58 (t, 1 H, <i>J</i> = 2.9)	4.87 (m, 1 H), 4.81 (m, 1 H), 4.66 (m, 2 H)*	4.12 (m, 1 H), 4.08 (m, 1 H), 3.89 (m, 1 H), 3.70 (m, 1 H)	13
8	4.93 (t, 1 H, $J = 1.9$), 4.84 and 4.76 (both dd, 2×1 H, J = 1.8 and 2.8)	4.80 and 4.79 (both dd, 2×1 H, J = 1.9 and 2.9) 4.55 (m, 3 H)**	4.52 (m, 1 H), 4.50 (m, 1 H), 4.55 (m, 3 H)**	4.25 (m, 1 H), 4.17(m, 1 H), 4.13 (m, 1 H), 4.04 (m, 1 H)	12

Table 1. ¹H NMR spectra of quatercymantrenyls, δ (J/Hz)

*Two α -protons give one signal. **Three protons give one signal.

and give individual signals. This means that these compounds have no symmetry elements and, hence, should be chiral. The spectrum of compound 7 has 12 oneproton and one two-proton signals (two of fourteen signals coincide). The spectrum of compound 8 contains 11 one-proton and one three-proton signals (three of fourteen signals coincide). In the spectra of compounds 5 and 6, the protons of two equivalent C_5H_3 rings form one set of the signals: a downfield signal with the "longrange" coupling constant ${}^{2}J_{H,H} = 1.8$ Hz and two doublets of doublets with the constants ${}^{2}J_{H,H} = 1.8$ Hz and ${}^{1}J_{\rm H,H} = 2.8$ Hz. It has been shown previously 1-4 that this set of signals is characteristic of bicymantrenyl derivatives containing a substituent at the β -position. Based on this, it can be supposed that in compounds 5 and 6 two $C_5H_4C_5H_3$ fragments are linked according to the β - β -type; however, the compounds differ in the mutual arrangement of the fragments (Scheme 2). The spectral data allow one to distinguish distinctly compounds 5 and 6 from their isomeric complexes 7 and 8. but it is impossible to assign a particular spectrum to this or another compound (5 or 6, similarly 7 or 8). Apparently, this can be established only from the X-ray diffraction study. Compound 5 (Scheme 2) is chiral and can be theoretically resolved into enantiomers. Compound $\mathbf{6}$ is a meso-form, because the molecule can be superimposed with its mirror image rotated by 180° around the axis crossing the inversion center and perpendicular to the central C-C bond.

The spectra of compounds 7 and 8, where all four Cp rings are nonequivalent, contain not one, but two, different sets of one triplet and two doublets (two different C_5H_3 rings) and two sets of the signals assigned to C_5H_4 (two different C_5H_4 rings). The signals in the spectra of compounds 5 and 6 can be easily assigned from the onedimensional ¹H NMR spectrum on the basis of the position and differences in multiplicity. By contrast, we managed to assign unambiguously the signals of the protons from all four rings in the spectra of compounds 7 and 8 using only two-dimensional correlation {¹H,¹H} NMR spectroscopy (COSY) combined with the phosphorus decoupling. In the spectra of complexes 7 and 8, one set of the signals for the C_5H_3 ring characteristic of β -substitution can be distinguished (triplet with ${}^{2}J_{H,H} = 1.8$ Hz in the low field and two doublets of doublets in the higher field) and one more set (two doublets of doublets and triplet in the higher field with ${}^{1}J_{H,H} = 2.8$ Hz). The latter is characteristic of the α -type substitution. It can be concluded that chiral complexes 7 and 8 probably have the "angular" structure and are formed due to the α - β -type coupling of two $C_5H_4C_5H_3$ fragments.

These conclusions agree with the data of the ${}^{31}P$ NMR spectra. In compounds 5 and 6, two phosphorus atoms are equivalent and give one sharp singlet with chemical shifts at 91.19 and 91.28 ppm, respectively. By contrast, the ${}^{31}P$ NMR spectrum of com-

pound 7 contains a broadened singlet at 92.00 ppm with a shoulder at 92.05 ppm. In the spectrum of compound 8, two phosphorus atoms are nonequivalent and give two individual singlets with equal intensities at 91.01 and 91.88 ppm.

Evidently, along with the products of coupling of β - β - and α - β -types, the formation of products of the α - α -type coupling is also possible. It is known that for the metallation of bicymantrenyl, the ratio of the substitution to the β - and α -positions is equal to -4: 1, *i.e.*, the fraction of lithium in two β -positions is equal to 0.8, and that in two α -positions is 0.2. Assuming that all three possible types (β - β , α - β and α - α) of coupling are equally probable, the probabilities of the formation of the coupling products according to the three types indicated will be 0.64 : 0.32 : 0.04 (taking into account that the products of the α - β -type coupling can be formed via two routes). In fact, the fraction of the products of the α - α -type coupling should be still lower, because the steric hindrance is higher for coupling to the α -position. Therefore, these complexes can be formed in very small amounts only and cannot be isolated.

To compare the reactivity, we metallated complex 2⁴ and compounds 5 and 6 with buthyllithium. It turned out that the metallation of complex 2 is not selective: after quenching with D_2O , deuterium inserts in all 14 positions in four Cp rings, but in different amounts. By contrast, complexes 5 and 6 are selectively metallated involving only six hydrogen atoms of two internal Cp rings. According to the ¹H NMR data, after quenching with D_2O , deuterium exists only in these positions. The selective metallation of complexes 5 and 6 allows selective synthesis of different derivatives with substituents only in central Cp-rings.

Experimental

All experiments were performed in an argon atmosphere. Initial complex 4 was obtained by a known procedure.⁷ Prior to use THF was distilled over benzophenone sodium ketyl. ¹H and ³¹P NMR spectra were obtained in CDCl₃ relative to Me₄Si on Bruker WP-200-SY (200 MHz for ¹H) and Bruker AMX-400 (400 MHz for ¹H) spectrometers.

Metallation and oxidative coupling of complex 4. A 2.2 M solution (1.2 mL) of buthyllithium (2.5 mmol) in hexane was added to a solution of compound 4 (0.86 g, 1.34 mmol) in THF (40 mL) at -60 to -65 °C. Anhydrous CuCl₂ (2.2 g, 16 mmol) was added 40 min later. The mixture was stirred for 3 h at -65 °C, heated to -20 °C, and quenched with 5% HCl. The reaction products were extracted with CH₂Cl₂. The extract was washed with 5% HCl and water, dried with CaCl₂. and evaporated. The residue was chromatographed on a column with Al_2O_3 . Elution by a benzene-heptane (1 : 1) mixture gave two fractions: complex 8 (0.07 g, 8%) and a mixture of 8 and starting 4 (0.11 g). Elution by a benzene-heptane (3 : 2) mixture gave two fractions: unreacted 4 (0.16 g, 19%) and complex 7 (0.05 g, (6%). Elution by a benzene-heptane (3:1) mixture resulted in a mixture of complexes 5 and 6 (0.14 g, 16%). Fractional crystallization from a toluenehexane mixture afforded complex 5 (0.04 g, 5%) in the precipitate and complex 6 (0.02 g, <2%) from the mother liquor. Complex 5 was isolated as yellow crystals with m.p. (decomp.) >275 °C. Found (%): C, 61.96; H, 3.75; P, 4.45. C₆₆H₄₄Mn₄O₁₀P₂. Calculated (%): C, 61.99; H, 3.47; P, 4.84. Complex 6 was isolated as yellow crystals with m.p. 116– 121 °C. Found (%): C, 61.92; H, 3.50; P, 4.54. C₆₆H₄₄Mn₄O₁₀P₂. Calculated (%): C, 61.99; H, 3.47; P, 4.84. Complex 7 was isolated as yellow crystals with m.p. (decomp.) >275 °C. Found (%): C, 61.82; H, 3.63; P, 4.68. C₆₆H₄₄Mn₄O₁₀P₂. Calculated (%): C, 61.99; H, 3.47; P, 4.84. Complex 8 was calculated as yellow platelets with m.p. 142– 154 °C (hexane). Found (%): C, 61.72; H, 4.28; P, 4.50. C₆₆H₄₄Mn₄O₁₀P₂. Calculated (%): C, 61.99; H, 3.47; P, 4.84.

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