rhodium complexes. Optimal conditions were found for carrying out the acyldemercuration both for  $R_2Hg$  and RHgX, where R = aryl and alkyl groups.

2. Convenient methods were developed for the synthesis of substituted benzophenones, alkylaromatic, unsaturated, and heterocyclic ketones.

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#### ORGANOMOLYBDENUM DERIVATIVES OF CYMANTHRENE

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It is well known that the alkyl, aryl, and acyl  $\sigma$ -derivatives of cyclopentadienyltricarbonylmolybdenum Cp(CO)<sub>3</sub>MoR and Cp(CO)<sub>3</sub>MoCOR (R = Alk, Ar) have a low thermal and oxidation stability [1-3]. The  $\sigma$ -phenyl derivative of molybdenum has not been isolated at all, because rupture of the  $\sigma$ -bond Mo-Ph and migration of the Ph-group into the cyclopentadienyl ring occur already at negative temperatures [4]. On the other hand, we have demonstrated that the  $\sigma$ -cymanthrenyl complexes of the transition metals (Ni, Fe, and W) are much more stable than their alkyl and aryl analogs [5-7]. This led us to the conclusion that the  $\sigma$ cymanthrenyl derivatives of cyclopentadienyltricarbonylmolybdenum can also be expected to be stable compounds. In the present work we have achieved the synthesis of a series of organomolybdenum derivatives of cymanthrene and investigated their properties.

$$Cp(CO)_3MoNa + (CO)_3MnC_5H_4COCl \rightarrow Cp(CO)_3MoCO - (I) Mn (CO)_3$$

The  $\sigma$ -acyl complex (I) has been obtained with a 55% yield by reacting the sodium cyclopentadienyltricarbonylmolybdate with the acid chloride of cymanthrenecarboxylic acid. Compound (I) is a yellow crystalline substance which melts without decomposition at 89.5-90°C. It does not change when kept in air for extended periods of time, i.e., it surpasses with respect to its stability not only the acyl derivatives of molybdenum Cp(CO)<sub>3</sub>MoCOAlk, which have not been isolated in pure form, but also the perfluoroacyl compounds Cp(CO)<sub>3</sub>MoCOAlkF which start to decompose when kept in air for several hours [8].

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2352-2358, October, 1984. Original article submitted July 8, 1983. When heated briefly in THF, the  $\sigma$ -cymanthrenoyl complex (I) is easily decarbonylated to give the  $\sigma$ -cymanthrenyl complex (II) which is stable like (I) as a solid. In solutions both complexes gradually decompose, particularly in light. The complexes (I) and (II) have been characterized by their IR and NMR spectra; their mass spectra have been published earlier [9]:



The  $\sigma$ -cymanthrenyl derivative (II) represents a heterobinuclear metal carbonyl complex, both fragments of which can undergo in principle photochemical substitution of the carbonyl ligands. We have investigated the photochemical reaction of (II) with PPh<sub>3</sub>, with substitution of the CO ligands in the organomolybdenum derivatives Cp(CO)<sub>3</sub>MoR [10] and in cymanthrene derivatives [11]; it was found that PPh<sub>3</sub> substitutes one CO group only at the Mo atom with the formation of the trans-phosphinedicarbonyl complex (III). A substitution of the CO ligand by PPh<sub>3</sub> in the cymanthrenyl fragment of compounds (II) and (III) does not take place. An analogous course of the photochemical reaction with PPh<sub>3</sub> has been observed earlier in the case of the  $\sigma$ -cymanthrenyl derivatives of tungsten Cp(CO)<sub>3</sub>WC<sub>5</sub>H<sub>4</sub>Mn(CO)<sub>3</sub> [7] and of iron Cp• (CO)<sub>2</sub>FeC<sub>5</sub>H<sub>4</sub>Mn(CO)<sub>3</sub> [6]. The structure of (III) was established by <sup>1</sup>H NMR (PMR). As in the case of other molybdenum dicarbonyl complexes Cp(CO)<sub>2</sub>(PR<sub>3</sub>')MoR, the signal of the Cp ring protons in (III) is shifted to the strong field (by 0.59 ppm) in comparison with the initial tricarbonyl complex (II); it appears as a doublet due to splitting at the P atom with a spinspin interaction constant JPH = 1.4 Hz, which is characteristic for trans-isomers [12].



Earlier investigations of the reactivity of  $\sigma$ -cymanthrenyl derivatives of Ni, Fe, and W [5, 6, 13] showed that the metal-carbon  $\sigma$ -bond is more resistant in these compounds toward electrophilic reagents than in the  $\sigma$ -alkyl and  $\sigma$ -aryl complexes of these metals. In the present work we have investigated the reaction of the  $\sigma$ -cymanthrenyl complexes of molybdenum (II) and (III) with Hg(II) salts and HCl in aqueous dioxane, and the reaction of (II) with I<sub>2</sub> under the conditions of rupture of the Mo-C  $\sigma$ -bond by these reagents in the  $\sigma$ -phenylphosphine-dicarbonyl derivative Cp(CO)<sub>2</sub> (PPh<sub>3</sub>)MoPh [14].



It was found that the complexes (II) and (III) were stable against HCl in aqueous dioxane; however, they showed different activities toward the Hg(II) salts. The Mo-C  $\sigma$ -bond in the tricarbonyl compound (II) was stable toward HgCl<sub>2</sub> and HgBr<sub>2</sub> even when refluxed in organic solvents. The phosphinedicarbonyl complex (III) reacts with mercuric chloride in benzene already at about 20° [however, more slowly than the  $\sigma$ -phenyl complex Cp(CO)<sub>2</sub>(PPh<sub>3</sub>)MoPh] to form the cyclopentadienyltricarbonylmolybdenum chloride and cymanthrenylmercuric chloride. Cp(CO)<sub>2</sub>• (PPh<sub>3</sub>)MoCl was obtained as a mixture of the trans- and cis-isomers (1:2) which were separated by chromatography on silica gel (the cis-isomer eluted first). The chlorides were attributed to the cis- and trans-isomers on the basis of the multiplet character of the signal of the Cp ring protons in the PMR spectrum [12]. The chloride that gave a single at  $\delta$  5.41 ppm was considered as the cis-isomer. The other isomer, the Cp ring protons of which appear as a doublet at  $\delta$  5.11 ppm (J = 2.2 Hz) was considered as the trans-isomer. The cis- and transisomers of Cp(CO)<sub>2</sub>(PPh<sub>3</sub>)MoCl differ also in the position and relative intensity of the valence oscillation bands of the CO groups in the IR spectra (1980 and 1982 cm<sup>-1</sup> in the cis-isomer and 1990 and 1909 cm<sup>-1</sup> in the trans-isomer). In the cis-isomer the high-frequency band is the more intensive, in the trans-isomer it is the low-frequency one; this is in agreement with the proposed Manning criterion [15] for the distinction between the cis- and trans-isomers of  $Cp(CO)_2(L)MX$  from their IR spectra. When heated in benzene the trans-isomer of  $Cp(CO)_2(PPh_3)MoC1$  is converted to the cis-isomer. Only the cis-isomer of  $Cp(CO)_2(PPh_3)MoC1$  has been described earlier [12, 16].

Thus, the investigations of the reactions of  $\sigma$ -cymanthrenyl complexes of molybdenum (II) and (III) with HCl in aqueous dioxane and with Hg(II) salts have shown that the Mo-C  $\sigma$ -bond in these compounds [particularly in (II)] is more stable toward these reagents than in the  $\sigma$ -phenyl complex Cp(CO)<sub>2</sub>(PPh<sub>3</sub>)MoPh.

The  $\sigma$ -cymanthrenyl derivative (II) reacts easily with I<sub>2</sub> in CHCl<sub>3</sub> at 20°. This leads not only to the rupture of the Mo-C  $\sigma$ -bond as observed earlier in the case of the methyl Cp(CO)<sub>3</sub>MoMe and phenyl Cp(CO)<sub>2</sub>(PPh<sub>3</sub>)MoPh complexes [1, 14], but also to the substitution of one CO group at the Mo atom by two I atoms with the formation of Cp(CO)<sub>2</sub>MoI<sub>3</sub> as the sole reaction product. In the case of an equimolar ratio of the reagents the yield of Cp(CO<sub>2</sub>)MoI<sub>3</sub> is 34%, while 25% of the initial complex (II) remains unaltered. When the amount of I<sub>2</sub> is increased (reagent ratio 1:2), the yield of Cp(CO)<sub>2</sub>MoI<sub>3</sub> increases to 63%. Cp(CO)<sub>2</sub>MoI<sub>3</sub> is not formed from Cp(CO)<sub>3</sub>MoI because the latter does not substitute the CO ligands by I under the conditions at which (II) reacts with I<sub>2</sub> (the exchange takes place only under irradiation with UV light [17]). Consequently, the substitution of the CO group by I takes place in the initial complex (II) and precedes the rupture of the Mo-C  $\sigma$ -bond in it.

Thermal rearrangement has been described for the  $\sigma$ -ethyl and  $\sigma$ -benzyl derivatives of cyclopentadienyltricarbonylmolybdenum, consisting in the migration of the  $\sigma$ -bonded group into the cyclopentadienyl ring with the formation of symmetrical and asymmetrical dimeric complexes [2, 18].  $\sigma$ -Phenyl(cyclopentadientyl)tricarbonylmolybdenum suffers such a rearrangement already during its preparation [4]

$$Cp(CO)_{3}MoR \rightarrow [RC_{5}H_{4}(CO)_{3}Mo]_{2} + RC_{5}H_{4}(CO)_{3}MoMo(CO)_{3}Cp$$
  
 $R = Et, CH_{2}Ph, Ph.$ 

In the present work we have studied the thermal decomposition of molybdenum  $\sigma$ -cymanthrenyl derivative (II) in a melt at 169-171°C. Under these conditions a product of the migration of the cymanthrenyl group into the cyclopentadienyl ring was obtained with a yield of 17%: the asymmetrical dimeric complex (IV). During thermolysis at temperatures above 175° the complex (IV) decomposes completely while at temperatures below 169° the thermolysis is negligible and the yield of (IV) decreases sharply. Other reaction products are cymanthrene (29%) and bis(cyclopentadienyltricarbonylmolybdenum) (32%). Besides this, small amounts of compound (V) are formed in the thermal decomposition of (II); the IR and PMR spectra of this compound are in good agreement with the structure of an asymmetrical dimeric complex which contains the cymanthrenoyl group as a substituent in the cyclopentadienyl ring. No binuclear fulvalene complex [C<sub>5</sub>H<sub>4</sub>(CO)<sub>3</sub>Mo]<sub>2</sub> was formed, analogous to the complex [C<sub>5</sub>H<sub>4</sub>(CO)<sub>3</sub>W]<sub>2</sub> [19], isolated in the thermal decomposition of  $\sigma$ -cymanthrenyl(cyclopentadienyl)tricarbonyltungsten.



The trinuclear complex (IV) which contains two Mo atoms and one Mn atom represents a light red crystalline substance which is stable in air in the solid state but which decomposes rapidly in solution. Its structure has been established by IR, PMR, and mass spectrometry. The IR spectrum of (IV) contains five absorption bands in the region of valence oscillations of the CO ligands. The PMR spectrum of (IV) in deuterochloroform consists of two triplets with  $\delta$  4.76 and 4.99 ppm due to the C<sub>5</sub>H<sub>4</sub> protons of cymanthrenyl, a singlet with  $\delta$ 

5.26 ppm, due to the Cp ring protons, which overlaps with the signal from two protons of the  $C_5H_4$  (CO)<sub>3</sub>Mo group, and a triplet with  $\delta$  5.44 ppm from two other protons of this group with an integral intensity ratio of 2:2:7:2. The mass spectrum of (IV) contains peaks of the ions  $[M - nCO]^+$  (n = 2, 5, 6, 8, 9) which are formed by splitting-off of carbonyl ligands from the molecular ion; peaks of the ions  $[M - nCO - Mn]^+$  (n = 3, 4, 6, 7, 9) which are formed when Mn is lost from partially or fully decarbonylated ions; peaks of ions formed when one or several molecules of hydrogen and/or acetylene are eliminated from these two types of fragment ions; peaks of Mo and Mn ions. The most intensive in the mass spectrum of (IV) is the ion  $[C_{10}H_{10}Mo_2]^+$  which is formed when the fragment  $C_5H_3Mn$  is lost from the fully decarbonyl-ated ion  $[M - 9CO]^+$ .

Compound (V) represents a light red crystalline substance which is analogous, with respect to its stability in air, to (IV) but is less stable thermally. The IR spectrum contains a band at 1667 cm<sup>-1</sup> that corresponds to valence oscillations of the acyl CO group. In the region of the C=O valence oscillations the IR spectrum of (V) is similar to that of (IV); however, all five vC=O bands are shifted toward the high-frequency region by 9-17 cm<sup>-1</sup>. The PMR spectrum of (V) in deuterochloroform is similar to that of (IV); it contains a triplet with  $\delta$  4.90 ppm, a singlet with  $\delta$  5.34 ppm, and two triplets with  $\delta$  5.52 and 5.90 ppm with an integral intensity ratio of 2:7:2:2. In comparison with (IV), the signals of the protons of the two monosubstituted C<sub>3</sub>H<sub>4</sub> rings in (V) are shifted toward the weak field by 0.14-0.46 ppm; this can be attributed to the unscreening effect of the acyl C=O group. Based on these data, the structure of an asymmetrical dimeric complex with a cymanthrenoyl group in the cyclopentadienyl ring has been proposed for compound (V).

### EXPERIMENTAL

All reactions were carried out in an atmosphere of dry clean Ar in absolute solvents. Chromatography was performed on neutral  $Al_2O_3$  (activity II) and SiO<sub>2</sub> (40/100). The compounds described above were identified by the melting points of samples mixed with the known substance and by the IR spectra. The IR spectra were taken on a UR-20 spectrometer, the PMR spectra of compounds (I) and (II) on a T-60 spectrometer (60 MHz); of compound (III) and the cis- and trans-isomers of Cp(CO)<sub>2</sub>PPh<sub>3</sub>MoCl on a Tesla BS-497 spectrometer (100 MHz); of compounds (IV) and (V) on a Varian XL-100 spectrometer (100 MHz); the internal standard was TMS. The IR and PMR spectra of the cis- and trans-isomers of Cp(CO)<sub>2</sub>PPh<sub>3</sub>MoCl were taken in CHCl<sub>3</sub>. The mass spectrum of (IV) was obtained on an MS-30 mass spectrometer using the DS-50 data treatment system; the temperature of the source was 250°, the ionizing voltage was 70 V, with direct introduction of the sample. The m/z values are quoted for ions containing the iso-topes <sup>98</sup>Mo and <sup>192</sup>Mo<sub>2</sub>.

<u>Preparation of Cp(CO)<sub>3</sub>MoCOC<sub>5</sub>H<sub>4</sub>Mn(CO)<sub>3</sub> (I).</u> A solution of Cp(CO)<sub>3</sub>MoNa in 70 ml THF [from 3.72 g Cp(CO)<sub>3</sub>MoI] was added to a solution of 3 g (CO)<sub>3</sub>MnC<sub>5</sub>H<sub>4</sub>COCl in 50 ml THF during 10 min and stirred for 75 min. The solution was filtered through a layer of Al<sub>2</sub>O<sub>3</sub> (2-3 cm), the THF stripped down to a volume of almost 10 ml, and the main quantity of (I) precipitated with petroleum ether. The mother liquor was chromatographed on plates coated with Al<sub>2</sub>O<sub>3</sub>, using a 1:1 mixture of benzene and petroleum ether as the mobile phase. Yield 0.01 g [Cp(CO)<sub>3</sub>Mo]<sub>2</sub>, 0.21 g (4.7%) (II),\* and 0.30 g (I). Total yield 2.61 g (55%)\* of yellow crystals with mp 89.5-90° (purified by precipitation from THF with pentane). Found, %: C 42.82; H 1.96; Mn 11.03. C<sub>17</sub>H<sub>9</sub>MnMoO<sub>7</sub>. Calculated, %: C 42.88; H 1.91; Mn 11.54. IR spectrum (CCl<sub>4</sub>, v, cm<sup>-1</sup>): 2040, 2030, 1970-1950, 1940 (C=O), 1629 (C=O). PMR spectrum (CHCl<sub>3</sub>,  $\delta$ , ppm, internal standard HMDS): 5.53 s (5H, Cp), 4.97 t (2H) and 4.70 t (2H, C<sub>5</sub>H<sub>4</sub>).

<u>Preparation of Cp(CO)<sub>3</sub>MoC<sub>5</sub>H<sub>4</sub>Mn(CO)<sub>3</sub> (II).</u> A solution of 0.33 g (I) in 20 ml THF was refluxed for 40 min, filtered through a layer of  $Al_2O_3$ , and the THF distilled off. The residue was dissolved in benzene and chromatographed on an  $Al_2O_3$  column. Benzene eluted 0.22 g (71%) of (II) in the form of yellow crystals with mp 146-147°C (with partial decomposition) (precipitated from THF with pentane). Found, %: C 42.89; H 2.14; Mn 12.01; Mo 20.92. C<sub>16</sub>H<sub>9</sub>Mn• MoO<sub>6</sub>. Calculated, %: C 42.88; H 2.02; Mn 12.26; Mo 21.41. IR spectrum (CC1<sub>4</sub>,  $\nu$ , cm<sup>-1</sup>): 2048, 2019, 1967, 1940, 1925 (C=O). PMR spectrum (CHCl<sub>3</sub>,  $\delta$ , ppm, internal standard HMDS): 5.47 s (5H, Cp), 4.87 t (2H), and 4.47 (2H, C<sub>5</sub>H<sub>4</sub>).

<sup>\*</sup>The yields of (I) and (II) were calculated on the basis of the amount of  $Cp(CO)_3MoI$  taken for the reaction.

Preparation of  $Cp(CO)_2(PPh_3)MoC_5H_4Mn(CO)_3$  (III). A solution of 0.70 g of (I) and 0.84 g PPh<sub>3</sub> in 120 ml THF was irradiated at 10-15° in a vessel made of Pyrex glass with a PRK-4 lamp for 8 h; the THF was stripped off and the residue chromatographed on Al<sub>2</sub>O<sub>3</sub> plates (mobile phase: benzene-petroleum ether 1:1). Yield 0.02 g (2.8%) (II) and 0.64 g (60%) (III) in the form of yellow crystals with mp 204-205° (with decomposition) (recrystallized from THF with pentane). Found, %: C 57.97; H 3.73; P 4.55; Mn 7.75. C<sub>33</sub>H<sub>24</sub>PMnMoO<sub>5</sub>. Calculated, %: C 58.08; H 3.55; P 4.54; Mn 8.05. IR spectrum (CHCl<sub>3</sub>,  $\vee$ , cm<sup>-1</sup>): 2016, 1970, 1930, 1882 (C=O). PMR spectrum (CDCl<sub>3</sub>,  $\delta$ , ppm): 4.88 d (5H, Cp, J<sub>PH</sub> = 1.4 Hz), 4.79 t (2H) and 4.59 t (2H, C<sub>5</sub>H<sub>4</sub>).

Reaction of (II) with HCl. A solution of 0.10 g (II) in 10 ml dioxane was treated with 2 ml concentrated HCl. The mixture was treated for 21 h with an aqueous  $Na_2CO_3$  solution and extracted with ether. The ether extracts were washed with water and dried with  $Na_2SO_4$ ; the ether was then distilled off and the residue chromatographed on  $Al_2O_3$ . Yield 0.10 g (quantitative) (II).

<u>Reaction of (III) with HCl.</u> A solution of 0.10 g (III) in 13 ml 90% aqueous dioxane containing the tenfold excess of HCl was kept at 20° for 48 h and treated as in the experiment with (II). The residue was chromatographed on SiO<sub>2</sub>. Yield 0.085 g (85%) (III).

Reaction of (II) with HgCl<sub>2</sub>. A solution of 0.18 g (II) and 0.12 g HgCl<sub>2</sub> in 10 ml benzene was refluxed for 5 h. The solvent was stripped off and the residue chromatographed on  $Al_2O_3$ . Yield 0.13 g (72%) (II).

Reaction of (II) with HgBr<sub>2</sub>. A solution of 0.18 g (II) and 0.15 g HgBr<sub>2</sub> in 15 ml acetone was refluxed for 11 h. The solvent was stripped off and the residue chromatographed on  $Al_2O_3$ . Yield 0.15 g (83%) (II).

<u>Reaction of (III) with HgCl<sub>2</sub>.</u> A solution of 0.10 g (III) and 0.04 g HgCl<sub>2</sub> in 25 ml benzene waskept at 20° for 2.5 h. The benzene was then stripped off and the residue chromatographed on a SiO<sub>2</sub> column. A mixture of benzene and petroleum ether eluted 0.05 g (78%) (CO)<sub>3</sub>MnC<sub>5</sub>H<sub>4</sub>HgCl, mp 134-135°C. CHCl<sub>3</sub> eluted 0.04 g (53%) of the cis-isomer of Cp(CO)<sub>2</sub>(PPh<sub>3</sub>). MoCl, mp 185-186°C (decomposes), the IR and PMR spectra of which were identical to the sample prepared by the procedure given in [16]. THF eluted 0.02 g (26.5%) of the trans-isomer of Cp(CO)<sub>2</sub>(PPh<sub>3</sub>)MoCl, mp 185-186° (decomposes) (recrystallized from CHCl<sub>3</sub> with pentane). The coincidence of the melting points of the cis- and trans-isomers of Cp(CO)<sub>2</sub>(PPh<sub>3</sub>)MoCl is evidently due to the transition of the trans-isomer to the cis-isomer during heating. This transition was observed also when a benzene solution of the trans-isomer was refluxed for a short time (25-30 min).

<u>Reaction of (II) with Iodine.</u> A solution of 0.20 g (II) in 5 ml CHCl<sub>3</sub> was treated with a solution of 0.24 g I<sub>2</sub> in 20 ml CHCl<sub>3</sub>. A brown precipitate was formed. After 1 h the precipitate was filtered off and reprecipitated from THF with pentane. Yield 0.17 g (63%) Cp• (CO)<sub>2</sub>MoI<sub>3</sub> which decomposes at >120° (see [17]). Found, %: C 14.15; H 1.026; I 63.59. C<sub>7</sub>H<sub>5</sub>• MoI<sub>3</sub>O<sub>2</sub>. Calculated, %: C 14.04; H 0.843; I 63.69. IR spectrum (THF, v, cm<sup>-1</sup>): 2080 and 2045 (C=O). PMR spectrum (deuteroacetone,  $\delta$ , ppm): 6.73 s (Cp). Reduction of the solution with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and chromatography on Al<sub>2</sub>O<sub>3</sub> gave 0.02 g (10%) (II).

Under the same conditions 0.20 g (II) and 0.12 g  $I_2$  gave 0.09 g (34%) Cp(CO)<sub>2</sub>MoI<sub>3</sub> and 0.05 g (25%) (II) remained unchanged.

<u>Thermal Decomposition of (II).</u> 0.90 g (II) was heated on an oil bath at  $169-171^{\circ}$  for 2.5 h in an ampul sealed under Ar. A fraction of the cymanthrene formed in the reaction sublimated and collected in the upper section of the ampul which was not immersed in the oil bath. After cooling the ampul was opened approximately in the middle. The cymanthrene was washed from the upper part of the ampul with petroleum ether and the solution chromatographed on  $Al_2O_3$ , yield 0.05 g cymanthrene. The contents of the lower part of the ampul were dissolved in THF, the solution filtered, and the THF stripped off. According to TLC the residue contained cymanthrene,  $[Cp(CO)_3MO]_2$ , (II), and two new red compounds. This mixture was separated by repeated chromatography on  $Al_2O_3$  plates with benzene-petroleum ether (1:1). Yield 0.07 g cymanthrene (total 0.12 g, 29%), mp 75.5-76.5°, 0.16 g (32%)  $[Cp(CO)_3MO]_2$ , mp 215-217° (decomposes), 0.04 g (4.4%) (II), 0.12 g (17%) (IV), and 0.05 g (6.9%) (V).

The complex (IV) was purified by reprecipitation from THF with hexane which gave a red crystalline substance; it started to darken at  $175^{\circ}$  and melted intensively with decomposition at  $189-191^{\circ}$ . Found, %: C 41.91; H 2.17. C<sub>24</sub>H<sub>13</sub>MnMo<sub>2</sub>O<sub>9</sub>. Calculated, %: C 41.64; H 1.89.

IR spectrum (THF, v, cm<sup>-1</sup>) 2022, 2016, 1942, 1918 (C=O). Mass spectrum (200°), m/z (ion, relative intensity, %): 636 (M<sup>+</sup> - 2CO, 1.2); 553 (M<sup>+</sup> - 3CO - Mn, 1.3); 552 (M<sup>+</sup> - 5CO, 3.2); 525 (M<sup>+</sup> - 4CO - Mn, 1.3); 524 (M<sup>+</sup> - 6CO, 0.6); 522 (M<sup>+</sup> - 6CO - H<sub>2</sub>, 1.3); 469 (M<sup>+</sup> - 6CO - Mn, 4.6); 468 (M<sup>+</sup> - 8CO, 5.0); 466 (M<sup>+</sup> - 8CO - H<sub>2</sub>, 4.9); 441 (M<sup>+</sup> - 7CO - Mn, 9.7); 440 (M<sup>+</sup> - 9CO, 20.3); 438 (M<sup>+</sup> - 9CO - H<sub>2</sub>, 30.1); 436 (M<sup>+</sup> - 9CO - 2H<sub>2</sub>, 29.9); 434 (M<sup>+</sup> - 9CO - 3H<sub>2</sub>, 26.4); 385 (M<sup>+</sup> - 9CO - Mn, 12.9); 383 (M<sup>+</sup> - 9CO - Mn - H<sub>2</sub>, 14.6); 381 (M<sup>+</sup> - 9CO - Mn - 2H<sub>2</sub>, 16.9); 379 (M<sup>+</sup> - 9CO - Mn - 3H<sub>2</sub>, 10.5); 359 (M<sup>+</sup> - 9CO - Mn - C<sub>2</sub>H<sub>2</sub>, 6.8); 357 (M<sup>+</sup> - 9CO - Mn - C<sub>2</sub>H<sub>2</sub> - H<sub>2</sub>, 4.2); 355 (M<sup>+</sup> - 9CO - Mn - C<sub>2</sub>H<sub>2</sub> - 2H<sub>2</sub>, 4.2); 322 (M<sup>+</sup> - 9CO - C<sub>5</sub>H<sub>3</sub>Mn, 100); 320 (M<sup>+</sup> - 9CO - C<sub>5</sub>H<sub>3</sub>Mn - H<sub>2</sub>, 99.7); 318 (M<sup>+</sup> - 9CO - C<sub>5</sub>H<sub>3</sub>Mn - 2H<sub>2</sub>, 53.9); 316 (M<sup>+</sup> - 9CO - C<sub>5</sub>H<sub>3</sub>Mn - 3H<sub>2</sub>, 24.4); 281 (MnC<sub>5</sub>H<sub>4</sub>C<sub>5</sub>H<sub>4</sub>Mo<sup>+</sup>, 5.4); 247 (Cp(CO)<sub>3</sub>Mo<sup>+</sup>, 21.1); 226 (C<sub>1</sub>O<sub>4</sub>H<sub>8</sub>Mo<sup>+</sup>, 22.8); 224 (C<sub>1</sub>O<sub>4</sub>H<sub>6</sub>Mo<sup>+</sup>, 17.6); 163 (CpMo<sup>+</sup>, 91.6); 98 (Mo<sup>+</sup>, 9.8), 55 (Mn<sup>+</sup>, 16).

The complex (V) was reprecipitated from THF with heptane to give a red crystalline substance which started to darken at 135° and decomposed violently above 145°; it was stable in air as a solid but decomposed rapidly in solutions. Found, %: C 42.65; H 2.01.  $C_{25}H_{13}MnMo_2$ •  $O_{10}$ . Calculated, %: C 41.69, H 1.82. IR spectrum (THF, v, cm<sup>-1</sup>): 2039, 2025, 1975, 1955, 1928 (C=O), 1667 (C=O).

### CONCLUSIONS

1. Stable organomolybdenum derivatives of cymanthrene  $Cp(CO)_3MoC_5H_4Mn(CO)_3$ ,  $Cp(CO)_3Mo \cdot COC_5H_4Mn(CO)_3$ , and  $Cp(CO)_2(PPh_3)MoC_5H_4Mn(CO)_3$  have been prepared.

2. The  $\sigma$ -bond Mo-C in the  $\sigma$ -cymanthrenyl derivatives of molybdenum Cp(CO)<sub>3</sub>MoC<sub>5</sub>H<sub>4</sub>Mn(CO)<sub>3</sub> and Cp(CO)<sub>2</sub>(PPh<sub>3</sub>)MoC<sub>5</sub>H<sub>4</sub>Mn(CO)<sub>3</sub> is more stable toward electrophilic reagents (hydrochloric acid, mercury salts) than in the  $\sigma$ -phenyl derivative Cp(CO)<sub>2</sub>(PPh<sub>3</sub>)MoPh.

3. The thermal decomposition of  $Cp(CO)_{3}MoC_{5}H_{4}Mn(CO)_{3}$  yields products of the migration of the cymanthrenyl group into the cyclopentadienyl ring  $(CO)_{3}MnC_{5}H_{4}C_{5}H_{4}(CO)_{3}MoMo(CO)_{3}Cp$  and  $(CO)_{3}MnC_{5}H_{4}COC_{5}H_{4}(CO)_{3}MoMo(CO)_{3}Cp$ .

4. The trans-isomer of Cp(CO)<sub>2</sub>(PPh<sub>3</sub>)MoCl has been isolated.

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