REACTIONS OF $Fe_2-\mu-(o-C_6H_4CH_2NC_6H_5)(CO)_6$ WITH TRIPHENYLPHOSPHINE AND THE CRYSTAL STRUCTURE OF $Fe_2-\mu-(o-C_6H_4CH_2NC_6H_5)P(C_6H_5)_3(CO)_5$

UDC 542.91:548.312.5:547.1'18:541.49

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The exchange of a carbonyl ligand for different donor ligands is the most characteristic reaction of carbonyl complexes of transition metals. In complexes with a square or octahedral structure for the inner sphere, ligand substitution frequently is subject to the trans effect owing to the presence of a carbon σ -bonded with the metal [1].

In order to study the substitution of carbonyl by triphenylphosphine, we chose the binuclear complex hexacarbonyl- μ -[o-phenylenemethylene(phenylamino)] diiron (I), in which one iron atom is π -bonded and the other is σ -bonded with the arene ring. The structure of compound (I) was determined previously using x-ray diffraction [2]. Although the geometry of the molecule in the crystal state is not determined only by the effect of the ligands on each other, in most cases it is possible to observe lengthening of the bonds in the position trans to the trans-active ligand. In complex (I), the longest Fe-CO bond (longer than the rest of such bonds by 0.03-0.04 Å) is the bond trans to the iron-arene σ bond. This made it possible to expect that it would be specificially the above indicated carbonyl group which would be substituted by triphenylphosphine.

However, carrying out the reaction under various conditions has not confirmed this hypothesis. Heating the reagents at 80° C in C_6H_6 leads to the product of complete substitution of the nitrogen-containing ligand by PPh₃ with formation of complex (II). The unusual nature of the displacement of the organic ligand bonded to the metal atom by a σ bond has been noted [3]. At the same temperature in n-heptane, compound (II) is formed in lower yield. At 20°C in n-heptane, substitution of one CO group by PPh₃ occurs with formation of complex (III), which is obtained in benzene at 20°C only in insignificant yields. The structure of (III) has been established by x-ray diffraction.



The structure of (III) is close to that found for (I) (Fig. 1): the Fe(CO)₃ and $Fe(CO)_2PPh_3$ fragments are interconnected by the single bond Fe-Fe of length 2.458(1) Å and the bridge ligand of $o-C_6H_4CH_2NPh$. The N atom and the $o-C_6H_4$ fragment are connected to both iron atoms, and the arene fragment is a σ,π bridge (the Fe¹-C¹¹ σ bond has length 2.023(6) Å, while the Fe-C π bonds have lengths 2.372(7) and 2.186(6) Å). The FeFeP angle in complex

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Fig. 1. The structure of pentacarbonyl(triphenylphosphine)- μ -[o-phenylenemethylene(phenylamino)]diiron.

(III) is equal to 143.6° and is comparable with the value of the $Fe^{1}Fe^{2}C^{5}$ angle in (I), 140.2°. From the characteristics of the geometry of (III), we may note some semibridge character for the carbonyl group $C^{3}-O^{3}$, which has a tendency toward coordination with the "foreign" Fe¹ atom in addition to coordination with "its own" Fe² atom (the Fe¹...C³ distance is 2.456(7) Å), which leads to substantial nonlinearity for the Fe²-C³-O³ fragments (the Fe²C³O³ angle is 164.1(6)°, the rest of the FeCO angles are in the range 174.5-178.8°), and also to an appreciable alternation of the C-C bonds in the benzene fragment C⁶-C¹¹ fragment: the C-C and C=C bonds alternate, having lengths 1.42 and 1.37 Å respectively, which completely agrees with the proposed type of coordination for this fragment with the iron atoms.

As a result of the x-ray diffraction study for compound (III), it was determined that substitution of the CO group occurs at the iron atom having a σ bond with the carbon atom of the arene ring; and the triphenylphosphine ligand occupies the position trans to the other iron atom.

The ortho-metallated complex with a bridge sulfur atom, which is similar in structure, at $\sim 25^{\circ}$ C also is attacked by PPh₃ at the iron atom which is σ bonded to the carbon; but in this case substitution of the CO ligand does not occur, but rather we see this ligand shift with insertion at the Fe-C σ bond (complex (IV)) [4]. Boiling compound (IV) in C₆H₆ leads to formation of thiolactone (V). In our case, the analogous substance should be N-phenyl-



phthalimidine; but instead of this substance we observe N-benzylideneaniline among the reaction products.

One reason for substitution of the carbonyl group at the Fe atom σ -bonded to the carbon is apparently the closeness of the arene ring. It has been proposed [5] that upon exchange of the CO for phosphine, the possibility of localization of the electron pair on the ring in the transition state facilitates addition of the electron pair from the incoming nucleophile. Furthermore, the electronic environment of the Fe¹ atom in compound (I) should differ from the environment of the Fe² atom: both have the same number of carbonyl ligands and are connected by a common bridge nitrogen atom, but the bridge arene ligand is π bonded with one Fe atom by two electrons and is σ bonded with the other Fe atom only by one electron. Despite some compensation [2], the environment of the iron atom which is σ bonded with the carbon in complex (I) remains electron-deficient, which may favor substitution of CO by the

ABLE 1.	Coordinates of	the Atoms (•1	_0 ⁴)*				والموادقات والمحافظ
Atom	X	Y	2	Atom	¥	Y	z
⁷ EEAXOÕÕÕÕÖÜÜÜÜÜÜÜÜÜÜÖÖÖÖÖÖÖÖ	$\begin{array}{c} 3338 (1) \\ 5269 (1) \\ 5269 (1) \\ 5269 (1) \\ 3338 (1) \\ 3338 (1) \\ 3328 (1) \\ 528 (1) \\ 528 (1) \\ 6718 (5) \\ 528 (5) \\ 6718 (5) \\ 528 (6) \\ 7718 (5) \\ 568 (7) \\ 568 (7) \\ 568 (7) \\ 568 (7) \\ 568 (7) \\ 568 (7) \\ 568 (6) \\ 66 (6) \\ 6$	$\begin{array}{c} 2256 \\ 23246 \\ 3148 \\ 900 \\ 3315 \\ 3315 \\ 3315 \\ 33246 \\ 13528 \\ 4107 \\ 4107 \\ 4338 \\ 4107 \\ 4338 \\ 4107 \\ 4338 \\ 4407 \\ $	$\begin{array}{c} 1974 (0) \\ 1914 (0) \\ 1933 (1) \\ 1933 (1) \\ 1933 (1) \\ 1933 (1) \\ 1933 (1) \\ 1933 (1) \\ 1933 (1) \\ 1933 (1) \\ 173 (3) \\ 173 (3) \\ 173 (3) \\ 173 (3) \\ 173 (3) \\ 173 (3) \\ 173 (3) \\ 177 (3) \\$	30000000000000000000000000000000000000	5200 (8) 4317 (8) 3913 (7) 3913 (7) 3328 (6) 530 (6) 530 (6) 532 (8) 9528 (2229 (6) 4014 (6) 4014 (6) 4014 (6) 4004 (5) 4004 (6) 4004 (6) 4149 (4) 4230 (4) 862 (6) 862 ($\begin{array}{c} 4687 \\ 4687 \\ 4373 \\ 4587 \\ 4373 \\ 4587 \\ 38667 \\ 38667 \\ 38667 \\ 338667 \\ 338667 \\ 338667 \\ 33856 \\ 44 \\ 33756 \\ 45 \\ 33756 \\ 44 \\ 33855 \\ 44 \\ 44 \\ 33855 \\ 44 \\ 33855 \\ 44 \\ 33855 \\ 44 \\ 33855 \\ 44 \\ 33855 \\ 44 \\ 33855 \\ 44 \\ 44 \\ 33855 \\ 44 \\ 44 \\ 44 \\ 33855 \\ 44 \\ 44 \\ 44 \\ 44 \\ 44 \\ 44 \\ 44 \\$

*The temperature factors may be obtained from the authors.

triphenylphosphine donor ligand. Such a substitution should lead to a more uniform electronic environment for both iron atoms in compound (III).

The fact that the substitution product (III) in C_6H_6 is formed in much lower yield is consistent with the reduction in the CO substitution rate observed in Mn complexes with an increase in the dielectric constant of the solvent [6].

From analysis of the data in [7-14], it also follows that in binuclear and polynuclear iron carbonyl complexes, the CO group found in the position trans to the Fe-Fe bond is the most easily substituted.

EXPERIMENTAL

The IR spectra were obtained on the UR-20 spectrophotometer; the mass spectra were taken on the MAT-311 A instrument with direct injection into the ion source at temperature 150°C and ionization energy 85 eV. The x-ray diffraction experiment was carried out on the Syntex-P1 diffractometer, $\lambda_{MOK\alpha}$, $\theta/2\theta$ scanning, $3^{\circ} \leq 2\theta \leq 50^{\circ}$. Crystals of (III) are monoclinic, a = 10.506(5), b = 15.182(8), C = 19.873(8) Å, β = 98.40(4)°, V = 3136(2) Å³, Z = 4, space group P2₁/c. The structure was deciphered by the heavy atom method and refined by the least squares method in the full-matrix anisotropic (P, Fe)-isotropic approximation to R = 0.071 (R_w = 0.085) for 3206 reflections with F² $\geq 3\sigma$. The final coordinates of the atoms are given in Table 1.

<u>Reaction of $Fe_2-\mu-(o-C_6H_4CH_2NPh)(CO)_6$ (I) with Triphenylphosphine.</u> The experiments were carried out in a 250 ml flask fitted with a reflux condenser, a magnetic stirrer, and tubing for inlet of inert gas. In all the experiments, we took 2.3 g (0.005 moles) of complex (I), 3.93 g (0.015 moles) PPh₃, and 150 ml solvent.

a) The reaction was carried out in n-heptane at 20°C for 10 days. According to TLC data, the starting materials remained in the reaction mixture. The precipitate formed was filtered off and recrystallized from C_6H_6 . We obtained 1.6 g of substance (III), mp 134°C (with decomp.), yield 46%. IR spectrum (v, cm⁻¹, KBr disk): 415 s, 422 s, 445 s, 467 s, 499 s, 506 s, 525 s, 585 s, 620 s, 645 s, 695 s, 745 s, 763 s, 800 s, 853 s, 895 s, 1001 s, 1032 s, 1093 s, 1120 s, 1164 s, 1188 s, 1210 s, 1225 s, 1250 s, 1284 s, 1300 s, 1313 s, 1335 s, 1390 s, 1400 s, 1435 s, 1490 s, 1530 s, 2833 s, 2934 s, 3006 s, 3040 s, 3061 s. The IR spectrum in the 1700-2200 cm⁻¹ region was taken in liquid paraffin: 1915 s, 1938 s, 1965 s, 1980, 1990, 2035 s, 2042 s (C≡O). The mass spectrum (m/z) (within the parentheses, we give the relative peak intensity in %): 583 (<1) $[M - 4C0]^+$, 581 (<1), 580 (1), 555 (2) $[M - 5C0]^+$, 461 (5), 433 (2) $[M - P(C_6H_5)_3]^+$, 431 (3), 430(10), 405(28) $[M - C0 - P(C_6H_5)_3]^+$, 402(18), 377(20) $[M - 2C0 - P(C_6H_5)_3]^+$, 374(26), $349(22) [M - 3CO - P(C_6H_5)_3]^+, 346(55), 321(47) [M - 4CO - P(C_6H_5)_3]^+, 318(100), 293(87)$ $[M - 5CO - P(C^{+}H^{>})_{3}]^{+}$, 262(100) $[P(C_{6}H_{5})_{3}]^{+}$, 183(100), 182(90), 181(100) $[o-C_{6}H_{4}CH_{2}NC_{6}H_{5}]^{+}$, 180(100), .164(65), 152(83), 133(46), 108(95), 107(87), 104(91), 91(49), 89(52), 78(95), 77(100), 76(46), 63(48), 56(88), 52(44), 51(100), 50(53). Found %: C 62.05; H 3.90; Fe 16.26; N 1.97%. C₃₆H₂₆Fe₂NO₅P. Calculated %: C 62.16; H 3.74; Fe 16.12; N 2.01%. We isolated 1.1 g of the starting complex (I) from the filtrate.

b) The experiment was carried out in C_6H_6 at 80°C for 24 h (up to disappearance of (I) according to TLC). The reaction mixture was filtered hot; the filtrate was evaporated to dryness. By fractional crystallization from C_6H_6 we obtained 3.23 g (65%) of compound (II), identified by elemental analysis, IR and mass spectra, and the melting point [15]. We isolated 0.83 g (92%) of N-benzylideneaniline.

c) In C_6H_6 at 20°C after 10 days, 0.196 g (6%) of complex (III) was formed; 1.26 g of compound (I) was recovered.

d) From the reaction products in n-heptane at 80° C (24 h), we isolated 0.96 g (19%) (II), 0.35 g (39%) N-benzylideneaniline, and 0.73 g (I).

CONCLUSIONS

1. Upon reaction of the complex hexacarbonyl- μ -[o-phenylenemethylene(phenylamino)]diiron with triphenylphosphine in n-heptane at 20°C, substitution of one carbonyl group by the phosphine ligand occurs. 2. By x-ray diffraction of the complex pentacarbonyl (triphenylphosphine)- μ -[o-phenylenemethylene(phenylamino)]diiron, we have shown that substitution of the carbonyl group occurs at the iron atom having a σ bond with the carbon atom of the arene ring; and the phosphine ligand occupies the position trans to the other iron atom.

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DISUBSTITUTED NORBORNADIENE π -COMPLEXES.

COMMUNICATION 1. SYNTHESIS AND SOME CHEMICAL PROPERTIES

OF 2,3-DISUBSTITUTED NORBORNADIENE COMPLEXES OF RHODIUM

UDC 542.91:547.1'13:541.49:546.97

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Among the disubstituted derivatives of norbornadiene, apparently the most available are 2,3-dicarboxy- and 2,3-dicarbomethoxynorbornadienes, which were first obtained by Diels and Alder [1, 2]. This explains their relatively wide use in direct synthesis of norbornadiene π -complexes of transition metals [3, 4]. There is no information on the reactivity of such π complexes in the literature. Accordingly, we have synthesized a number of new 2,3-disubstituted norbornadiene complexes of Rh and have studied some of their chemical properties.

As the key compound, we chose (2,3-dicarbomethoxynorbornadiene)cyclopentadienylrhodium (I), obtained in two steps using a previously developed method [5]. In the course of an investigation of the reactivity of diester (I), we found that when exposed to <math>20% H₂SO₄ it

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