3. Crystals (III) $AgBr_2C_{10}H_{13}OS$, triclinic, size up to 1 mm, $\alpha = 12.767(7)$, b = 7.807(2), c = 7.077(1) Å; $\alpha = 105.39(2)$, $\beta = 91.15(2)$, $\gamma = 81.05(2)^\circ$, V = 671(1) Å³, d_{calc} = 1.34 g/cm³, Z = 2. Space group PI. The structure was determined by analysis of the Patterson function (Ag and Br atoms), and subsequent electron density syntheses (S, 0, C). Refinement by full-matrix least squares led to an R-factor of 0.057. In the difference synthesis of the electron density, eight of the 13 H atoms were objectively localized. The interatomic distances are given in Table 4.

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Re(III) COMPLEXES IN THE SYNTHESIS OF PLATINUM ACETATE COMPLEXES AND THE STRUCTURE OF [PPh_Pt(OAc)_]?

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Reaction of tetrachlorodiacetatodirhenium dihydrate with triphenylphosphineplatinum (II) triacetatoargentate(I) produces a new binuclear platinum complex with acetate bridges, bis[(μ^2 -acetato)acetatotriphenylphosphine]diplatinum(II). The new complex is characterized by x-ray structural analysis, IR, and PMR spectroscopies. The Re(III) complex in this reaction is not only the source of chloride ions, which are necessary for precipitation of silver, and the acetate acceptor, but also the silver(I) reductant which is oxidized during the reaction to Re(IV).

Binuclear complexes of platinum(II) are of interest as starting compounds for preparation of catalytically active multinuclear systems. In contrast to the well known and structurally characterized palladium complexes with bridging acetate groups, platinum complexes of the type $[LPt(OAc)_2]_2$ (L = PR₃, allyl) have not been prepared. Moreover, their preparation using traditional synthesis methods [1-4] have not succeeded [5, 6]. We studied reaction of PPh₃Pt(OAc)₃Ag with Re₂(OAc)₂X₄·2H₂O (X = C1, Br) in order to discover synthetic routes to binuclear platinum acetate complexes.

EXPERIMENTAL

Solvents were purified by standard methods [7]. $PPh_3Pt(OAc)_3Ag(I)$ was prepared by reaction of AgOAc with $[PPh_3PtCl_2]_2$ in AcOH. $Re_2(OAc)_2X_4$ (X = Cl, Br) was prepared as in [8].

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Atom	X	Y	Z	B _{equiv} , Å ²
D+	0.07024(3)	0.09576(6)	0.34929(3)	3 44 (2)
D	0,3373(2)	0,4641(3)	0.1670(2)	32(2)
<u>_</u>	0.4024(4)	0.2417(9)	0.2772(4)	3.8(5)
02	0,0038(5)	0.237(1)	0.1770(4)	5.4(5)
Õ3	0,4644 (5)	0.461(1)	0.1377(5)	6.3(6)
04 04	0.1011(0) 0.1287(7)	-0.004(1)	0.4582(5)	7.2(7)
Ci	0.0660(7)	0.282(1)	0.2196(7)	3.9(7)
\tilde{C}^2	0,0000(7)	0.388(1)	0.1981(7)	6.3(8)
C ³	0,4348 (8)	0.436(2)	0.0757(6)	3.8(8)
Č4	0,4615 (9)	0.334(2)	0.0508 (8)	10(1)
C ⁵	0,2539(6)	0.033(1)	0.3961 (5)	2,8(6)
Č	0,1818(6)	0.465(1)	0.0950(6)	3,9(7)
č	0.3865(7)	0.018(2)	0.4532(7)	5,1(8)
č	0,3916(8)	0.138(2)	0.4878 (7)	5,3(9)
Ȱ	0.3266(7)	0.205(1)	0.4767 (6)	4,1(9)
\tilde{C}^{10}	0.2569(7)	0.152(1)	0,4298(6)	4,2(7)
Č ¹¹	0.3422 (7)	0.291(1)	0.1424(6)	3,6(7)
\tilde{C}^{12}	0.4076 (8)	0.222(2)	0,1840 (8)	5,7 (9)
C13	0.418(1)	0.084(2)	0.1682(8)	8(1)
Č14	0.362(1)	0.014(2)	0,1145 (8)	7(1)
Č15	0.2953 (9)	0,091 (2)	0,0730(7)	6,9(9)
Č16	0.2852(7)	0,230(1)	0,0876(6)	4,2(7)
\tilde{C}^{17}	0.3272(6)	0.453(1)	0,2400(6)	3,6(7)
C 18	0.2036(6)	0,063(1)	0,2474(6)	4,7(7)
C19	0.2113(7)	0,061(2)	0,1902(7)	6,0(9)
Č ²⁰	0,3136(8)	0,445(2)	0,3508(7)	6.3(9)
C ²¹	0.3425 (8)	0.331(2)	0,3363(7)	5,6(9)
C ²²	0,3494(7)	0,333(2)	0,2790(7)	4,6(8)

TABLE 1. Positional and Thermal Atomic Parameters in $[PPh_3 - Pt(OAc)_2]_2$

PMR spectra were taken on a Bruker WP-80 instrument (for saturated solutions with TMS as internal standard). IR spectra between 4000-400 cm⁻¹ were recorded on a Specord IR-75 instrument using KBr pellets.

Synthesis of $(PPh_3)_2Pt(OAc)_2$. A 0.1 g $(1.35\cdot10^{-4} \text{ mole})$ portion of $PPh_3Pt(OAc)_3Ag$ and 0.07 g $(2.7\cdot10^{-4} \text{ mole})$ portion of PPh_3 were dissolved in 50 ml AcOH. A 0.049 g $(1.35\cdot10^{-4} \text{ mole})$ portion of $Re(CO)_5Br$ in 20 ml AcOH was added to the solution. After 3 h, the precipitate of AgBr was filtered and the mother liquor was evaporated to dryness. From the dried residue, $(PPh_3)_2Pt(OAc)_2$ was extracted with benzene.

<u>Synthesis of [PPh₃Pt(OAc)₂]₂ (II).</u> A 0.2 g $(2.7 \cdot 10^{-4} \text{ mole})$ portion of PPh₃Pt(OAc)₃Ag was dissolved with heating in 100 ml absolute benzene. A fine suspension (ground in a mortar) of 0.045 g $(0.67 \cdot 10^{-4} \text{ mole})$ of Re₂(OAc)₂Cl₄·2H₂O (or Re₂(OAc)₂Br₄·2H₂O) in absolute benzene (ratio Ag:Cl = 1:1) was added to the cooled solution. The mixture remained in an argon atmosphere for 3 days. The precipitate was filtered off and the mother liquor was evaporated on a rotary evaporator to half its volume. Hexane was added until a precipitate formed. After 5-10 min, a small quantity of dark precipitate formed in the solution. This was filtered off. The remaining light yellow solution was evaporated to 10 ml. Complex (II) was precipitated by hexane as a finely crystalline product. The yield based on platinum was quantitative.' Found: C 44.82; H 3.7; Pt 34.21; and P 5.1%. C_{4.4}H_{4.2}O₈P₂Pt₂. Calculated: C 45.91; H 3.65; Pt 33.91; and P 5.39%. IR spectrum (KBr, v, cm⁻¹): 1648, 1630, 1595, 1570, 1430, 1375 (OAC⁻), 1490, 1440, 1110, 770-520 (PPh₃).

Electronic absorption spectra were recorded on a Specord UV-VIS instrument between 50.0-12.5 kK. The structural study of compound (II) was carried out on a Syntex P2₁ autodiffractometer (MoK_a radiation, $\theta/2\theta$ scanning, $2\theta_{max} = 50^{\circ}$). The crystals belong to the monoclinic system, space group C2/c, a = 20.933(2), b = 9.787(1), c = 23.634(3), $\beta = 120.44(8)$, V = 4774.4 Å³, Z = 4, number of nonzero reflections 2034. The structure was solved by the heavy atom method. The positions of the platinum and phosphorus atoms were found from the distribution of interatomic vectors. The oxygen and carbon atoms were found from electron density distributions. The atomic coordinates were refined by anisotropic least squares until R_{hkl} = 0.043 (Table 1).

RESULTS AND DISCUSSION

Reaction of the $PPh_3Pt(OAc)_3Ag$ complex with reagents which contain chloride ions and are capable of precipitating silver as AgCl leads to formation of the anionic fragment

	w, deg	11,9(4) 13,8(5) 13,9(5) 013,9(6) 02,4(6) 07,2(6)
	Angle	PtPC ⁵ PtPC ¹⁷ C ⁵ PC ¹¹ C ⁵ PC ¹¹ C ⁵ PC ¹¹
	e, deg	89,9(3) 89,3(3) 93,3(3) 89,5(4) 87,5(4) 87,5(4) 112(1) 1213(1) 124(2)
$h_3Pt(OAc)_2]_2$	Ang1e	PPt0 ¹ PPt0 ³ 0 ² Pt0 ³ 0 ³ C ³ O ⁴ 0 ³ C ³ O ⁴
s w in [P]	ω, deg	116,5 (1) 81,7 (3) 73,8 (3) 93,8 (3) 93,8 (3) 94,1 (3) 126 (1) 117 (1) 117 (1)
d and Angles	Angle	PtPtP PtPt0 PtPt00 PtPt00 01C100 01C1C2 02C1C2
listances	d, A	1,24(2) 1,26(2) 1,20(2) 1,29(2) 1,42(3)
teratomic I	Bond	00000000000000000000000000000000000000
nportant Ir	d, A	3,101(1) 2,209(4) 2,039(9) 2,11(1) 3,03(1) 3,03(1)
TABLE 2. LI	Bond	Pt-Pt Pt-P Pt-0' Pt-0' Pt-03 Pt-03 Pt-0'

_
2
(OAc)
Pt(
[PPh;
in
З
Angles
and
φ
Distances
Interatomic
Important
2.
ABLE



Fig. 1. Structure of [PPh₃Pt(OAc)₂]₂.

 $[Pt(OAc)_3PPh_3]^-(III)$ [9]. The presence of three acetate groups and the PPh₃ molecule on the Pt atom renders its square planar environment stable. Formation of the $[PPh_3Pt(OAc)_2]_2$ complex in the absence of acetate ligand acceptors is improbable. Dimerization of the co-ordinatively unsaturated PPh₃Pt(OAc)₂ fragments with formation of the binuclear complex with bridging acetate groups can be expected after removal of OAc⁻ from the complex anion (III). The binuclear Re(III) acetate was chosen as the Cl⁻ donor and OAc⁻ acceptor.

Reaction of a solution in absolute C_6H_6 of $PPh_3Pt(OAc)_3Ag$ with cis-Re₂(OAc)₂Cl₄·2H₂O (IV) produces a complex for which the elemental analysis is consistent with the formula $(PPh_3)_2Pt_2(OAc)_4$ as the sole platinum-containing reaction product

$$\frac{PPh_{3}Pt(OAc)_{3}Ag}{(I)} \xrightarrow{Re_{2}(OAc)_{2}X_{4} \cdot 2H_{2}O} (PPh_{3})_{2}Pt_{2}(OAc)_{4}}{(II)}$$
(1)

X = Cl, Br.

Besides this, a dark precipitate and a small quantity of dark green product which contains rhenium and is soluble in benzene are formed. The dark precipitate consisted of unreacted $\text{Re}_2(\text{OAc})_2\text{Cl}_4$ (IV) which was washed away with hot $\text{C}_2\text{H}_5\text{OH}$ and acidified HOAc. The residue, according to elemental analysis, was a mixture of AgCl and Ag. The elemental analysis and IR spectrum of products which contain rhenium showed that compounds of general formula $[\text{Re}(\text{OAc})_4\text{Cl}_m]_n$ ($\ell \geq 2$, $m \leq 4$) are formed. These contain a larger number of OAc⁻ groups than the starting Re(III) complex (vCO 1560, 1545, 1530, 1440, and 1420 cm⁻¹).

The data obtained show that the ligand exchange reaction is also complicated by a redox reaction between Ag(I) and the Re(III) complex [10]. Comparison of electronic absorption spectra of products which contain rhenium in 8 N HCl solution with those of [11] showed that bands corresponding to monomeric forms of Re(IV) (32.33 max, 27.20 sh) and bands indicating the presence of Re₂(III) complexes (38.8 max, 14.25 max) are present. The occurrence of an IR band at 920 cm⁻¹ indicates formation of ReO₂. Thus, the starting Re(III) is partially oxidized to Re(IV) during the reaction.

The reaction occurs more vigorously and reduction of Pt(II) as well as silver begins with reaction of complex (I) with $Re(CO)_5Br$. Addition to the system of an equimolar quantity of PPh_3 leads to formation of $(OAc)_2Pt(PPh_3)_2$ and carbonylphosphine rhenium complexes along with silver reduction

$$PPh_3Pt(OAc)_3Ag + PPh_3 \xrightarrow{\text{Re}(CO)_5Br} (OAc)_2Pt(PPh_3)_2 + Ag^0.$$

In reaction (1), the Re(III) complex acts as a stronger Lewis acid than Pt(II). It strips an acetate ligand from the $[Pt(OAc)_3PPh_3]^-$ anion which is formed and causes its dimerization to complex (II). The dimeric rhenium fragment which is formed after loss of chloride does not react with the platinum anion with formation of heteronuclear complexes [9]. Reaction of $PPh_3Pt(OAc)_3Ag$ with the trans isomer of complex (IV) or analogous bromide complexes produces complex (II) as the sole platinum-containing reaction product.

Single crystals of complex (II) were grown from benzene-hexane solution in order to refine the structure and mode of OAc⁻ group coordination. The crystals consist of neutral

binuclear $[PPh_3Pt(OAc)_2]$ complexes (Fig. 1). The closest surroundings of each platinum atom consists of three O atoms from acetate groups and the P atom of triphenylphosphine. These form a square plane. Two of the acetate groups are bridging and are located in a position cis to each other. One of the O atoms of the third acetate group enters the inner sphere of the platinum atom, whereas the second O atom interacts weakly with the central atom. The dihedral angle between the $O^{1}O^{2}O^{3}P$ planes of the two halves of the dimer is 42.8° and is dictated by the fixed distance between O atoms of the bridging acetate groups and by intramolecular contacts (shortest distances: $C^{11}-C^{12}$, 3.53; $O^{3}-C^{11}$, 3.10; and $O^{3}-C^{13}$, 3.07 Å). The platinum atoms are displaced from the $O^{1}O^{2}O^{3}P$ plane by 0.11 Å toward each other. Repulsion between O^{3} atoms and C^{11} and C^{12} atoms of one of the phenyl rings leads to a shift of the O^{3} and P atoms in opposite directions parallel to the Pt-Pt line. As a result, the Pt-Pt-P angle increases to 116.5° whereas the Pt-Pt-O^{3} angle decreases to 98.1°. Preservation of the planar environment of the platinum atom is achieved by a parallel shift of the bridging acetate groups such that the Pt-Pt-O^{1} angle becomes larger (81.7°, 0¹ atom in the position trans to O^{3} atom) and the Pt-Pt-O² angle becomes smaller (73.8°, 0² atom in the position trans to the P atom) (Table 2).

Two features draw attention upon examination of the structure of complex (II). The Pt atoms are displaced from the planes toward each other, and the Pt atom interacts with the 0⁴ atom. The approach of the Pt atoms can be explained first by a Pt-Pt bonding interaction and second by a tendency toward a decrease of Pt-O-C angles at O atoms of the bridging acetate groups. The distance between Pt atoms (3.101(1) Å) is apparently typical for weak interaction without electronic bonding. Therefore, the displacement of platinum atoms from the planes is probably caused by the decrease of Pt-O-C angles and their approximation to the optimal values. The C-C bond lengths in the phenyl rings are 1.36-1.45 Å and the C-C-C angles are 116-123°.

Thus, complex (II) in the solid is the trans isomer. Signals of the three OAc groups at 1.44, 1.47, and 1.55 ppm are observed in the PMR spectrum of complex (II) in CD_2Cl_2 . If only the trans isomer existed in solution, then only two OAc⁻ group signals would be observed since the bridging groups in this case would be equivalent. The appearance in the spectrum of the third signal indicates a cis-trans isomerization of the complex in CD_2Cl_2



Reduction of complex (II) by formic acid led initially to exchange of acetate ligands by formate

$$[PPh_3Pt(OAc)_2]_2 + 4HCOOH \rightleftharpoons [PPh_3Pt(OOCH)_2]_2 + 4AcOH$$

GLC showed that formation of HOAc in a quantity corresponding to exchange of all OAc⁻ groups by HCOO⁻ occurs after 45 min in solution. Reduction of complex (II) occurs with an induction period of 6 h and is accompanied by appearance of benzene (GLC monitoring). Thus, formation of AcOH is related to exchange of acetate ligands and not to reduction of complex (II).

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NEW CHIRAL SYNTHON OF ELECTROPHILIC GLYCINE AND ITS REACTIONS WITH METALLOORGANIC, C-H, N-H, AND O-H COMPOUNDS FOR THE ASYMMETRIC SYNTHESIS OF α -SUBSTITUTED α -AMINO ACIDS

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A new chiral synthon of the electrophilic glycine - the Ni(II) complex of the Schiff base of L-N-benzylprolylorthoaminobenzophenone with α-bromoglycine was synthesized. The reaction of this complex with nucleophiles led to the isolation of complexes of L- and D-2-amino-2-dimethylaminoacetic acid, L- and D-2amino-2-phenoxyacetic acid, 3,3-di(carbethoxy)alanine, and norleucine. The decomposition of the 3,3-di(carbethoxy)alanine and norleucine complexes led to the synthesis of L-aspartic acid and L-norleucine with the enantiomeric purity of 80 and 68% correspondingly.

Reactions proceeding via the carbanions of derivatives of glycine and alanine have been intensively utilized for the asymmetric synthesis of α -amino acids [1]. Far fewer investigations were devoted to reactions proceeding via the carbocation (the utilization of electrophilic chiral synthons) [2-7]; however they may prove to be effective for the synthesis of some α -amino acids which cannot be obtained via the carbanions. We undertook to attempt the isolation of electrophilic synthons of glycine starting from the previously described [8] Ni(II) complex of the Schiff base of L-N-benzylprolylorthoaminobenzophenone and glycine (I). The present work describes the synthesis of the Ni(II) complex of the Schiff base of L-N-benzylprolylorthoaminobenzophenone and α -bromoglycine (II), and its reactions with malonic ester, methanol, phenol, dimethylamine, and metalloorganic compounds.

RESULTS AND DISCUSSION

The interaction of (I) with bromine in the presence of water in MeOH led to the redcolored complex (III) with the diastereomeric excess of L,L > 95% (Scheme 1)



 $R = OMe(III), n-Bu(V), NMe_2(VI), OPh(VII), CH(COOEt)_2(VIII).$

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