Synthesis, structure, and properties of organoplatinum(II) derivatives of diphenyl ether

T. V. Baukova,[a]* *N. A. Oleinikova,*[a] *and L. G. Kuz'mina*[b]

[a]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Science,*
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085
[b]*N. S Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Science,*
31 Leninsky prosp., 117907 Moscow, Russian Federation.
Fax: +7 (095) 954 1279

New mono- and disubstituted organoplatinum(II) derivatives of diphenyl ether, *cis*-$(PhOC_6H_4$-*o*$)PtCl(PPh_3)_2$ and (*o*-$C_6H_4OC_6H_4$-*o*)$Pt(PPh_3)_2$, were synthesized by the reaction of 2,2′-dilithium diphenyl oxide with *cis*-$Cl_2Pt(PPh_3)_2$. Transmetallation of $(PhOC_6H_4$-*o*$)AuPPh_3$ with *cis*-$Cl_2Pt(PPh_3)_2$ was studied using ^{31}P NMR monitoring. This reaction proceeds with the retention of configuration to afford $ClAuPPh_3$ and *cis*-$(PhOC_6H_4$-*o*$)PtCl(PPh_3)_2$ under kinetically controlled conditions. The latter complex irreversibly isomerizes into the *trans* isomer in the presence of equimolar quantities of $ClAuPPh_3$, whereas, in the presence of free PPh_3, this isomerization is reversible. The structures of the obtained diphenyl oxide derivatives of platinum were confirmed by ^{31}P NMR and FAB mass spectrometry. It was established by X-ray structural analysis that in the *cis*-$(PhOC_6H_4$-*o*$)PtCl(PPh_3)_2$ complex, the Pt atom is in a nearly square-planar coordination, and secondary intramolecular Pt...O interaction occurs.

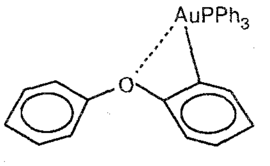
Key words: hypercoordination organoplatinum(II) compounds, diphenyl ether, synthesis, X-ray diffraction study, isomerization, ^{31}P NMR and FAB mass spectrometry.

Previously we synthesized hypercoordinated σ-organogold(I) compounds of a new class, mono- and diaurated *ortho*-derivatives of diphenyl ether of three different types (**1**, **2**, and **3**), and performed a comparative study of their molecular and electronic structures (Ref. 1).

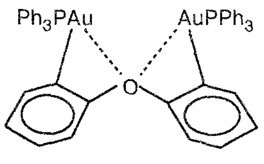
It was established that complexes **1** and **2** are stabilized through additional intramolecular bonds between the Au^I atoms and the lone electron pairs of the O atom of the organic ligand; complex **3** is stabilized through aurophilic Au...Au interaction in the three-membered carbometallocycle of the molecule.[1]

In an effort to estimate the effect of the nature of the metal on the character of the secondary interactions of the metal atom with the O atom of the organic ligand in complexes of types **1** and **2** (when the Au^I atom is replaced by a Pt^{II} atom), in this work we for the first time synthesized and studied the structures of the corresponding hypercoordinated mono- and disubstituted organoplatinum(II) *ortho*-derivatives of diphenyl ether.

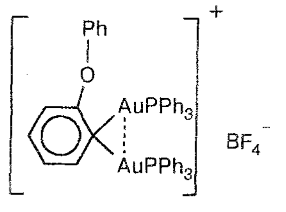
We synthesized the platinum complexes,
cis-$(PhOC_6H_4$-*o*$)PtCl(PPh_3)_2$ (*cis*-**4**)
and (*o*-$C_6H_4OC_6H_4$-*o*)$Pt(PPh_3)_2$ (**5**), by the reaction of *cis*-$Cl_2Pt(PPh_3)_2$ with the 2,2′-dilithium derivative of diphenyl ether, which was prepared by metallation of diphenyl ether with *n*-BuLi[2] in an ether—THF medium.



1



2



3

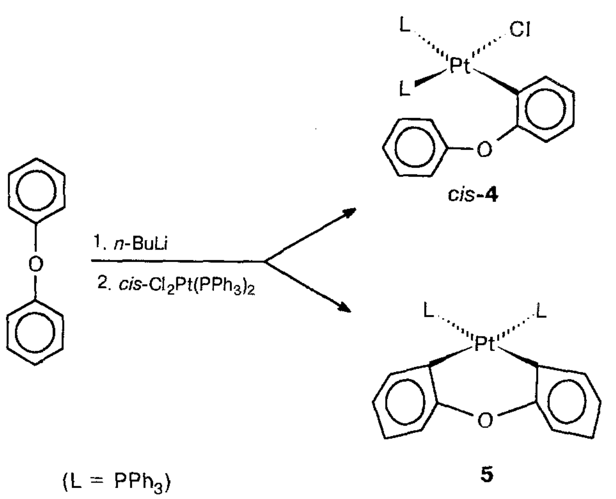
The reaction affords a mixture of complexes *cis*-**4** and **5**. However, predominantly complex *cis*-**4** or **5** may be obtained depending on the time of the reaction.

Thus, when the reaction with *cis*-$Cl_2Pt(PPh_3)_2$ proceeds for approximately 1.5 h, the *cis* configuration of the initial complex is retained and the monosubstituted

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 1814—1820, October, 1994.

derivative of platinum *cis*-**4** is predominantly formed. To prepare predominantly disubstituted derivative **5**, an increase in the time of the reaction to two days is required.

The structures of compounds *cis*-**4** and **5** were confirmed by elemental analysis, ^{31}P NMR, and FAB (fast-atom bombardment) mass spectrometry. The structure of complex *cis*-**4** was established by X-ray diffraction analysis.



Results and Discussion

The structure of the *cis*-**4** complex is shown in Fig. 1; the bond lengths and bond angles are given in Tables 1 and 2.

In complex *cis*-**4**, the mutual *cis* arrangement of the two PPh_3 ligands occurs. The Pt atom is in a slightly tetrahedrally distorted planar-square coordination: the dihedral angle between the planes P(1)PtP(2) and Cl(1)PtC(1) is 7.3°.

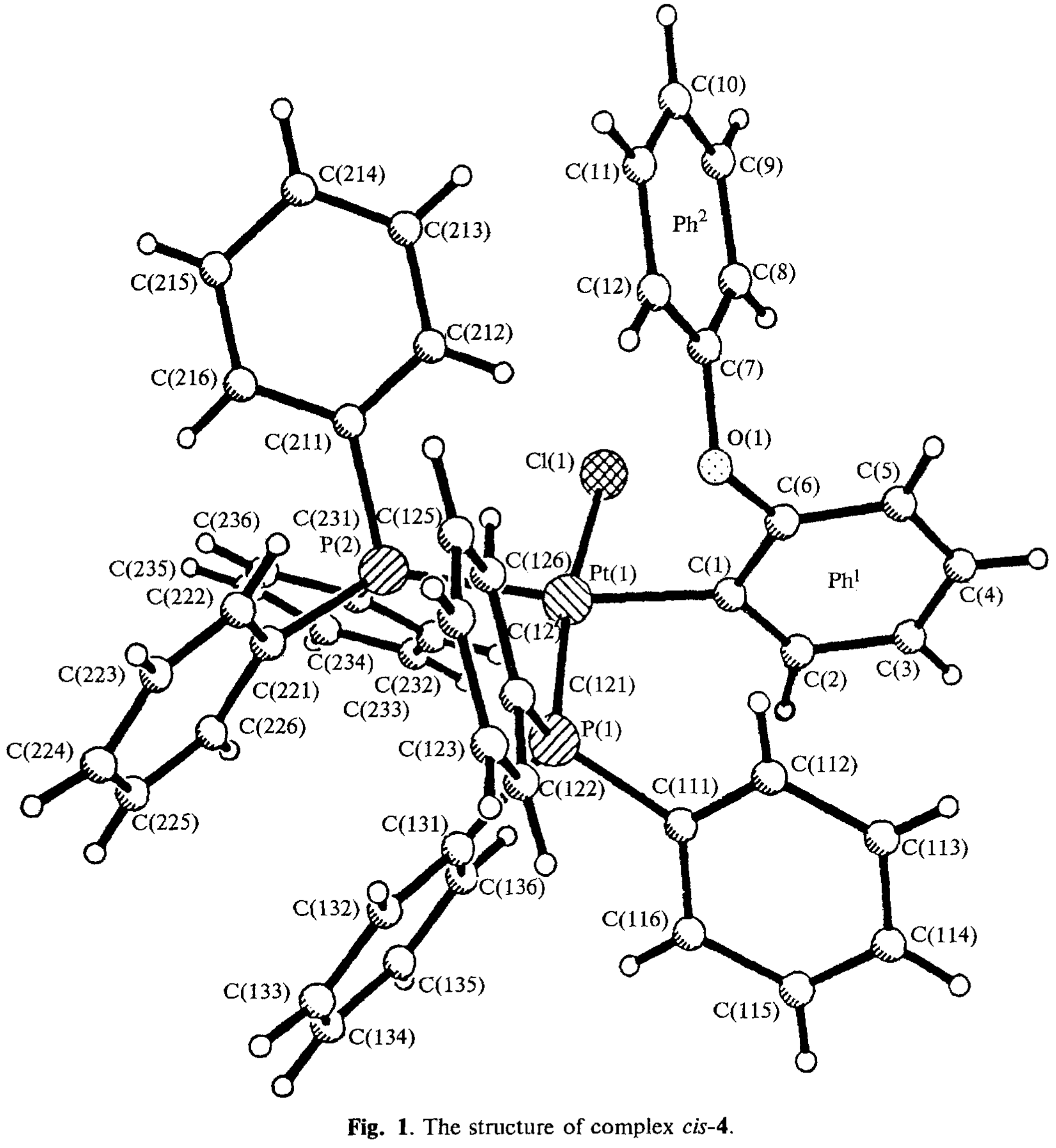


Fig. 1. The structure of complex *cis*-**4**.

Table 1. Bond lengths (*d*) in complex *cis*-**4**

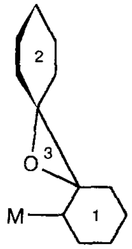
Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
Pt(1)—P(1)	2.230(2)	P(1)—C(121)	1.820(8)	C(212)—C(213)	1.37(2)
Pt(1)—Cl(1)	2.352(2)	P(2)—C(211)	1.837(9)	C(214)—C(215)	1.37(2)
P(1)—C(111)	1.83(1)	P(2)—C(231)	1.83(1)	C(221)—C(222)	1.38(1)
P(1)—C(131)	1.81(1)	O(1)—C(7)	1.36(1)	C(222)—C(223)	1.39(2)
P(2)—C(221)	1.837(9)	C(1)—C(6)	1.38(1)	C(224)—C(225)	1.38(2)
O(1)—C(6)	1.40(1)	C(3)—C(4)	1.36(2)	C(231)—C(232)	1.34(2)
C(1)—C(2)	1.39(1)	C(5)—C(6)	1.38(2)	C(232)—C(233)	1.39(2)
C(2)—C(3)	1.38(2)	C(7)—C(12)	1.38(2)	C(234)—C(235)	1.32(3)
C(4)—C(5)	1.34(2)	C(9)—C(10)	1.35(2)	C(131)—C(136)	1.41(1)
C(7)—C(8)	1.37(2)	C(11)—C(12)	1.38(2)	C(133)—C(134)	1.36(2)
C(8)—C(9)	1.36(2)	C(111)—C(116)	1.39(2)	C(135)—C(136)	1.37(2)
C(10)—C(11)	1.36(2)	C(113)—C(114)	1.37(3)	C(211)—C(216)	1.36(2)
C(111)—C(112)	1.38(2)	C(115)—C(116)	1.38(2)	C(213)—C(214)	1.35(2)
C(112)—C(113)	1.41(2)	C(121)—C(126)	1.39(1)	C(215)—C(216)	1.37(2)
C(114)—C(115)	1.33(4)	C(123)—C(124)	1.37(2)	C(221)—C(226)	1.39(2)
C(121)—C(122)	1.39(1)	C(125)—C(126)	1.37(1)	C(223)—C(224)	1.36(2)
C(122)—C(123)	1.39(1)	C(131)—C(132)	1.39(1)	C(225)—C(226)	1.38(2)
C(124)—C(125)	1.36(2)	C(132)—C(133)	1.39(2)	C(231)—C(236)	1.34(3)
Pt(1)—P(2)	2.354(2)	C(134)—C(135)	1.36(2)	C(233)—C(234)	1.32(2)
Pt(1)—C(1)	2.044(9)	C(211)—C(212)	1.38(2)	C(235)—C(236)	1.38(4)

Table 2. Bond angles (ω) in complex *cis*-**4**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
P(1)—Pt(1)—P(2)	99.35(8)	C(211)—P(2)—C(221)	101.4(4)	C(211)—C(216)—C(215)	122.0(1)
P(1)—Pt(1)—C(1)	90.5(3)	C(221)—P(2)—C(231)	103.7(5)	P(2)—C(221)—C(226)	122.1(8)
P(2)—Pt(1)—C(1)	168.9(3)	Pt(1)—C(1)—C(2)	121.6(7)	C(221)—C(222)—C(223)	120.5(9)
Pt(1)—P(1)—C(111)	114.9(3)	C(2)—C(1)—C(6)	116.9(8)	C(223)—C(224)—C(225)	120.0(1)
Pt(1)—P(1)—C(131)	113.0(3)	C(2)—C(3)—C(4)	122.0(1)	C(221)—C(226)—C(225)	120.0(1)
C(111)—P(1)—C(131)	101.2(4)	C(4)—C(5)—C(6)	119.0(1)	P(2)—C(231)—C(236)	124.0(1)
Pt(1)—P(2)—C(211)	109.5(3)	O(1)—C(6)—C(5)	118.7(9)	C(231)—C(232)—C(233)	122.0(1)
Pt(1)—P(2)—C(231)	112.4(4)	O(1)—C(7)—C(8)	125.1(9)	C(233)—C(234)—C(235)	118.0(2)
C(211)—P(2)—C(231)	106.2(5)	C(8)—C(7)—C(12)	119.0(1)	C(231)—C(236)—C(235)	123.0(3)
C(6)—O(1)—C(7)	119.1(8)	C(8)—C(9)—C(10)	122.0(1)	C(112)—C(113)—C(114)	120.0(2)
Pt(1)—C(1)—C(6)	121.1(7)	C(10)—C(11)—C(12)	121.0(1)	C(114)—C(115)—C(116)	122.0(2)
C(1)—C(2)—C(3)	120.0(1)	P(1)—C(111)—C(112)	118.1(8)	P(1)—C(121)—C(122)	120.8(7)
C(3)—C(4)—C(5)	120.0(1)	C(112)—C(111)—C(116)	120.0(1)	C(122)—C(121)—C(126)	119.1(8)
O(1)—C(6)—C(1)	118.4(8)	C(8)—C(9)—C(10)	122.0(1)	C(122)—C(123)—C(124)	120.0(1)
C(1)—C(6)—C(5)	123.0(1)	C(10)—C(11)—C(12)	121.0(1)	C(124)—C(125)—C(126)	122.0(1)
O(1)—C(7)—C(12)	115.5(9)	P(1)—C(111)—C(112)	118.1(8)	P(1)—C(131)—C(132)	123.4(7)
C(7)—C(8)—C(9)	119.0(1)	C(112)—C(111)—C(116)	120.0(1)	C(132)—C(131)—C(136)	118.5(9)
C(9)—C(10)—C(11)	118.0(1)	C(111)—C(112)—C(113)	118.0(1)	C(132)—C(133)—C(134)	121.0(1)
C(7)—C(12)—C(11)	119.0(1)	C(113)—C(114)—C(115)	121.0(2)	C(134)—C(135)—C(136)	121.0(1)
P(1)—C(111)—C(116)	121.6(8)	C(111)—C(116)—C(115)	119.0(1)	P(2)—C(211)—C(212)	119.7(7)
C(7)—C(8)—C(9)	119.0(1)	P(1)—C(121)—C(126)	120.1(7)	C(212)—C(211)—C(216)	118.0(1)
C(9)—C(10)—C(11)	118.0(1)	C(121)—C(122)—C(123)	119.6(9)	C(212)—C(213)—C(214)	122.0(1)
C(7)—C(12)—C(11)	119.0(1)	C(123)—C(124)—C(125)	120.0(1)	C(214)—C(215)—C(216)	120.0(1)
P(1)—C(111)—C(116)	121.6(8)	C(121)—C(126)—C(125)	119.6(9)	P(2)—C(221)—C(222)	118.5(7)
P(1)—Pt(1)—Cl(1)	171.90(8)	P(1)—C(131)—C(136)	117.9(7)	C(222)—C(221)—C(226)	119.4(9)
P(2)—Pt(1)—Cl(1)	87.32(8)	C(131)—C(132)—C(133)	119.0(1)	C(222)—C(223)—C(224)	120.0(1)
Cl(1)—Pt(1)—C(1)	83.3(3)	C(133)—C(134)—C(135)	120.0(1)	C(224)—C(225)—C(226)	120.0(1)
Pt(1)—P(1)—C(121)	115.8(3)	C(131)—C(136)—C(135)	120.0(1)	P(2)—C(231)—C(232)	120.6(9)
C(111)—P(1)—C(121)	102.2(4)	P(2)—C(211)—C(216)	122.1(8)	C(232)—C(231)—C(236)	115.0(2)
C(121)—P(1)—C(131)	108.3(4)	C(211)—C(212)—C(213)	120.0(1)	C(232)—C(233)—C(234)	120.0(1)
Pt(1)—P(2)—C(221)	122.0(3)	C(213)—C(214)—C(215)	118.0(1)	C(234)—C(235)—C(236)	121.0(3)

The Pt—P(1) and Pt—P(2) bond lengths (2.230 and 2.354 Å, respectively) are essentially different, which is due to the different electron-acceptor properties of the ligands, the Cl atom, and the diphenyl oxide C atom,

Table 3. Selected geometric parameters (dihedral angles between planes 1, 2, and 3) and the M...O distances (M = Au and Pt) for complexes **1**, **2**, and *cis*-**4**



Compound	Angle 1/2 /deg	Angle 1/3 /deg	Angle 2/3 /deg	Distance M...O/Å	Orbital O
1	99.2	83.8	4.9	3.23	p
2	100.6	75.5	6.9	3.04	sp^2
				3.25	p
cis-**4**	104.5	67.4	12.7	3.16	p

which are in a *trans* orientation with respect to the triphenylphosphine ligands. In the other previously studied analogous planar-square *cis* complexes of Pt^{II}, in which the Cl ligands are *trans* to the phosphine ligands, the Pt—P bond lengths are 2.228 and 2.229 Å (Ref. 3), and 2.237 and 2.238 Å (Ref. 4). In Pt complexes in which the carbon atoms of organic ligands are *trans* with respect to the bond under consideration, the Pt—P bond lengths are 2.322 and 2.337 (Ref. 5), and 2.321 and 2.326 (Ref. 6), and 2.282 Å (Ref. 7). The variety of Pt—P bond lengths for the two given groups of structures (2.228—2.238 and 2.282—2.337 Å) are substantially different; the bond lengths that we determined coincide with the lower limit of the former range and slightly exceed the upper limit of the latter one. The Pt—Cl bond length (2.352 Å) is very close to those reported previously: 2.344, 2.360 (Ref. 3), 2.345, and 2.356 Å (Ref. 4); the Pt—C(1) bond (2.044(9) Å) is slightly shorter than those reported previously: 2.09, 2.11 Å (Ref. 5), and 2.064 Å (Ref. 7).

The plane of the benzene ring C(1)...C(6) in complex *cis*-**4** is nearly orthogonal to the mean coordination plane of the Pt atom; the dihedral angle between these planes is 84.2°.

Let us consider the conformation of the PhOPh ligand in detail and compare it with those reported for $(AuPPh_3)C_6H_4OPh$ (**1**) and $(AuPPh_3)C_6H_4OC_6H_4(AuPPh_3)$ (**2**).[1] The selected geometric parameters for the PhOPh ligand in complexes *cis*-**4**, **1**, and **2** are given in Table 3. The dihedral angles between the phenyl planes in the three structures are nearly the same (104.5 in *cis*-**4**, 99.2 in **1**, and 100.6° in **2**). One of the phenyl rings (Ph^2) (in *cis*-**4** and **1**, this ring is the ring not coordinated to the metal atom) is nearly coplanar with the COC plane (the dihedral angles in *cis*-**4**, **1**, and **2** are 12.7, 4.9, and 6.9°, respectively), whereas the second phenyl ring (Ph^1) is substantially twisted (the dihedral angles in *cis*-**4**, **1**, and **2** are 67.4, 83.8, and 75.5°, respectively). The reported data point to the qualitative similarity of the conformations of the diphenyl oxide ligand in these three structures.

Our semi-empirical quantum-chemical calculations of the free molecule of diphenyl ether by the MNDO method showed that in this molecule, the plane of one ring (Ph^2) is coplanar with the COC plane, whereas the plane of the second ring (Ph^1) is normal to the COC plane. This geometry of the free PhOPh molecule is governed by both electronic factors (the conjugation between the lone electron pair in the p orbital of the O atom and the π^* orbitals of the Ph^2 benzene ring) and steric factors. When the Ph^1 ring is twisted out of the PhO plane by 90°, the steric interactions are minimal. However, the molecular-mechanics calculations of the conformational possibilities of the Ph^1 ring with the fixed conformation of the Ph^2 ring (the Ph^2 plane is coplanar with the COC plane) demonstrated that rotation of the Ph^2 group about the C—O bond from the calculated value of 90° to ~40° is virtually free.

Therefore, in molecules of *cis*-**4**, **1**, and **2** with the found conformations of the diphenyl oxide ligand, on the one hand, the steric interactions are minimized and, on the other hand, this conformation is favorable for O...π-system (the Ph ring) electron interaction.

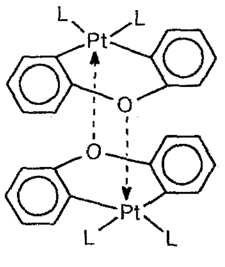
The O—C(7) bond length (1.36(1) Å) is smaller than the O—C(6) bond length (1.40(1) Å) which indicates conjugation between the O atom and the Ph^2 benzene ring in *cis*-**4**. This effect was also found in the molecule of complex **1** (see Ref. 1). In the structures of the platinum complex *cis*-**4** and gold complexes **1** and **2**, the p orbital of the lone electron pair of the O atom involved in conjugation with the Ph^2 benzene ring points toward the axial position of the metal atom. The Pt...O distance (3.16 Å), is comparable to the sum of the van der Waals radii of these atoms (~3.1 Å) and is attributable to a secondary bond. The analogous distances in gold derivatives **1** and **2** are 3.23 and 3.04 (in **1**), and 3.25 Å (in **2**), which also corresponds to secondary Au...O bonds.[1]

In the ^{31}P NMR spectrum of platinum complex *cis*-**4**, the signals of an AX system of two nonequivalent phosphorus nuclei of phosphine ligands (the chemical shifts are 16.89 and 20.64 ppm) and the corresponding side signals (splitting by the ^{195}Pt magnetic isotope, the natural abundance is 33.8 %, the spin is 1/2) were observed. In the spectrum of disubstituted platinum complex **5**, the signal of two equivalent phosphorus atoms of the PPh_3 ligands occurs (23.52 ppm) with corresponding splitting by the ^{195}Pt nuclei.

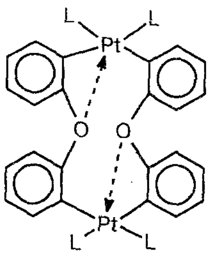
The FAB mass spectrometric characteristics point to a substantial difference in the structures of mono- and disubstituted platinum complexes *cis*-**4** and **5**. The mass spectrum of *cis*-$(PhOC_6H_4\text{-}o)PtCl(PPh_3)_2$ (*cis*-**4**) has a molecular ion peak (*m/z* 924) and peaks corresponding to its successive fragmentation associated with the loss of ligands at the Pt atom.

In mass spectrum of disubstituted platinum complex **5**, both the molecular ion peak of the mononuclear unit $O(C_6H_4)Pt(PPh_3)_2$ (*m/z* 888) and the peaks of heavier ions (high intensity peaks) are observed, such as $[M+Pt+2PPh_3]^+$ (*m/z* 1606), $[M+H+PhOC_6H_4+2PPh_3]^+$ (*m/z* 1582), $[M+H+C_6H_4OC_6H_4+Pt]^+$ (*m/z* 1253), *etc.*, which correspond to the successive fragmentation of the dimeric bimetallic platinum complex of the same molecular formula, $\{O(C_6H_4)_2Pt(PPh_3)_2\}_2$.

Based on the different character of the mass-spectral data for complexes *cis*-**4** and **5**, it may be suggested that disubstituted complex **5** (unlike monosubstituted complex *cis*-**4**) in the solid state (or at least under conditions of FAB mass-spectrometric study) exhibits a dimeric structure with secondary intermolecular Pt...O bonds, for example, of the type **5a** or **5b** (rather than intramolecular Pt...O bonds, as in the case of monosubstituted complex *cis*-**4**). The formation of such dimeric bimetallic structures is typical in particular of acetylacetonate complexes of Pt^{II} and Pt^{IV} (see Refs. 8, 9).



5a



5b

In an effort to perform a comparative study of the chemical features of Au^I and Pt^{II} organic derivatives of diphenyl ether and to examine the possibility of the synthesis of monosubstituted platinum derivative **4** from the corresponding gold derivative **1**, we studied the reaction between gold complex **1** and *cis*-$Cl_2Pt(PPh_3)_2$ at a 1 : 1 ratio in CH_2Cl_2. This interaction (after 28 days) results in transmetallation and exchange of the Au atom in **1** with the Pt atom (Eq. 1).

$$\mathbf{1}\ \xrightarrow[-\,\mathrm{ClAuPPh_3}]{cis\text{-}\mathrm{Cl_2Pt(PPh_3)_2}}\ cis\text{-}\mathbf{4}\ \xrightarrow{\mathrm{ClAuPPh_3}}\ trans\text{-}\mathbf{4} \qquad (1)$$

It was established that under kinetically controlled conditions, the reaction proceeds with the retention of the *cis* configuration of the initial platinum complex and affords complex *cis*-**4**. As indicated above, pure complex *cis*-**4** is stereochemically stable; however, under the conditions of reaction (1) in the presence of $ClAuPPh_3$, *cis*-**4** completely isomerizes into *trans* isomer **4**. ^{31}P NMR monitoring of reaction (1) allows observation of the successive accumulation in the reaction mixture of first *cis* isomer **4** and then *trans* isomer **4**.

A special-purpose experiment demonstrated that complex *cis*-**4** irreversibly isomerizes into complex *trans*-**4** (yield is 83 %) in the presence of equimolar quantities of $ClAuPPh_3$ (under the same conditions) after 20 days.

Taking into account the duration of transmetallation (1) and the possible presence of traces of free PPh_3 in the reaction mixture (as a result of insignificant decomposition of complexes **1** and **4**), which is in principle capable of catalyzing *cis-trans* isomerization of square-planar platinum complexes,[10,11] we specially examined the possibility of isomerization of platinum complex *cis*-**4** into *trans*-**4** under the action of PPh_3.

It turns out that in the presence of traces of PPh_3, complex *cis*-**4** (in CH_2Cl_2) undergoes no isomerization into the *trans* isomer. However, when the reaction mixture is boiled in the presence of equimolar quantities of PPh_3, *cis-trans* isomerization proceeds but it is reversible. The process terminates after just 7 days (according to ^{31}P NMR data), when equilibrium between *cis* and *trans* complexes **4** in the ratio of 4 : 1 is established (Eq. 2).

$$\begin{tikzcd}
cis\text{-}(\mathrm{PhOC_6H_4}\text{-}o)\mathrm{PtCl(PPh_3)_2} \arrow[d, shift left, "\mathrm{PPh_3}"] \arrow[d, leftarrow, shift right, "cis\text{-}\mathbf{4}\ (80\ \%)"'] \\
{[\mathrm{PhOC_6H_4}\text{-}o)\mathrm{PtCl(PPh_3)_3}]} \arrow[d, shift left] \arrow[d, leftarrow, shift right, "\mathbf{4b}"'] \\
{[\mathrm{PhOC_6H_4}\text{-}o)\mathrm{Pt(PPh_3)_3}]^+\mathrm{Cl}^-} \arrow[d, shift left, "-\,\mathrm{PPh_3}"] \arrow[d, leftarrow, shift right, "\mathbf{4c}"'] \\
trans\text{-}(\mathrm{PhOC_6H_4}\text{-}o)\mathrm{PtCl(PPh_3)_2} \\
trans\text{-}\mathbf{4}\ (20\ \%)
\end{tikzcd} \qquad (2)$$

A similar situation is known for *cis-trans* isomerization of other aryl complexes of platinum of the type $ArPtHal(PPh_3)_2$.[10,11]

The different effects of free PPh_3 and $ClAuPPh_3$ on the equilibrium composition of mixtures of isomers in reactions (1) and (2) points to the fact that they are actually not catalysts of the process, which affect its rate, but are directly involved in the reaction and determine (differently) the equilibrium of the isomerization.

Experimental

^{31}P NMR spectra were recorded on a Bruker CXP 200 instrument (81 MHz) in CH_2Cl_2, with a 85 % H_3PO_4 solution as the external standard. Mass spectra were measured on a Kratos concept instrument, the energy of bombarding atoms (Cs) was 8 keV; 3-nitrobenzyl alcohol was used as the matrix.

Compounds **4** and **5** were synthesized under a dry argon atmosphere. The solvents were distilled just prior to use over sodium benzophenone ketyl under an argon atmosphere.

The reaction was monitored by TLC on Silufol UV-254 plates (Czechoslovakia). The plates were developed by heating.

***Cis*-chloro-2-phenoxyphenylbis(triphenylphosphine)platinum** (*cis*-**4**). A solution of the 2,2′-dilithium derivative of diphenyl ether prepared by boiling a 1.78 *N* hexane solution (2.15 mL, 3.8 mmol) of *n*-BuLi for 5 h with diphenyl ether* (0.28 g, 1.6 mmol) in 8 mL of ether and 5 mL of THF, was added portionwise with stirring to a suspension of *cis*-$Cl_2Pt(PPh_3)_2$ (0.50 g, 0.64 mmol) in 17 mL of THF. Then the reaction mixture was stirred for 1 h and decomposed with water. The organic extract was dried with calcined K_2CO_3 and evaporated at reduced pressure to dryness. The oily residue was treated with pentane (3×5 mL) and then dried to afford 0.54 g of a mixture of *cis*-**4** and **5** in a ~4 : 1 ratio (according to the ^{31}P NMR spectrum) as a powdered yellow material. The product was reprecipitated from a minimum quantity of $CHCl_3$ with excess petroleum ether. The precipitate was isolated, washed with pentane, and dried. Reprecipitation from a chloroform solution with ether afforded *cis*-**4** (0.39 g, 68 %), m.p. 174—175 °C (with decomposition). Found (%): C, 62.29; H, 4.43; P, 6.70. $C_{48}H_{39}ClOP_2Pt$. Calculated (%): C, 62.37; H, 4.28; P, 6.70. ^{31} P NMR (δ, *J*/Hz): 16.89 (d, P_A—$^{194,196,198}Pt$ $^2J_{P(A)-P(X)}$ = 15); 16.89 (dd, $^2J_{P(A)-P(X)}$ = 15, $^1J_{P(A)-{}^{195}Pt}$ = 4388); 20.64 (d, P_X—$^{194,196,198}Pt$ $^2J_{P(X)-P(A)}$ = 15); 20.64 (dd, $^2J_{P(X)-P(A)}$ = 15, $^1J_{P(X)-{}^{195}Pt}$ = 1740). Mass spectrum, *m/z* (I_{rel} (%)): 924 $[M]^+$ (50), 888 $[M-Cl]^+$ (30), 755 $[M-PhOC_6H_4]^+$ (10), 719 $[M-PhOC_6H_4-Cl]^+$ (100), 626 $[M-PPh_3-Cl]^+$ (15), 456 $[M-PhOC_6H_4-Cl-PPh_3]^+$ (30).

The combined mother liquors were evaporated to dryness; the residue was reprecipitated from a chloroform solution with ethanol to afford **5** (0.09 g, 15 %), m.p. 122—123 °C (with decomposition, from a $CHCl_3$—EtOH mixture). Found (%): C, 65.35; H, 4.86; P, 6.03. $C_{48}H_{38}OP_2Pt$. Calculated (%): C, 64.93; H, 4.31; P, 6.01. ^{31} P NMR (δ, *J/Hz*): 23.52 (s, P—$^{194,196,198}Pt$); 23.52 (d, $^1J_{P-{}^{195}Pt}$ = 2100). Mass spectrum, *m/z*, (I_{rel} (%)): 1606 $[M+Pt+2PPh_3]^+$ (20), 1582 $[M+H++PhOC_6H_4+2PPh_3]^+$ (18), 1508 $[M+PhOC_6H_4+PPh_3+PPh_2]^+$ (100), 1344 $[M+Pt+PPh_3]^+$ (24), 1320 $[M+H+PhOC_6H_4++PPh_3]^+$ (35), 1253 $[M+H+C_6H_4OC_6H_4+Pt]^+$ (7), 1178 $[2Pt+3PPh_3+H]^+$ (20), 888 $[M+H]^+$ (10), 719 $[M-PhOC_6H_4]^+$ (90), 455 $[M-PhOC_6H_4-PPh_3]^+$ (42), 378 $[M-PhOC_6H_4-PPh_3-Ph-nH]^+$ (48).

Diphenyl oxide-2,2′-diylbis(triphenylphosphine)platinum (5). A solution of the 2,2′-dilithium derivative of diphenyl ether obtained by boiling a 1.80 *N* hexane solution (1.20 mL, 2.1 mmol) of *n*-BuLi, diphenyl ether (0.16 g, 0.9 mmol) in 4 mL of ether, and 2 mL of THF, was added portionwise with stirring to a suspension of *cis*-$Cl_2Pt(PPh_3)_2$ (0.20 g, 0.25 mmol) in 15 mL of THF. The reaction mixture was stirred for 3 h, stored for 2 days at +5 °C, then filtered off, and treated with water. The organic layer was isolated, and the aqueous layer was extracted with ether. The combined organic extracts were dried with calcined K_2CO_3 and evaporated *in vacuo* to dryness. The residue was treated with pentane (5×10 mL) and reprecipitated from $CHCl_3$ with ethanol to afford **5** (0.08 g, 36 %) as a powdered yellow material, m.p. 123—125 °C (with decomposition, from a $CHCl_3$—EtOH mixture).

Complex **4** (m.p. 174—175 °C with decomposition, from a $CHCl_3$—hexane mixture) was isolated from the mother liquors in a 0.02 g (9 %) yield.

The reaction of 2-(triphenylphosphinaurio)diphenyl oxide (1) with *cis*-$Cl_2Pt(PPh_3)_2$. A solution of complex **1** (0.20 g, 0.3 mmol) and *cis*-$Cl_2Pt(PPh_3)_2$ (0.25 g, 0.3 mmol) in 20 mL of CH_2Cl_2 was stirred for 28 days. The course of the reaction was monitored every 2 days by TLC in benzene (R_f for complexes: **1** 0.66; $ClAuPPh_3$ 0.54; *cis*-**4** 0.3; *trans*-**4** 0.2; *cis*-$Cl_2Pt(PPh_3)_2$ 0) and by recording ^{31}P NMR spectra of the reaction mixture (δ; complex **1** 43.15 (s); *cis*-$Cl_2Pt(PPh_3)_2$ 3.89 (s, P—$^{194,196,198}Pt$), 13.89 (d, $^1J_{P-{}^{195}Pt}$ = 2678 Hz); $ClAuPPh_3$ 33.15 (s); after 5 days the signal of an unidentified intermediate complex appears in the spectrum at 28.86 ppm, then the signal gradually increases, and disappears at the end of the reaction) After the completion of the reaction, the ^{31}P NMR spectrum shows only signals of phosphorus of the $ClAuPPh_3$ complex and *trans*-**4**.

The reaction solution was filtered off and evaporated *in vacuo* to dryness. For separating the components, the solid residue, which is a mixture of $ClAuPPh_3$ and *trans*-**4**, was twice chromatographed on plates (17×24 cm) with Al_2O_3 (Brockmann II) in benzene. Elution with chloroform and evaporation of the solutions afforded $ClAuPPh_3$ (0.12 g, 75 %), m. p. 243—244 °C (from a $CHCl_3$—petroleum ether mixture) (see Ref. 12: m. p. 243—244 °C; from a $CHCl_3$—petroleum ether mixture), and *trans*-**4** (0.29 g, 89 %), m.p. 238—240 °C (with decomposition, from a CH_2Cl_2—petroleum ether mixture). Found (%): C, 61.83; H, 4.49. $C_{48}H_{39}ClOP_2Pt$. Calculated (%): C, 62.37; H, 4.28. ^{31}P NMR (δ, *J*/Hz): 22.80 (s, P—$^{194,196,198}Pt$); 22.80 (d, $^1J_{P-{}^{195}Pt}$ = 3022).

Prepared platinum complexes **4** and **5** are stable in air, soluble in most of organic solvents, and almost insoluble in petroleum ether.

Crystals of *cis*-$(PhOC_6H_4\text{-}o)PtCl(PPh_3)_2$ (*cis*-**4**) are monoclinic, at 20 °C a = 12.135(3), b = 17.948(5), c = 18.805(8) Å, β = 105.29(3)°, V = 3951(2) Å^3, d_{calc} = 1.55 g cm^{-3}, Z = 4, space group is $P2_1/c$.

The unit cell parameters and intensities of 9303 reflections, of which 4747 had $I > 2\sigma(I)$, were measured on a four-circle automated Enraf-nonius CAD-4 diffractometer (graphite monochromator, ω-scanning technique, θ_{max} = 27°).

---

* Under the conditions used in this work, the yield of the 2,2′-dilithium derivative of diphenyl ether[2] was ~50 % (determined in a blank experiment by carboxylation).

Table 4. Atomic coordinates and equivalent isotropic temperature parameters (B_{eq}) for compound *cis*-**4**

Atom	x	y	z	B_{eq}/Å^2
Pt(1)	0.8129(0)	0.2808(0)	−0.859(0)	2.64(1)
P(1)	0.9019(2)	0.2868(1)	0.0340(1)	3.75(9)
P(2)	0.9427(2)	0.2043(1)	−0.1255(1)	3.1(1)
Cl(1)	0.7110(2)	0.2919(1)	−0.2105(1)	4.0(1)
O(1)	0.5995(6)	0.2267(4)	−0.0330(4)	4.2(3)
C(1)	0.6773(7)	0.3386(5)	−0.0684(5)	2.6(3)
C(2)	0.6657(8)	0.4150(5)	−0.0808(6)	3.8(5)
C(3)	0.568(1)	0.4503(6)	−0.0754(8)	7.1(7)
C(4)	0.481(1)	0.4126(7)	−0.0583(8)	4.4(6)
C(5)	0.488(1)	0.3385(7)	−0.0483(7)	4.1(5)
C(6)	0.5870(9)	0.3023(5)	−0.0519(6)	4.0(4)
C(7)	0.5322(8)	0.1758(5)	−0.0780(5)	3.4(4)
C(8)	0.468(1)	0.1894(6)	−0.1484(6)	7.0(7)
C(9)	0.406(1)	0.1330(7)	−0.1883(7)	8.9(9)
C(10)	0.403(1)	0.0640(7)	−0.1604(7)	6.9(7)
C(11)	0.470(1)	0.0495(6)	−0.0917(8)	7.3(8)
C(12)	0.534(1)	0.1048(7)	−0.0490(7)	5.1(6)
C(111)	0.856(1)	0.3638(5)	0.0837(5)	6.0(6)
C(112)	0.753(1)	0.3573(7)	0.1012(5)	4.9(6)
C(113)	0.714(2)	0.419(1)	0.1347(7)	7.9(6)
C(114)	0.778(2)	0.4821(9)	0.1497(7)	7.9(8)
C(115)	0.877(2)	0.4872(7)	0.1329(8)	7.9(7)
C(116)	0.921(1)	0.4287(6)	0.1010(6)	11.0(1)
C(121)	0.8837(7)	0.2064(4)	0.0887(5)	2.2(3)
C(122)	0.9217(8)	0.2081(5)	0.1653(5)	3.5(4)
C(123)	0.9082(9)	0.1454(6)	0.2059(5)	4.3(5)
C(124)	0.8544(9)	0.0832(6)	0.1707(7)	4.2(5)
C(125)	0.8170(9)	0.0821(5)	0.0961(6)	3.7(5)
C(126)	0.8289(8)	0.1427(5)	0.0543(5)	3.6(4)
C(131)	1.0532(8)	0.3056(5)	0.0515(5)	3.8(4)
C(132)	1.1352(9)	0.2744(7)	0.1096(5)	3.7(4)
C(133)	1.248(1)	0.2974(8)	0.1226(6)	3.8(5)
C(134)	1.280(1)	0.3491(9)	0.0793(7)	5.1(6)
C(135)	1.201(1)	0.3792(7)	0.0215(7)	6.9(7)
C(136)	1.0882(9)	0.3578(6)	0.0060(5)	5.0(5)
C(211)	0.8685(8)	0.1207(5)	−0.1704(5)	4.0(5)
C(212)	0.7536(9)	0.1119(5)	−0.1766(6)	3.7(5)
C(213)	0.699(1)	0.0493(7)	−0.2099(8)	5.3(6)
C(214)	0.754(1)	−0.0045(7)	−0.2374(7)	7.8(8)
C(215)	0.868(1)	0.0034(9)	−0.2298(9)	7.9(6)
C(216)	0.925(1)	0.0648(8)	−0.1946(8)	3.7(5)
C(221)	1.0683(8)	0.1633(5)	−0.0607(5)	3.0(4)
C(222)	1.0520(9)	0.1053(5)	−0.0164(5)	3.9(5)
C(223)	1.143(1)	0.0760(6)	0.0370(6)	4.9(6)
C(224)	1.251(1)	0.1026(8)	0.0434(8)	4.2(6)
C(225)	1.269(1)	0.1602(9)	−0.0011(9)	7.9(5)
C(226)	1.178(1)	0.1905(7)	−0.0533(8)	3.1(5)
C(231)	1.002(1)	0.2502(7)	−0.1943(6)	5.5(6)
C(232)	0.979(1)	0.3217(6)	−0.2116(6)	4.4(5)
C(233)	1.021(1)	0.3583(7)	−0.2644(7)	6.4(7)
C(234)	1.084(2)	0.323(1)	−0.300(1)	7.9(8)
C(235)	1.105(3)	0.251(1)	−0.286(2)	16.0(2)
C(236)	1.066(3)	0.216(1)	−0.232(2)	16.0(1)

The structure of complex *cis*-**4** was solved by the heavy-atom method and isotropically refined by the full-matrix least-squares method. At this stage of the refinement, the correction for absorption of X-rays by the crystal was applied according to the DIFABS method[13] (μ(Mo-Kα) = 21.3 cm^{-1}).

Further anisotropic refinement was performed by the full-matrix least-squares method. The difference electron density synthesis revealed all of the hydrogen atoms; however, in further refinement, the calculated coordinates of these atoms were used. The final anisotropic refinement of the structure of *cis*-**4** was performed by the full-matrix least-squares method taking into account all hydrogen atoms with fixed positional and temperature parameters. The final R values are: R = 0.0380, R_w = 0.0388 for 4616 reflections with $F > 2.5\sigma(F^2)$. The following weighting scheme was used: $w = (\sigma^2 F_o + 0.0016F_o{}^{2})^{-1}$.

All calculations were carried out on an IBM PC/AT computer using the SHELX program package.[14]

Atomic coordinates for nonhydrogen atoms and their equivalent isotropic temperature parameters are given in Table 4.

We would like to thank A. L. Blyumenfel'd and P. V. Petrovskii for recording the ^{31}P NMR spectra, and D. V. Zagorevskii and K. V. Kazakov for measuring the mass spectrometric characteristics.

This work was supported by the International Science Foundation (Project No. MDV 000).

References

1. T. V. Baukova, N. A. Oleinikova, D. A. Lemenovskii, and L. G. Kuz'mina, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 729 [*Russ. Chem. Bull.*, 1993, **43**, 681 (Engl. Transl.)].
2. K. Oita and H. Gilman, *J. Am. Chem. Soc.*, 1957, **79**, 339.
3. N. Walker and D. Stuart, *Acta Crystallogr.*, 1983, **39A**, 158.
4. G. M. Sheldrick (1986), SHELX86, Program for the solution of crystal. struct., Gottingen, Germany.
5. K. Azam, G. Ferguson, S. M. Ling, M. Parvez, R. J. Puddenphatt, and D. Srokowski, *Inorg. Chem.*, 1985, **24**, 2799.
6. A. L. Balch, R. R. Guimerans, J. Linehan, and F. E. Wood, *Inorg. Chem.*, 1985, **24**, 2021.
7. A. T. Hatton, P. G. Pringle, and B. Shaw, *J. Chem. Soc., Dalton Trans.*, 1985, 1677.
8. A. G. Swallow and M. R. Truter, *Proc. Roy. Soc.*, 1960, A, **254**, 205.
9. B. N. Figgis, J. Lewis, R. F. Long, R. Mason, R. S. Nyholm, P. J. Pauling, and G. B. Robertson, *Nature*, 1962, **195**, 1278.
10. J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1959, 4020.
11. D. M. Rundhi, in *Comprehensive Coordination Chemistry*, Ed. G. Wilkinson, Pergamon Press. G. Brit., 1967, **5**, 399 and 497.
12. C. Kowala and J. M. Swan, *Austral. J. Chem.*, 1966, **19**, 547.
13. J. M. Wisner, T. J. Bartczak, J. A. Iberg, J. J. Low, and W. A. Goddard, *J. Am. Chem. Soc.*, 1986, **108**, 347.
14. R. D. W. Kemmit, S. Mason, J. Fawcett, and D. R. Russel, *J. Chem. Soc., Dalton Trans.*, 1992, 851.

Received June 30, 1994