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## Redox properties of gold(I) compounds with organic ligands

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### Abstract

Redox properties of numerous organogold compounds of different structures containing one, two, or three gold atoms are discussed on the basis of published reports and unpublished experimental electrochemical data obtained by the authors.

*Key words:* Gold; Electrochemistry

### 1. Introduction

There are several reviews [1,2] and one monograph [3] dedicated to reviewing the many studies on the synthesis of organogold compounds (OGC) and the description of their properties. The chemistry of gold-containing clusters has also been extensively developed.

Interest in organogold chemistry has been growing steadily thanks to the intensive development of microelectronics, which requires conducting coatings on ceramic substrates of various configurations. To form these coatings a laser power source is used. This provides the possibility of depositing metallic gold in strictly determined locations, from its compounds in gas phase or solution [4–6]. In addition, some OGC are used as antiarthritic drugs [7,8] and some have antitumour properties [9].

Compounds with a single gold atom are classified according to the oxidation state of the metal: Au<sup>I</sup>, Au<sup>II</sup>, Au<sup>III</sup> and Au<sup>V</sup>. Gold(I) and gold(III) compounds are the most stable, while the oxidation state Au<sup>II</sup> is very rare [10–13]. Oxidation state Au<sup>V</sup> is found in the fluoride complexes AuF<sub>6</sub><sup>-</sup> and AuF<sub>5</sub>. Most of the mononuclear OGC described upto now contain the metal in the oxidation state Au<sup>I</sup> or Au<sup>III</sup>, although there is a large number of clusters containing gold–gold

bonds, in which one cannot assign an oxidation state to any particular metal atom.

As a metal, gold differs from other metals in that dissolved oxygen does not oxidize it, either in acidic or in alkaline aqueous media, unless there is a ligand capable of coordination with it. This is why gold is considered the most noble metal. However, in the presence of such substances as cyanides or phosphines accompanied with halide ions the oxidation of gold proceeds easily and stable compounds of monovalent gold (Au(CN)<sub>2</sub>, Ph<sub>3</sub>PAuCl, etc.) are formed (the coordination number of gold(I) is usually two). Thus our data show that one can remove a gold film from a platinum electrode in a solution containing chloride ions and triphenylphosphine at potentials less than +2.0 V.

Our laboratory is carrying out a programme on the synthesis and investigation of properties of the organic derivatives of gold. In this paper we wish to generalize our previous data on the electrochemical behaviour of these compounds in non-aqueous solution. We believe that studies of the reactions of OGC on electrodes will contribute much to a more detailed understanding of their “ordinary” homogeneous chemical reactions.

There have been a few studies on the electrochemical behaviour of OGC and just two of them should be mentioned here. The first concerns the cathodic reactions of sandwich dicarbonyl complexes of gold, namely (n-(3)-1,2-B<sub>9</sub>C<sub>2</sub>H<sub>11</sub>)<sub>2</sub>Au(Et<sub>4</sub>N)<sub>2</sub> and (n-(3)-1,2-B<sub>9</sub>C<sub>2</sub>H<sub>11</sub>)<sub>2</sub>AuPPh<sub>3</sub>Me [14]. These complexes are reduced

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TABLE 1. Redox potentials of gold(I) complexes at a Pt-electrode (MeCN, 0.05 M Et<sub>4</sub>NBF<sub>4</sub>, Ag/AgCl/KCl (sat.) ref. electrode, 20°C)

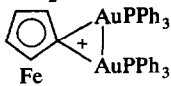
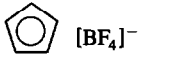
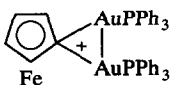
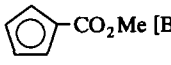
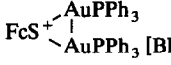
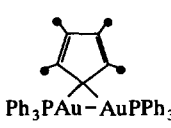
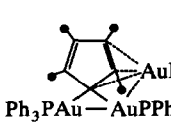
|    | Compound   | $E_{1/2}^{ox}$ , V                          | $-E_{1/2}^{red}$ , V     | Ref. |
|----|--|---|--------------------------|------|
| 1  | ClAuPPh <sub>3</sub>   | 1.58  | 1.76(0.12 <sup>a</sup> ) | 15   |
| 2  | BrAuPPh <sub>3</sub>   | 1.31  | 1.71(0.16 <sup>a</sup> ) | 15   |
| 3  | BrAuPEt <sub>3</sub>   | 1.38  | 1.76                     | 15   |
| 4  | IAuPPh <sub>3</sub>  | 1.05  | 1.54(0.22 <sup>a</sup> ) | 15   |
| 5  | MeAuPPh <sub>3</sub>   | 1.59  | 1.63(e <sup>a</sup> )    | 15   |
| 6  | PhAuPPh <sub>3</sub>   | 1.61 1.97                                   | 1.73(e <sup>a</sup> )    | 15   |
| 7  | 4-MeOC <sub>6</sub> H <sub>4</sub> AuPPh <sub>3</sub>  | 1.28 1.71                                   | e                        | 15   |
| 8  | 4-FC <sub>6</sub> H <sub>4</sub> AuPPh <sub>3</sub>  | 2.00  | e                        | 19   |
| 9  | 4-FC <sub>6</sub> H <sub>4</sub> AuPPhFc <sub>2</sub>  | 0.61 0.80 2.09                              | e                        | 19   |
| 10 | 4-FC <sub>6</sub> H <sub>4</sub> AuPFc <sub>3</sub>  | 0.57 0.72 0.86 2.13                         | e                        | 19   |
| 11 | NCAuPPh <sub>3</sub>   | 2.25  | e(0.78 <sup>a</sup> )    | 20   |
| 12 | NCCH <sub>2</sub> AuPPh <sub>3</sub>   | 2.24  | e(0.98 <sup>a</sup> )    | 20   |
| 13 | NCCH(COOEt)AuPPh <sub>3</sub>  | 2.17  | e(0.79 <sup>a</sup> )    | 20   |
| 14 | (NC) <sub>2</sub> C(AuPPh <sub>3</sub> ) <sub>2</sub>  | 2.21  | e(0.80 <sup>a</sup> )    | 20   |
| 15 | (NC) <sub>2</sub> CMeAuPPh <sub>3</sub>  | 2.30  | 1.91(1.00 <sup>a</sup> ) | 20   |
| 16 | NCPPh <sub>2</sub> CAuPPh <sub>3</sub>   | 1.22  | 1.67(0.58 <sup>a</sup> ) | 20   |
| 17 | (NC) <sub>2</sub> PhCAuPPh <sub>3</sub>  | 0.86  | 1.57(0.69 <sup>a</sup> ) | 20   |
| 18 | FcAuPPh <sub>3</sub>   | 0.24  | e                        | 21   |
| 19 | (2-O <sub>2</sub> NFc)AuPPh <sub>3</sub>   | 0.81  | 1.66 <sup>b</sup>        | 21   |
| 20 |   | 0.68 1.62                                   | 1.62                     | 21   |
|    |   |   |                          |      |
| 21 |    | 0.88 1.81                                   | 1.77                     | 21   |
|    |   |   |                          |      |
| 22 |   | 0.72 2.21                                   | 2.21                     | 21   |
| 23 | C <sub>5</sub> Ph <sub>4</sub> HAuPPh <sub>3</sub>   | 0.48 1.36 1.97                              | 1.84                     | d    |
| 24 |   | 1.52 (1.94 <sup>c</sup> )                   | e                        | d    |
| 25 |   | 0.79 1.08 1.41<br>2.04 (0.84 <sup>c</sup> ) | 1.36                     | d    |
| 26 | MeCONHAuPPh <sub>3</sub>   | 1.89 2.65                                   | 1.77                     | d    |
| 27 | ClCH <sub>2</sub> CONHAuPPh <sub>3</sub>   | 1.99 3.20                                   | 1.80                     | d    |
| 28 | PhCONHAuPPh <sub>3</sub>   | 2.27 2.59                                   | 1.92                     | d    |
| 29 | 4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> NHAuPPh <sub>3</sub>   | 1.44  | 1.37 1.76                | d    |
| 30 | 4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> N(AuPPh <sub>3</sub> ) <sub>2</sub>  | 2.50  | 1.43 1.84                | d    |
| 31 | 4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> N <sup>+</sup> H(AuPPh <sub>3</sub> ) <sub>2</sub> [BF <sub>4</sub> ] <sup>-</sup> | 1.36  | 1.43 1.65                | d    |
| 32 | 4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> N <sup>+</sup> (AuPPh <sub>3</sub> ) <sub>3</sub> [BF <sub>4</sub> ] <sup>-</sup>  | 1.41  | 1.51 1.75                | d    |
| 33 | 2-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> NHAuPPh <sub>3</sub>   | 1.54  | 1.65                     | d    |
| 34 | 4-MeC <sub>6</sub> H <sub>4</sub> N <sup>+</sup> (AuPPh <sub>3</sub> ) <sub>3</sub> [BF <sub>4</sub> ] <sup>-</sup>                | 0.95  | 1.87                     | d    |

TABLE 1. (continued)

|    | Compound   | $E_{1/2}^{\text{ox}}$ , V | $-E_{1/2}^{\text{red}}$ , V | Ref. |
|----|--|---------------------------|-----------------------------|------|
| 35 | (MeCO) <sub>2</sub> CHAuPPh <sub>3</sub>               | 2.00                      | 1.64                        | d    |
| 36 | MeCOCH(AuPPh <sub>3</sub> )COPh                        | 2.05                      | 1.60                        | d    |
| 37 | (PhCO) <sub>2</sub> CHAuPPh <sub>3</sub>               | 1.96                      | 1.56                        | d    |
| 38 | ( <sup>t</sup> BuCO) <sub>2</sub> CHAuPPh <sub>3</sub> | 1.86                      | 1.60 1.78                   | d    |

<sup>a</sup> Reduction at a mercury dropping electrode.

<sup>b</sup> Reduction of the nitro-group.

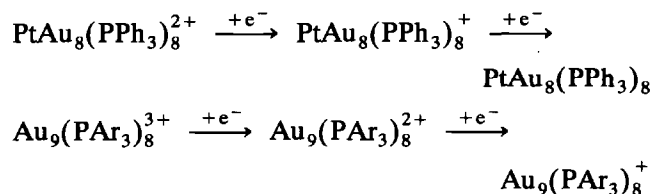
<sup>c</sup> CH<sub>2</sub>Cl<sub>2</sub> – MeCN (10:1).

<sup>d</sup> Authors' unpublished data.

<sup>e</sup> No reduction.

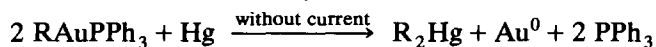
Fc = ferrocenyl

reversibly in two single-electron steps that corresponds to consecutive processes Au<sup>III</sup>/Au<sup>II</sup> and Au<sup>II</sup>/Au<sup>I</sup>. (–0.62, –0.98 V and –0.62, –0.84 V, respectively; a platinum cathode, acetonitrile, the Bu<sub>4</sub>NClO<sub>4</sub> background, and a saturated calomel electrode). The second paper presents the study of the reduction of three gold-containing clusters MAu<sub>8</sub>(PAR<sub>3</sub>)<sub>8</sub><sup>n+</sup> (where M = Pt, Au, Ar = Ph, Ph, 4-MeOC<sub>6</sub>H<sub>4</sub>, n = 2, 3, 3, respectively) on a platinum cathode [15]. Two reversible single-electron transfer stages are also observed in this case:



The values of the redox-step potentials in acetone are –1.51, –1.62 V, –0.96, –0.99 V and –1.06, –1.13 V, respectively.

The redox potentials (a platinum electrode, acetonitrile) of 39 organoderivatives of gold(I) with various organic ligands have been measured in our laboratory. The obtained data are listed in Table 1. As the transmetallation reaction between metallic mercury and some of the gold complexes (GC), namely (1–7), takes place, a mercury cathode appears to be of limited usefulness for studies of gold(I) compounds.



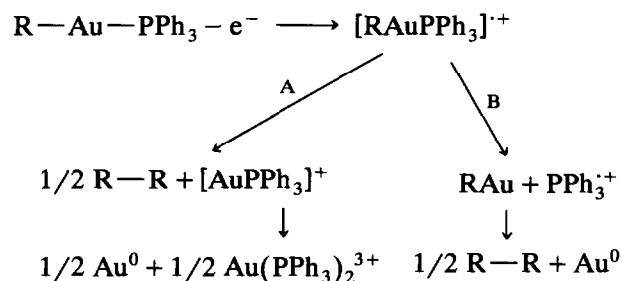
Thus, the redox potential measured on a mercury electrode characterizes the reduction not of the OGC themselves, but of the respective organomercury compounds [15].

It is better to measure electrochemical potentials of OGC using platinum, gold or glassy-carbon electrodes. The data obtained on platinum or gold electrodes are almost similar, therefore Table 1 presents only that for the case of a platinum electrode (acetonitrile, Ag/AgCl/KCl/KCl sat., Et<sub>4</sub>NBF<sub>4</sub>).

## 2. Oxidation of organogold compounds

### 2.1. Alkyl- and arylgold(I) complexes

We have made a preliminary determination of the oxidation potentials of monovalent gold halides stabilized with the triphenylphosphine ligand (compounds (1–6) in Table 1). However, our data are not in accordance with those in the literature [16]. In this report, the electrochemical oxidation of gold(I) chlorides was reported to proceed as an irreversible two-electron process leading to the derivatives of trivalent gold. On the contrary, our results indicate that the oxidation and reduction waves of all OGC should be considered as single-electron processes (this was established by comparing the oxidation current with that of ferrocene in equal concentration) [15]. Consequently, the electrochemical oxidation of these compounds does not cause any changes of the gold oxidation state. Thus, one can suggest two alternative ways for the electrochemical oxidation of OGC to take place:



As is obvious from this scheme it is very difficult to make an unambiguous choice between these two mechanisms of electrooxidation. It should be expected that the contribution of one or other pathway of this reaction depends on the nature of the organic radical and the degree of coordination of the triphenylphosphine to the gold atom. Only the fact that the reduction of the triphenylphosphine cation-radical is observed (by cyclic voltammetry (CVA)) would confirm that the oxidation proceeds by path B. The closeness of the oxidation potentials of the OGC to that of free triph-

enylphosphine (1.24 V in acetonitrile, silver chloride reference electrode) would give indirect evidence of path B operating, while the closeness to the oxidation potential of the respective organic anion would indicate the probability of path A.

The peak corresponding to the reduction of the triphenylphosphine radical cation has in fact been observed on the cathodic branches of the cyclic voltammogram of the oxidation of compounds 1–5. In spite of our failure to observe triphenylphosphine cation-radical reduction in the case of 6 and 7 we suggest that they also are oxidized by path B, the respective OGC being oxidized considerably more easily than the corresponding hydrocarbons (for instance, 6 is oxidized 700 mV earlier than benzene).

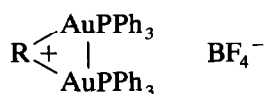
Evidently, path A is what actually occurs in the case of compounds 8–10, their oxidation potentials being close to that of fluorobenzene (2.40 V for 4-FC<sub>6</sub>H<sub>4</sub><sup>-</sup> according to our data). We must admit also that oxidation of the Au–C bond in 9 and 10 is preceded by oxidation of two or three ferrocenyl groups.

## 2.2. Gold(I) compounds with organic ligands containing CN-groups

In the case of the oxidation of 11–17 an irreversible single-electron wave can be observed. Compounds 11–15 are oxidized at considerably anodic potentials, approximately one volt greater than the free triphenylphosphine oxidation potential. These compounds are oxidized over the very same region of potentials where the oxidation of such anions as CN<sup>-</sup> or CH<sub>2</sub>CN<sup>-</sup> is observed (2.20 and 2.05 V, respectively). That is why we consider them to undergo electrooxidation by path A. This means that at the electrochemical stage of the reaction an electron is removed from the Au–C bond. On the contrary in the case of the electrooxidation of 16 and 17 the CVA shows a reduction peak on the reverse cathodic scan that corresponds to the reduction of the triphenylphosphine cation radical. Thus these compounds are evidently oxidized by path B.

## 2.3. The ferrocenyl derivatives of gold

Cationic complexes containing three-member metal-lacycles with two atoms of gold linked together represent a particularly interesting class of OGC.



R = Ar, vinyl, C<sub>5</sub>H<sub>4</sub>FeC<sub>5</sub>H<sub>5</sub>, C<sub>5</sub>H<sub>4</sub>Mn(CO)<sub>3</sub>

These compounds are easily prepared and sufficiently stable [17]; the structure of diaurated ferrocene was established by X-ray analysis [18].

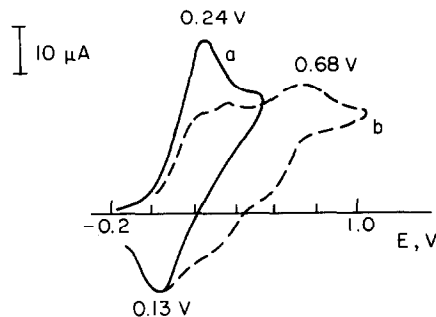
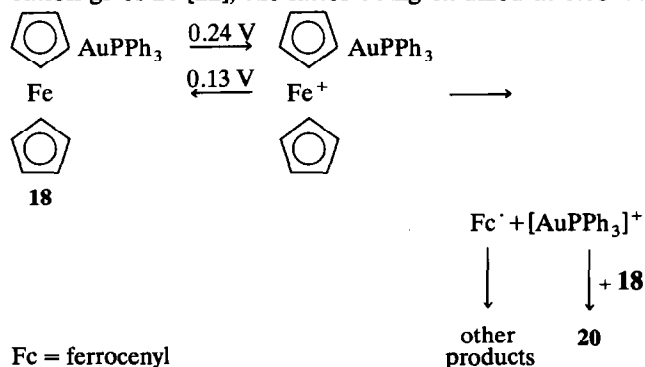


Fig. 1. The CVA curves of electrooxidation of complex 28 (10<sup>-3</sup> mole/l, MeCN, platinum electrode, Et<sub>4</sub>NBF<sub>4</sub> background, Ag/AgCl/KCl sat., 200 mV/s, 20°C). a = the first scanning; b = the fourteenth scanning.

It is the unusual structure of such compounds that makes them of the greatest interest, and worthy of special attention. The most remarkable peculiarity of their structure is the presence of the four-coordinated carbon atom of the sp<sup>2</sup>-type.

Diaurated ferrocenes can be oxidized rather easily. The CVA oxidation curve for compound 18 is presented in Fig. 1a. A reduction peak ( $E_{pc} = 0.13$  V) on the cathodic section of this curve can clearly be seen. Its height is 70% of that on the anodic section ( $E_{pa} = 0.24$  V). The character of the CVA curve testifies that the process of oxidation of compound 18 is quasireversible (the EC mechanism). It should be noted that with multiple scanning over the potential region the polarization picture changes (see Fig. 1b) and an additional peak appears at 0.68 V. Taking into account the fact that the oxidation potential of 20 is also 0.68 V one can hypothesize the following mechanism for the electrooxidation.

First of all the oxidation of the ferrocenyl fragment takes place. This is reversible, and some of the oxidized product may decompose with formation of the AuPPh<sub>3</sub><sup>+</sup> cation. On reacting with the initial complex 18 this cation gives 20 [22], the latter being oxidized at 0.68 V:

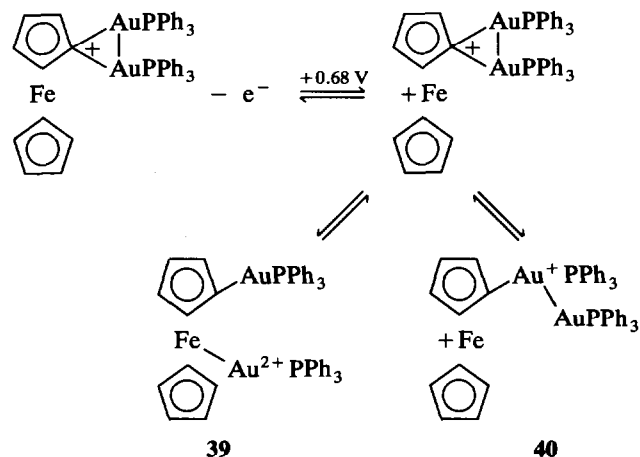


Fc = ferrocenyl

Such changes of the polarization picture are not observed for compound 19. Evidently, the potential of 0.81 V corresponds to a quasireversible transformation of 19 into the respective ferrocenyl cation.

The mechanism of oxidation of cationic complexes **20–22** was studied in detail, with **20** used as a model. To clarify this mechanism we have plotted the CVA curves starting from the potential of  $-1.60$  V (see Fig. 2). There is a peak 5 observed on the anodic section of the curve at the potential of  $0.24$  V besides the peak 1 which corresponds to the oxidation of compound **20**. If the direction of the polarization is inverted after peak 5 (point C in Fig. 2), cathodic peak 6 is observed. On comparing Figs. 1 and 2 one can hypothesize peaks 5 and 6 to correspond to a quasireversible redox-conversion of compound **18**. When the polarization direction is inverted at point B (see Fig. 2) peaks 2 and 3 are observed on the cathodic section of the CVA curve. With repeated scanning from point D peaks 5 and 6 disappear. This means that peak 5 is related to the electroreduction of the product formed at the potential represented by peak 4. From our viewpoint these results are best interpreted as follows.

Peaks 1 and 3 have similar height and peak 3 is related to the peak 1 since it disappears, in the case of potential reverse, before peak 1. Thus peak 3 should be assigned to the reduction of the product of the oxidation at the potential of peak 1. However, the difference between the potentials of peaks 1 and 3 is rather great ( $350$  mV) and the observed polarization picture does not change with multiple scanning over the potential region from  $-0.50$  to  $+1.10$  V. All these effects may be caused by certain structural changes as presented on the scheme below, which do not include any fragmentation of the dication.



Both structures **39** and **40** contain the gold atoms in different valent states. It seems to be possible that the moving force of the formation of structure **39** is the strong trend of the formation of structure **39** is the strong trend of the complex to preserve the 18-electron shell of the iron atom.

If these mechanistic assumptions are true, peak 3 of the CVA curve corresponds to the reduction of **39** or

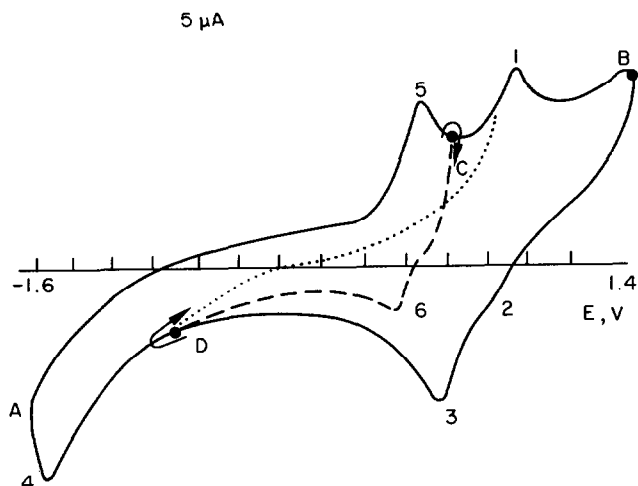


Fig. 2. The CVA curves of complex **20** ( $6 \times 10^{-4}$  mole/l,  $200$  mV/s).

**40** resulting in the restoration of the initial compound **20**.

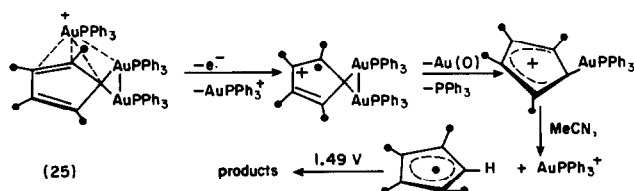
The oxidation of **21** and **22** proceeds by a similar mechanism.

#### 2.4. Aurated derivatives of tetraphenylcyclopentadiene

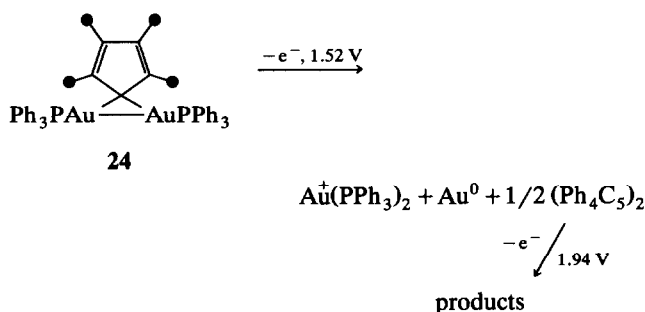
Compound **24** is hardly soluble in acetonitrile. That is why it was studied in a mixture MeCN:  $\text{CH}_2\text{Cl}_2$  (1:10). All the waves of oxidation of compounds **23–25** are irreversible and single-electron. The potentials of the second and the third waves of oxidation of compound **23** being similar to the potentials of oxidation of the corresponding non-aurated compound, we suggest both to be oxidized similarly:

Only the reversible wave is observed for compound **25** in acetonitrile: methylene chloride mixture. On triple scanning of the potential area two additional peaks appear and the polarization picture coincides with that observed for the first time in pure acetonitrile. Taking into account the fact that in this case a metal gold film is deposited on the platinum electrode surface one can suppose that the oxidation of the cationic complex **25** proceeds as follows: the transfer of an electron from the initial complex **25** causes the destabilization of the cluster cation and the latter decomposes by means of a consequent extrusion of all the gold atoms from the molecular frame. Evidently, this process can be well

described by the following scheme:

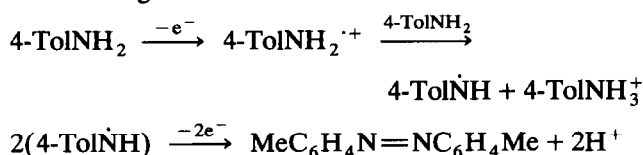


Compound **24** is oxidized in two successive steps. The fact that a metal gold film is deposited on the electrode surface makes it possible to propose the following route of oxidation:



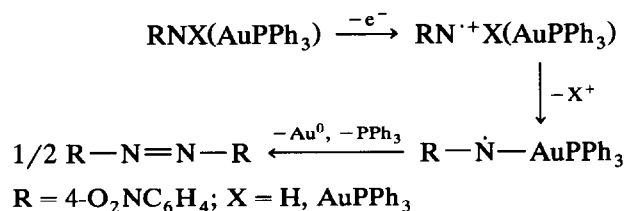
### 2.5. Aurated derivatives of para- and ortho-substituted anilines

There exists a paper dedicated to the anodic behaviour of the substituted anilines [23]. According to the results presented there, the oxidation proceeds as either a one- or two-electron transfer depending on whether the substituents have an electron releasing or withdrawing effect:

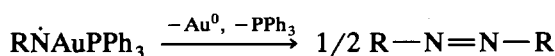
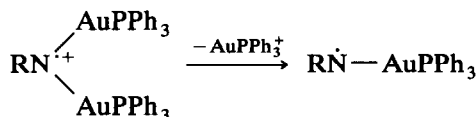
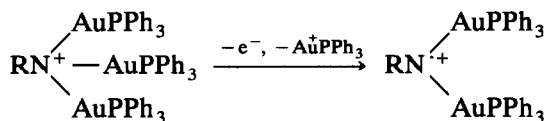


The oxidation of nitroanilines proceeds in a similar manner, but in this case the proton acceptor is a molecule of the solvent (acetonitrile).

When oxidising compounds **29–32** metallic gold appears on the surface of the platinum electrode. This, and the fact that the number of electrons transferred within the oxidation process is reduced from two in the case of nitroaniline to one in the case of its aurated derivative, makes it possible to propose the following scheme:



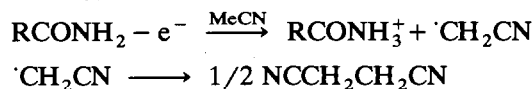
Compound **32** is described in the literature as a cluster in the form of a distorted pyramid with the nitrogen atom located on the top and the gold atoms forming the base [24]. The electron pair of the nitrogen atom being oxidized in this compound, it should not, by the way, be considered as a kind of ammonium quaternary salt.



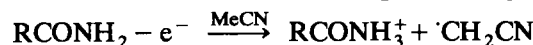
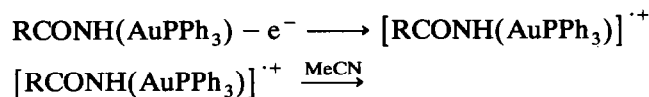
Compound **34** is oxidized in the very same manner as compound **32**. Our data suggest **31** dissociates in solution to give compound **29** and triphenylphosphine-gold(I) cation. The observed wave corresponds to the oxidation of compound **29**.

### 2.6. Monoaurated derivatives of carboxylic acid amides

This class of substances is represented here by compounds **26–28** (Table 1). In accordance with the literature data carboxylic acid amides are oxidized irreversibly, with one electron transferred:



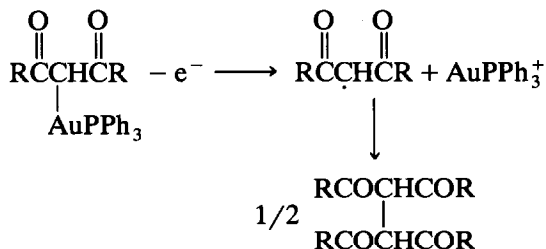
We have shown that the oxidation of N-aurated amides is an irreversible two single-electron transfer step process. The potentials of the second oxidation step of the compounds under consideration coincide with the potentials of the only wave of the corresponding non-aurated amide oxidation. In the case of compounds **26–28** the process can be formalized as the following:



### 2.7. Aurated derivatives of $\beta$ -diketones

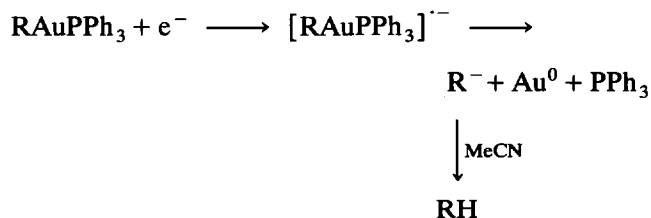
The compounds related to this class of OGC are oxidized irreversibly with one electron transferred. Their electrooxidation potentials do not differ practi-

cally from those of the respective C-H compounds (except compound 37; the difference between its oxidation potential and that of  $(t\text{BuCO})_2\text{CH}_2$  is 650 mV). We therefore consider the aurred compounds of this class to be oxidized by path A:



### 3. Reduction of gold(I) complexes

The reduction of almost all the OGC that we have studied proceeds as an irreversible single-electron transfer process:

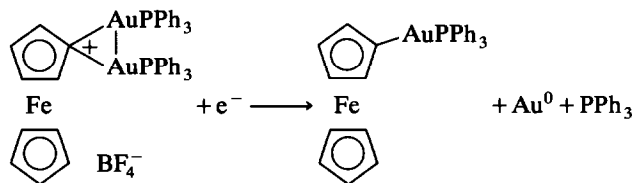


While the electroreduction proceeds, a platinum electrode is rapidly coated with a metallic gold film. In some cases one can observe the reduction wave of free triphenylphosphine ( $-2.66$  V on a gold electrode). When the CVA was applied we observed the peaks of oxidation of the respective anions  $\text{R}^-$  which are rather stable in acetonitrile (the reduction of compounds 15, 17, 23, 26–28, 35–39). The formation of a sufficiently stable  $[\text{RAuPPh}_3]^{-\bullet}$  anion radical was detected only in the case of compound 16 ( $E_{\text{pa}} - E_{\text{pc}} = 60$  mV,  $i_a/i_c = 1$ ). There is a number of substances among the compounds of interest which undergo the reduction by mechanisms other than the one mentioned above. These mechanisms will be discussed below.

#### 3.1. Diaurated ferrocenes

As it is obvious from Table 1 monoaurated ferrocenes are not reduced under the conditions employed (the observed wave for 19 corresponds to the reversible reduction of the  $\text{NO}_2$  group). Compounds 20–22 are reduced in one single-electron step and there is a peak observed on the back scan of the CVA reduction curve which corresponds to the oxidation of

monoaurated ferrocene 18. Thus, the reduction of the diaurated ferrocenes can be described by the equation:

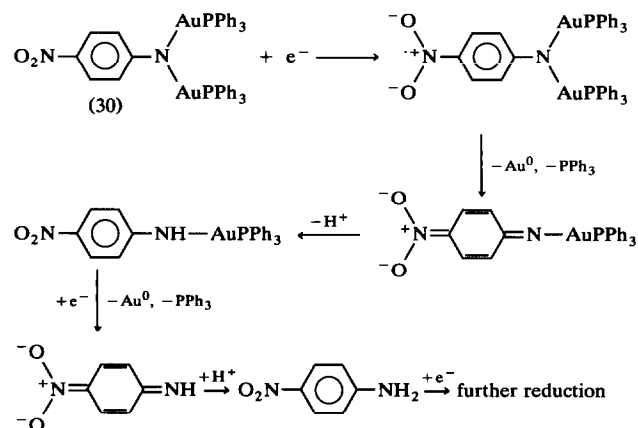


Triaurated tetraphenylcyclopentadiene is reduced in approximately the same manner to give the diaurated derivative (which is not reduced further) and metallic gold.

#### 3.2. Aurated derivatives of substituted anilines

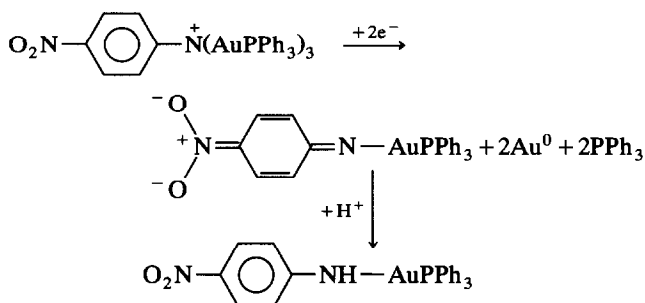
In accordance with our data non-aurated *p*-nitroaniline gives two waves of reduction at  $-1.32$  V ( $1 e^-$ ) and at  $-1.78$  V ( $2.2 e^-$ ), with the first being reversible while the second is not. As indicated in Table 1 the first wave potentials of the reduction of compounds 29–32 are of certain cathodic values (all these waves are the single-electron ones). As the number of  $\text{AuPPh}_3$  groups in a OGC molecule increases the stability of the anion radical formed at the first step of the reduction falls ( $i_a/i_c = 0.5$  for 29; this ratio becomes zero for 32). Meanwhile the number of the electrons transferred at the second electrochemical step increases ( $n_c = 2.8$  for 29 and 4 for 30 and 32).

Hence, on the basis of the experimental facts mentioned above we propose the following mechanism for the reduction of the compounds under consideration which includes an intramolecular electron transfer step:



It is clear from this scheme that each act of electron transfer is followed by the formation of metallic gold and the regeneration of a molecule which is electrochemically active over the same potential region. This causes the increase in number of electrons transferred at the second electrochemical stage.

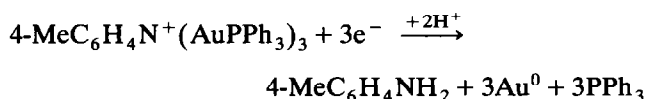
Compound 32 is reduced similarly:



The anion radical formed at the first cathodic step can be considered not only as a result of protonation by acetonitrile or of admixture of water but also as a result of intramolecular transfer of the  $\text{AuPPh}_3^+$  group from the nitrogen atom to the oxygen of the nitrogroup. This is what may cause the decrease of stability of the initially formed anion radical as the number of  $\text{AuPPh}_3$  groups attached to the nitrogen atom increases.

The reduction of compound 33 proceeds in an analogous manner. The only special feature of the case is the fact that, while being electrochemically reduced, both the monoaurated derivative and non-aurated nitroaniline itself present the only wave of reduction (reversible two- or single-electron one, respectively).

The reduction of compound 34 is easily formalized by the following equation:



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