Electrochemical Studies of Gold(I) and Gold(III) Complexes of Bis(diphenylphosphines)

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Cyclic voltammograms of gold complexes of bis(diphenylphosphines) were recorded using a gold working electrode. The $E_{\frac{1}{2}}$ values *vs.* a saturated calomel electrode (s.c.e.) (and the peak-to-peak separations) for the PF_6 salts of the following complexes were obtained: bis[1,2-bis(diphenylphosphino)benzene]gold(I), 0.463 (37); bis[1,2-bis(diphenylphosphino)-ethene]gold(I), 0.572 V (37); bis[1,2-bis(diphenylphosphino)ethane]gold(I), 0.458(30); bis[1,3-bisdiphenylphosphino)propane]gold(I), 0.752 V (35 mV). The first couple is electrochemically reversible and the last three show quasi-reversibility for the two-electron redox process to form the corresponding gold(III) complex. Spectroelectrochemistry of bis[1,2-bis(diphenylphosphino)-benzene]gold(I) revealed only two u.v.-absorbing species in solution, and the limiting spectra are those of the tetrahedral gold(I) complex and the square-planar gold(III) complex. A facile pseudo-rotation between the two geometries is proposed. Cyclic voltammetry of the chloride or bromide salt of bis[1,2-bis(diphenylphosphino)benzene]gold(I) demonstrated that halide ion adds to the gold(III) complex but dissociates from it upon reduction back to the starting gold(I) complex. Based on electrochemical behaviour, the order of increasing lability of the gold(III) complexes is as listed above.

Both linear and chelated gold complexes of bis(diphenylphosphines) are active against a number of animal tumours.[1,2] The mechanism of action of these complexes is not known, but it appears to be different from that of cisplatin *cis*-$PtCl_2(NH_3)_2$.[2] The linear gold compounds are represented by [ClAu($Ph_2PCH_2CH_2PPh_2$)AuCl] and the chelated compounds by bis[1,2-bis(diphenylphosphino)ethane]gold(I), $[Au(dppe)_2]^+$, which has been shown to be a potent cardiovascular toxin and a possible uncoupler of oxidative phosphorylation.[3] The chelated complex was shown to form from the linear complex in blood plasma.[4] This complex also was shown to cause a rapid initial increase in cellular respiration and a decrease in total cellular ATP content in rat hepatocytes,[5] and a study using isolated rat-liver mitochondria demonstrated a rapid collapse of the inner mitochondrial membrane potential.[6] These data suggest that the mitochondria may be the target of $[Au(dppe)_2]^+$.

As part of our investigation of the physical and structural parameters of these complexes, we determined the electrochemical behaviour of a number of gold complexes of bis-(diphenylphosphines). The ligands and the abbreviations used are as shown. Since uncoupling of oxidative phosphorylation has been suggested as a mechanism of cytotoxicity, the electrochemical data may be of use in constructing activity relationships. In addition, although four-co-ordinate complexes of gold(I) have been known for some time, the tetrahedral geometry of gold(I) complexes was demonstrated by *X*-ray crystallography only fairly recently,[7] and studies on the physical and reactivity properties of these complexes are lacking. Furthermore, considerable interest exists in the parameters of electron transfer involving couples with large changes between the geometries of the redox pair.[8]

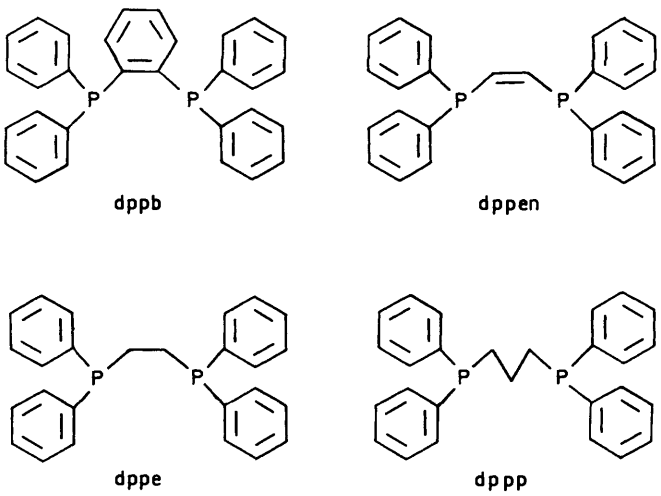

Table 1. Cyclic voltammetric data * collected at a scan rate of 10 mV s^{-1} and gold concentration of *ca.* 0.1 mmol dm^{-3}

Couple	$E_{\frac{1}{2}}$ (V *vs.* s.c.e.)	$E_p^a - E_p^c$ (mV)
$[Au(dppb)_2]^{1+,3+}$	0.463	37
$[Au(dppen)_2]^{1+,3+}$	0.572	37
$[Au(dppe)_2]^{1+,3+}$	0.458	30
$[Au(dppp)_2]^{1+,3+}$	0.752	35

* $E_{\frac{1}{2}} = 0.5(E_p^a + E_p^c)$.

Results

The cyclic voltammograms (c.v.s) of the tetrahedral gold(I) complexes with non-complexing anions showed chemically reversible behaviour for two-electron couples. By chemically reversible we mean that the electrochemical oxidation process has associated with it an electrochemical reduction process that regenerates the starting material. Table 1 gives the best estimate of the thermodynamic $E_{\frac{1}{2}}$ values vased on the voltages at minimum separation of the peak anodic (E_p^a) and cathodic

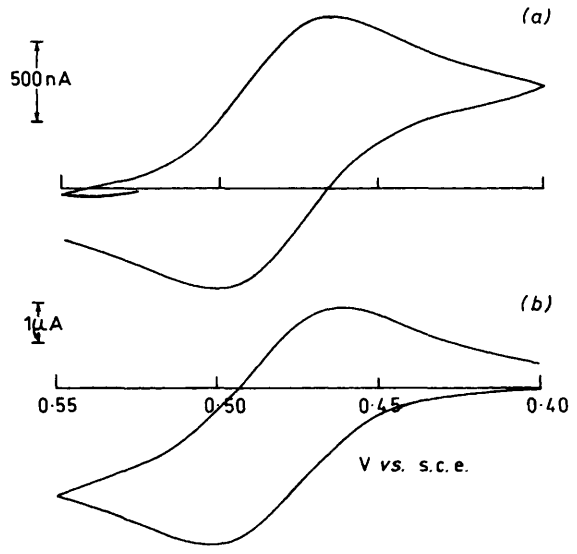

Figure 1. Cyclic voltammograms of (*a*) 0.1 mmol dm^{-3} $[Au(dppb)_2]$-$[ClO_4]_3$ at a scan rate of 100 mV s^{-1} in acetonitrile with 0.1 mol dm^{-3} tetrabutylammonium hexafluorophosphate as supporting electrolyte and (*b*) $[Au(dppb)_2]PF_6$ under the same conditions

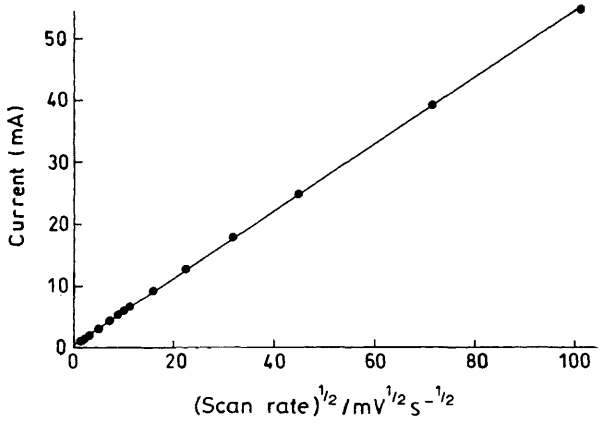

Figure 2. Plot of current *versus* the square root of the scan rate for cyclic voltammograms of $[Au(dppb)_2]PF_6$

Table 2. Effects of scan rate and concetration on the ratio I_{pa}/I_{pc} and the peak-to-peak separation in cyclic voltammograms of $[Au(dppp)_2]PF_6$

Scan rate (mV s^{-1})	Concentration (mmol dm^{-3})	$E_p^a - E_p^c$ (mV)
10	0.06	35
250	4.0	341
		I_{pa}/I_{pc}
250	0.5	2.39
250	1.0	2.57
250	2.0	2.90
250	4.0	3.24
500	0.125	1.91
250	0.125	2.17
100	0.125	2.97
50	0.125	5.98

(E_p^c) current. A cyclic voltammogram of $[Au(dppb)_2][ClO_4]_3$ is shown in Figure 1(*a*), and Figure 1(*b*) shows a cyclic voltammogram of $[Au(dppb)_2]PF_6$. For $[Au(dppb)_2]PF_6$ the current varied linearly with the square root of the scan rate from

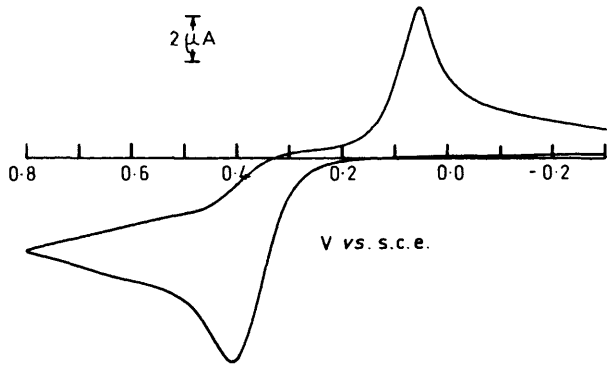

Figure 3. Cyclic voltammogram of 0.5 mmol dm^{-3} $[Au(dppb)_2]Cl$ recorded at 100 mV s^{-1}

2 mV s^{-1} to over 10 V s^{-1} (Figure 2). Thus, a diffusion-controlled, reversible (or nernstian) electrochemical process is indicated for this couple.[9] However, at scan rates greater than about 100 mV s^{-1} the peak-to-peak separation also varied directly (but not linearly) with scan rate, indicating the system becomes quasi-reversible under these conditions. No linear relationship between the current and the square root of the scan rate was found for the other three couples, which are thus described as quasi-reversible.[9] At slow scan rates, all four couples show peak-to-peak separations of less than 40 mV, which is near the value of 29 mV expected for a reversible two-electron couple. For $[Au(dppb)_2]PF_6$, $[Au(dppen)_2]PF_6$, and $[Au(dppe)_2]PF_6$ the ratio of the peak current in the reduction process (I_{pa}) to that in the oxidation process (I_{pc}) was 1.0:1 at any scan rate. For $[Au(dppp)_2]PF_6$ the I_{pa}/I_{pc} ratio varied depending on the scan rate and concentration of the complex (see below).

For $[Au(dppb)_2]PF_6$ and $[Au(dppen)_2]PF_6$ the concentration of complex in solution had almost no effect on the c.v.s. For $[Au(dppe)_2]PF_6$ and $[Au(dppp)_2]PF_6$ the higher the concentration the broader were the peaks and the greater their separation in the c.v.s. In addition, for $[Au(dppp)_2]PF_6$ the I_{pa}/I_{pc} ratio was increased for a given scan rate and range by increasing the concentration of complex. Similarly, their ratio was increased for a given concentration and scan range by decreasing the scan rate. The data are summarised in Table 2. The same effects caused by increasing the complex concentration also were caused by adding small amounts of dppp, the free phosphine, to dilute solutions of $[Au(dppp)_2]PF_6$. The peak separations in the c.v.s also were dependent on the type of solid electrode used. A 0.1 mol dm^{-3} solution of $[Au(dppb)_2]$-PF_6 scanned at 10 mV s^{-1} showed peak separations of 37, 58, and 79 mV for a gold, platinum, and glassy carbon electrode, respectively.

The presence of chloride or bromide with any of the four complexes caused totally irreversible behaviour; none of the reduction waves for the oxidised complex was seen. Instead, a new reduction peak at much more negative potentials was present. For the chloride salt of $[Au(dppb)_2]^+$ (0.5 mmol dm^{-3}), E_p^c occurred at 0.077 V at a scan rate of 100 mV s^{-1} (Figure 3), and for the bromide salt of the same complex under the same conditions E_p^c occurred at 0.059 V. Repeated cycling of the potential in the presence of chloride showed that, following reduction, the starting material is regenerated. Addition of halide ion beyond 1 equivalent produced no further effect. Addition of $[Au(dppb)_2]ClO_4$ to solutions of $[Au(dppb)_2]Cl$ produced both the reversible and irreversible waves. The interaction of the halides was only with the gold(III) complexes since solution spectra of the gold(I) complexes with halide counter ions were identical to those with non-complexing

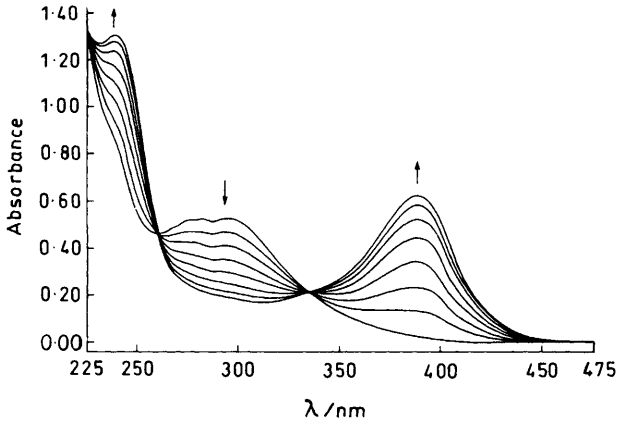

Figure 4. Spectroelectrochemical oxidation of $[Au(dppb)_2]PF_6$. The spectra were recorded before application of the oxidising potential (1.26 V) and at 1.0-min intervals thereafter

anions. The spectra showed no changes on dilution from 300 to 3 μmol dm^{-3}.

The bulk electrolysis of $[Au(dppb)_2]PF_6$ showed that 1.81 and 1.83 electrons per gold were removed on oxidation in two separate experiments at 700 mV. The electrochemical oxidations took more than 50 min to go to completion. Electrolysis of $[Au(dppen)_2]PF_6$ also was done, but the oxidation product of $[Au(dppen)_2]PF_6$ was not completely stable over the entire time course of the electrolysis. The product decomposed into another oxidisable compound after the bulk of the original oxidation was complete. The results indicated that >1.7 electrons per gold were passed in the initial oxidation. The oxidation products of $[Au(dppe)_2]PF_6$ and $[Au(dppp)_2]PF_6$ were too unstable to attempt a bulk electrolysis.

The spectroelectrochemistry of $[Au(dppb)_2]PF_6$ is shown in Figure 4. The initial spectrum is that for the tetrahedral gold(I) complex. When an oxidising potential of 1.26 V was applied to the gold minigrid the four peaks of the electronic spectrum of the gold(I) complex [294, 281, 276, and 272 (sh) nm] decreased in intensity and two new peaks at 387 and 239 nm appeared. Three isosbestic points at 335, 260, and 220 nm also were present. The spectra continued to change for 9 min. The oxidising potential was removed at 20 min, and from 9 to 30 min no change in the spectra was observed. The two limiting spectra observed for the spectroelectrochemistry were the same as those found for $[Au(dppb)_2]PF_6$ and $[Au(dppb)_2][ClO_4]_3$ recorded under the same conditions. The spectrum of $[Au(dppb)_2][ClO_4]_3$ also could be generated from a solution of $[Au(dppb)_2]PF_6$ by chemical oxidation with nitrosonium ion generated from $NaNO_2$ and perchloric acid in acetonitrile.

Discussion

The complex $[Au(dppb)_2]^+$ may be oxidised smoothly and cleanly by either chemical or electrochemical methods to $[Au(dppb)_2]^{3+}$. The electrochemical reaction is classically reversible for a two-electron couple. We find this redox behaviour quite striking because the complex undergoes a significant change in geometry from tetrahedral to square planar upon oxidation. The electronic spectrum of the oxidised material may be generated from the reduced species electrochemically as in the spectroelectrochemical experiment or chemically as in the oxidation by nitrosonium ion. Either method gives an electronic spectrum identical to that obtained from the isolated and fully characterised gold(III) complex in the same solvent and at the same ionic strength. Cyclic voltammetry of $[Au(dppb)_2]^{3+}$ yields a voltammogram identical in shape and peak positions to that of the reduced complex. This observation further supports the conclusion that the two complexes are the two halves of a single redox couple. Bulk electrolysis and the peak-to-peak separation of 37 mV confirm that this is a two-electron couple. The fact that $I_{pa}/I_{pc} = 1.0$ for all scan rates implies that the couple is chemically reversible. Of the four sets of redox pairs, only this one appears to be truly chemically and electrochemically reversible.

We know of no other mononuclear complexes that shows such dramatic geometry changes upon oxidation or reduction yet displays reversibility. However, some bimetallic complexes that undergo chemically reversible redox reactions accompanied by geometry changes have been studied. For example, the rhodium(I) phosphido-bridged dimer $[\{Rh(\mu\text{-}Bu^t_2P)(CO)_2\}_2]$ containing one tetrahedral and one square-planar metal centre undergoes a one-electron reduction followed by an isomerisation reaction and a second one-electron reduction to give a dimer with two tetrahedral rhodium(0) centres.[10] Reoxidation of this complex occurs first with two one-electron transfers followed by isomerisation back to the starting complex. Collman *et al.*[11] reported the chemically reversible two-electron reduction of a phosphido-bridged iron(I) dimer, $[\{Fe(\mu\text{-}Ph_2P)(CO)_3\}_2]$. The geometry about the iron(I) centres is approximately octahedral with an iron–iron bond, but the geometry abut the iron(0) centres is trigonal bipyramidal with no iron–iron interaction. It was speculated that addition of the first electron leads to breakage of the metal–metal bond, followed by a change in geometry that renders the second reduction more anodic than the first.

The behaviour we observed contrasts with that reported in an earlier study of the electrochemical reductions of bis[1,2-bis(dimethylphosphino)benzene]gold(III) and the arsine analogue of the same complex.[12] Only totally irreversible electrochemical reductions were observed for the gold(III) complexes. Complexes of these ligands with other metals also were investigated by the same authors. They reported that many one-electron electrochemical redox reactions involving retention of geometry were reversible, but that no one- or two-electron reactions involving a change in geometry were reversible.

The excellent behaviour of the $[Au(dppb)_2]^{1+,3+}$ redox couple suggests that the complex in both oxidation states is quite stable. In the spectroelectrochemical experiment the oxidised species generated underwent no detectable change as judged by the electronic spectrum for more than 10 min after the oxidising potential was discontinued. Generation of the gold(III) complex by chemical oxidation yields a complex of similar stability. The lack of an effect of varying the complex concentration suggests that both $[Au(dppb)_2]^{3+}$ and $[Au(dppen)_2]^{3+}$ are stable and kinetically inert, in contrast to the results for $[Au(dppp)_2]^{1+,3+}$ (see below). However, the presence of coordinating ions causes the oxidation of $[Au(dppb)_2]^+$ to be irreversible. If the starting material were the chloride salt of $[Au(dppb)_2]^+$, a new oxidised species was generated, but upon reduction the starting $[Au(dppb)_2]^+$ was regenerated as judged by the cyclic voltammogram. It appears that the complex undergoes oxidation with rapid addition of chloride and reduction with elimination of chloride. We prepared and characterised by single-crystal *X*-ray diffraction the new complex $[AuCl(dppb)_2]Cl_2 \cdot H_2O$. The geometry about the Au^{III} is square pyramidal (Au–Cl 2.7 Å; next shortest Au ··· Cl distance 6.8 Å)[13] and is one of the few examples of this geometry for Au^{III} known to us.[7a,12,14,15]

Under appropriate conditions of dilute solutions and slow scan rates, the other three complexes, $[Au(dppen)_2]^+$, $[Au(dppe)_2]^+$, and $[Au(dppp)_2]^+$, also showed quasi-reversible behaviour. By quasi-reversible behaviour we mean that the current is not proportional to the square root of scan rate, that the peak-to-peak separation is dependent on the scan rate, and

that these systems show characteristics of reversible processes at slow scan rates. In addition, $[Au(dppp)_2]^+$ shows characteristics of a totally irreversible system in the sense that no reduction wave is observed following oxidation at fast scan rates in concentrated solution.[9] The ratio I_{pa}/I_{pc} was 1.0 for $[Au(dppb)_2]^+$, $[Au(dppen)_2]^+$, and $[Au(dppe)_2]^+$ for all scan rates, but that for $[Au(dppp)_2]^+$ varied as a function of scan rate. The c.v.s of $[Au(dppe)_2]^+$ and $[Au(dppp)_2]^+$ also were affected markedly by changing the concentration of complex in solution. Increased concentration broadened the c.v. peaks and widened their separation, as did the addition of free dppp. This indicates adsorption of the complex or, more likely, adsorption of the free phosphine onto the surface of the electrode leading to poor electrode response. In addition, the I_{pa}/I_{pc} ratio for $[Au(dppp)_2]^+$ increased due to loss of the oxidised species with increasing concentration of the complex. Since the rate for first-order decomposition of an electrochemically generated species is independent of concentration and gives a constant I_{pa}/I_{pc} ratio for a constant scan rate and range, a higher-order process is operating. Phosphine dissociation from the oxidised complex and reduction of the gold(III) species by the free phosphine is a plausible mechanism for the observed behaviour.

The values of $E_{\frac{1}{2}}$ measured for these complexes imply strong stabilisation of both oxidation states. Warren and Bennett[12] previously cited the strong σ-donating properties and the rigidity of the ligand as contributing to the stability and the resulting high reduction potential (+0.11 V *vs.* saturated calomel electrode, s.c.e.) for bis[1,2-bis(dimethylphosphino)benzene]gold(III). Replacing the methyl groups on the phosphorus with phenyl groups leads to a value of $E_{\frac{1}{2}}$ of 0.46 V and apparently even more stabilisation, although it is difficult to compare quantitatively the reduction potential for the irreversible process to $E_{\frac{1}{2}}$ for the reversible process. This may be a surprising result since one expects that the more electron-withdrawing phenyl groups will result in a weaker σ donor. The increase in stability may result from a metal-to-ligand charge transfer involving π orbitals of the non-bridging phenyl groups. The absorption at 387 nm in acetonitrile solutions of bright yellow $[Au(dppb)_2][ClO_4]_3$ is best assigned to such a process. The colourless bis[1,2-bis(dimethylphosphino)benzene]gold(III) ion has no absorption lower in energy than 320 nm.[10] The $E_{\frac{1}{2}}$ value for $[Au(dppp)_2]^{1+,3+}$ is the most positive and may be surprising since the rigidity of the ligand is lost. The extra stabilisation may be due to the ability of the propyl ring to maximise the chelate angle or to reduce repulsive interactions among crowded phenyl groups.

Two recent studies are relevant to the results reported here. The first is an investigation of the fluxionality of $[Rh(dppe)_2]$ by e.s.r. spectroscopy.[16] Observed e.s.r. data were modelled well by assuming fluxionality between two sets of phosphorus nuclei in one of two models. In the first model, two pairs of Rh–P bond lengths vary over distances and times larger than normal vibrational modes. In the second model, the pairs of Rh–P equatorial and axial donors in a trigonal-bipyramidal arrangement with the odd electron interchange through a pseudo-rotation. The second study is an n.m.r. investigation of the exchange kinetics getween gold(I) and monodentate phosphines.[17] Complexes with one, two, and three co-ordinated phosphines were detected. The various species undergo exchange with one another *via* an associative mechanism.

We propose that a pseudo-rotation is involved in the reversible oxidation of $[Au(dppb)_2]^+$. The rigidity of the ligand presumably favours this mode of rearrangement over others and it ensures that the ligand cannot dissociate during the process unless both gold–phosphine bonds are broken nearly simultaneously. The complex $[Au(dppen)_2]^+$ should have a similar mechanism. The fact that its oxidation product is slightly less stable than $[Au(dppb)_2]^{3+}$ may be due to the decrease in steric bulk or to resultant small changes in geometry. Since only single two-electron reactions are observed, reduction by the second electron must be more thermodynamically favoured than reduction by the first. Therefore, it is likely that addition of the first electron leads to a substantial change in geometry toward tetrahedral and a lowering of the energy of the lowest-unoccupied molecular orbital; otherwise, the more anodic addition of the second electron to form a square-planar gold(I) complex is required.

The complexes $[Au(dppe)_2]^+$ and $[Au(dppp)_2]^+$ have available to them, in additon to the pseudo-rotation, a stepwise mechanism of dissociation whereby one end of the phosphine may dissociate and be rotated away from the metal, followed by dissociation of the other phosphorus. Dissociation of phosphines from both of these complexes in both oxidation states may be significant and could account for the irreversibility of the c.v.s under some conditions. When the complex at high concentration is oxidised the gold becomes susceptible to reduction by the phosphine from the dissociated complex or from phosphine added to the reaction solution. Reduction also could occur through a second-order interaction as proposed earlier for the gold(I) monodentates.[17] Thus, a decreased reduction wave would be seen on the reverse electrochemical sweep. This mechanism may operate during the bulk electrolysis of $[Au(dppen)_2]^+$, during which a second oxidisable species appears. Further evidence is that a small amount of dppp or PPh_3 (but not dppb) added to solutions of the oxidised complexes causes them to be reduced to the gold(I) complexes. Phosphines that can co-ordinate to the empty axial sites of the square-planar gold(III) complexes can cause reduction.[18] The ligand dppb cannot co-ordinate to the oxidised complexes because of its rigidity and the orientation of the lone electron pairs on the phosphorus atoms. In addition to the rigidity of the ligand, the steric bulk also may be important since replacing the four non-bridging phenyl groups on the phosphorus atoms of dppb with methyl groups results in irreversibility in the c.v. of the gold(III) complex.[10] Bulk electrolysis of $[Au(dppen)_2]^+$ was attempted but could not be completed due to the instability of the product. The products of the electrochemical oxidation of $[Au(dppe)_2]^+$ and $[Au(dppp)_2]^+$ were too unstable to conduct bulk electrolysis. Considering all of the above results, the order of increasing lability of the oxidised complexes in solution is $[Au(dppb)_2]^{3+} < [Au(dppen)_2]^{3+} < [Au(dppe)_2]^{3+} < [Au(dppp)_2]^{3+}$. Thus, lability decreases with increasing rigidity and steric bulk of the chelate ring.

The order of the activity of the complexes in destroying the inner membrane potential of isolated rat-liver mitochondria is the same as the order of lability.[6] That is, the more labile the complex, the more active it is.

These complexes in both oxidation states present many opportunities for further study. Investigations of the fluxionality and of the kinetics of the electrochemical and chemical redox processes are two such areas. The novel structures and reactivities of these complexes could be pursued. In addition, the remarkable reversibility of $[Au(dppb)_2]^+$ toward electrochemical and chemical oxidation suggests the complex may be useful in catalytic roles.

Experimental

Reagents.—All chemicals and solvents were reagent grade or were of the highest purity commercially obtainable. Tetra-n-butylammonium hexafluorophosphate (the supporting electrolyte for the electrochemical studies) was recrystallised from ethyl acetate. Cyclic voltammetry on a blank solution of $NBu^n_4PF_6$ showed no electrochemical activity between −0.7 and 1.5 V. The phosphine ligands were obtained from Strem Chemicals, tetra-alkylammonium salts from G. Frederick Smith Co., and chloroauric acid from Johnson Matthey.

Physical Measurements.—Cyclic voltammetry (c.v.) and bulk electrolysis (b.e.) were done with a Bioanalytical Systems Inc. BAS-100 electrochemical analyser at a gold electrode (c.v.) or a platinum-gauze electrode (b.e.) in acetonitrile solution containing 0.1 mol dm^{-3} $NBu^n_4PF_6$ as supporting electrolyte. Potentials are *versus* an aqueous KCl saturated calomel electrode (s.c.e.) unless otherwise noted. Spectroelectrochemistry was done with an optically transparent thin-layer electrode (o.t.t.l.e.) using a gold minigrid as described elsewhere,[19] a Princeton Applied Research model 174 polarographic analyser, and a Hewlett-Packard 8450A UV/VIS spectrophotometer. An oxidising potential of 700 mV *vs.* Ag–AgCl was applied and spectra were recorded as a function of time. Electronic spectra were obtained with a Perkin-Elmer Lambda-5 UV/VIS spectrophotometer.

Syntheses.—**CAUTION:** These complexes have been shown to be potent cardiovascular and hepatic toxins. They should be handled only with adequate ventilation while wearing gloves and a dust mask.

The first four complexes listed below were synthesised by a method similar to that published.[20]

(*a*) $[Au(dppe)_2]PF_6$. A 1.7 mol dm^{-3} solution (3 cm^3) of 2,2′-thiodiethanol in acetone was added to $HAuCl_4$ (1.0 g) dissolved in ethanol. To this solution were added 0.15 mol dm^{-3} NaOH in ethanol–water (1:1) (18 cm^3). The solution was stirred for 1.5 h, and then dppe (2.38 g) in hot acetone (50 cm^3) was added. The mixture was stirred overnight and then filtered to remove a white precipitate. Acetone was added to the filtrate to bring the total volume to 110 cm^3. To this solution were added NH_4PF_6 (2.05 g) in water (20 cm^3). More water was added to bring the final volume to 220 cm^3. After allowing the solution to stand for 2 h, fine white platelets were filtered off washed in acetone–water (1:1), and dried to give $[Au(dppe)_2]PF_6 \cdot Me_2CO$ (2.70 g, 91%). A full single-crystal *X*-ray structure was determined and will be reported in a future publication.[13] $\lambda_{max.}$(acetonitrile) 282 ($\varepsilon = 3.19 \times 10^4$) and 273 (sh) nm ($\varepsilon = 3.11 \times 10^4$ dm^3 mol^{-1} cm^{-1}).

(*b*) $[Au(dppen)_2]PF_6$. A 1.7 mol dm^{-3} solution (14 cm^3) of 2,2′-thiodiethanol in acetone was added to $HAuCl_4$ (3.0 g) dissolved in ethanol. To this solution were added acetone (10 cm^3) and water (1 cm^3). The solution was stirred for 2 h, taken to near dryness on a rotary evaporator, and redissolved with the addition of water (*ca.* 25 cm^3). Then dppen (6.05 g) in hot acetone (100 cm^3) was added, and the mixture stirred overnight. To this solution was added NH_4PF_6 (6.1 g) in water (80 cm^3). After allowing the solution to stand for 3 h, fine yellow needles were filtered off, washed in acetone–water (1:1) and then in diethyl ether, and dried. This complex was redissolved in acetonitrile (200 cm^3), and mixed with NH_4PF_6 (3.5 g) in water (15 cm^3). More water was added to precipitate the complex. This product was recrystallised from acetone by the addition of ether–hexane (1:1). Yield 7.05 g (79%). A full single-crystal *X*-ray structure was determined and will be reported in a future publication.[13] $\lambda_{max.}$(acetonitrile) 267 ($\varepsilon = 3.23 \times 10^4$), 272 (sh) ($\varepsilon = 3.16 \times 10^4$), and 288 (sh) nm ($\varepsilon = 2.59 \times 10^4$ dm^3 mol^{-1} cm^{-1}).

(*c*) $[Au(dppp)_2]PF_6$. A 1.7 mol dm^{-3} solution (4 cm^3) of 2,2′-thiodiethanol in acetone was added to $HAuCl_4$ (1.0 g) dissolved in water. The solution was cooled to 0 °C and dppp (2.23 g) in acetone (25 cm^3) was added. The mixture was stirred for 20 min, warmed slowly to 45 °C, and stirred for 20 min. The solution was cooled to room temperature and filtered. To this solution was added NH_4PF_6 (2.1 g) in water (15 cm^3). Another 40 cm^3 of water were added, and the solution was stored overnight at 4 °C. A gummy solid was filtered from the cold solution, and washed with acetone–water (1:1) and then with ether. The dried solid was redissolved in acetone (15 cm^3) and ether (10 cm^3) was added. After 2 h, 1.77 g of crystalline material were removed by filtration. Addition of another 5 cm^3 of ether resulted in a second crop of 0.95 g of product. The isolated crystals were washed with acetone–ether (2:3) and then with ether. Total yield: 2.72 g (91%). $\lambda_{max.}$(acetonitrile) 286 ($\varepsilon = 2.84 \times 10^4$) and 274 (sh) nm ($\varepsilon = 2.61 \times 10^4$ dm^3 mol^{-1} cm^{-1}).

(*d*) $[Au(dppb)_2]PF_6$. A 1.9 mol dm^{-3} solution (2 cm^3) of 2,2-thiodiethanol in acetone was added to $HAuCl_4$ (0.6 g) dissolved in water. The solution was diluted with acetone (25 cm^3), cooled to 0 °C, and dppb (1.35 g) in methylene chloride (30 cm^3) added. The mixture was stirred for 2 h, and then reduced to about 2 cm^3 on a rotary evaporator. Acetone (10 cm^3) was added and the solution was filtered. Acetone was added to the filtrate to bring the volume to 25 cm^3. To this solution was added NH_4PF_6 (1.2 g) in water (25 cm^3), and the solution was stored overnight at 4 °C. A viscous oil was isolated by decanting the remaining solution, and the oil was washed with acetone–water (1:1). The oil was redissolved in acetone (5 cm^3), and ether and hexane were added slowly until precipitation ceased. The solid was filtered off and dried, dissolved in acetone, and ether added until the solution became turbid. After this mixture was allowed to stand for 2 weeks at room temperature, 1.56 g (86%) of crystalline material were removed by filtration. A full single-crystal *X*-ray structure was determined and will be reported in a future publication.[13] $\lambda_{max.}$(acetonitrile) 293 ($\varepsilon = 2.94 \times 10^4$) and 278 nm ($\varepsilon = 2.91 \times 10^4$ dm^3 mol^{-1} cm^{-1}).

(*e*) $[Au(dppb)_2]Cl$. Tetraethylammonium dichloroaurate(I) was prepared according to a literature procedure.[21] A solution of 0.74 g of it and dppb (1.70 g) in methylene chloride (10 cm^3) was stirred for 2 h and then toluene (15 cm^3) was added slowly. The solution was filtered, and additional toluene (15 cm^3) was added. This solution was allowed to stand overnight and then was filtered again. The product was crystallised from the filtrate by adding ether slowly until the solution became turbid and then allowing the solution to stand. Yield: 2.17 g (97% as the toluene solvate). The identity of this complex was confirmed by elemental analysis and by u.v. spectroscopy.

(*f*) $[Au(dppb)_2]Br$. Tetraethylammonium dibromoaurate(I) was prepared according to a literature procedure.[10] A solution of 0.52 g of it and dppb (0.97 g) in methylene chloride (15 cm^3) was stirred for 1 h and then toluene (15 cm^3) was added slowly. The solution was filtered and several volumes of toluene were added. The product was crystallised by allowing this solution to stand. Yield: 1.21 g (91% as the toluene solvate). The identity of this complex was confirmed by elemental analysis and u.v. spectroscopy.

(*g*) $[Au(dppb)_2][ClO_4]_3$. A solution of $HAuCl_4$ (0.14 g) in methanol (1 cm^3) was added to $[Au(dppb)_2]Cl$ (0.5 g) in methanol (10 cm^3). A brown solid immediately precipitated. The mixture was refluxed for 5 min and became a yellow solution containing a dark solid. The mixture was cooled and filtered, and 70% $HClO_4$ (2 cm^3) was added to the filtrate. The liquid was refluxed for 5 min, then allowed to stand at room temperature overnight. The crystalline precipitate was filtered off and washed with methanol and ether. Yield (0.54 g 92%). This product was dissolved in acetonitrile and recrystallised by vapour diffusion with ether. A full single-crystal *X*-ray structure was determined and as for the previous gold complexes will be the subject of a future publication.[13] $\lambda_{max.}$(acetonitrile) 387 ($\varepsilon = 3.43 \times 10^4$) and 239 nm ($\varepsilon = 7.52 \times 10^4$ dm^3 mol^{-1} cm^{-1}). **CAUTION:** Although we have had no adverse experiences, the perchlorate salt should be treated as potentially explosive.

(*h*) $[AuCl(dppb)_2]Cl_2$. A solution of NBu^n_4Cl (0.26 g) and $[Au(dppb)_2][ClO_4]_3$ (0.21 g) in methylene chloride (20 cm^3) was stirred for a few minutes at room temperature, then filtered, and the filtrate dried on a rotary evaporator. Acetonitrile (2

cm^3) was added to the oily residue. Some solid precipitated from this mixture; another volume of acetonitrile was then added to the mixture. After standing for 6 d, the solution was filtered and 89 mg of dark yellow crystals were isolated. This complex was characterised as the monohydrate by a full single-crystal *X*-ray structure analysis. $\lambda_{max.}$(acetonitrile) 380 nm ($\varepsilon = 2.78 \times 10^4$ $dm^3\ mol^{-1}\ cm^{-1}$).

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