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Supplementary Material Available: Listing of observed and calculated structure factors for $(\text{CF}_3)_2\text{C}_2\text{CO}_2(\text{CO})_5(\text{MeCN})$ (8 pages). Ordering information is given on any current masthead page.

Electrochemical Reduction of the Gold Cluster $\text{Au}_9(\text{PPh}_3)_8^{3+}$. Evidence for an $\text{E}_r\text{E}_c\text{R}$ Mechanism. Formation of the Paramagnetic Gold Cluster $\text{Au}_9(\text{PPh}_3)_8^{2+}$

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Abstract: The gold cluster compound $\text{Au}_9(\text{PPh}_3)_8^{3+}$ can be reduced at a platinum electrode in various solvents (CH_3CN , CH_2Cl_2 , acetone). Controlled potential electrolysis delivered $n = 2$. In acetonitrile the unipositive gold cluster compound $\text{Au}_9(\text{PPh}_3)_8\text{PF}_6$ precipitated on the electrode, thus providing a method for larger scale preparation. Application of recently developed theories of pulse and cyclic voltammetry and convolution of linear sweep and cyclic voltammetry shows that the reduction in acetone follows an EE reaction path with $E_{1/2}(1) = -0.36$ V and $E_{1/2}(2) = -0.40$ V vs. a Ag-AgCl reference electrode. From the difference in half-wave potentials, it follows that the conproportionation constant $K_c = 4.7$ for the equilibrium $\text{Au}_9(\text{PPh}_3)_8^{3+} + \text{Au}_9(\text{PPh}_3)_8^+ \rightleftharpoons 2\text{Au}_9(\text{PPh}_3)_8^{2+}$ and that in mixing the 3+ and 1+ ions in a 1:1 molar ratio a large amount of the paramagnetic 2+ cluster should be formed. Indeed, an ESR experiment conducted at 20 K revealed a signal at $g_{av} = 1.982$.

In recent years interest in this¹ and other laboratories² has focused on the preparation, characterization, molecular structure determination, and reactivity of gold cluster compounds. In contrast with most other metal clusters containing carbonyl as the prominent ligand,³ the peripheral atoms in these gold clusters are coordinated with tertiary phosphines.

These gold clusters show a large variety of interconversion reactions. The $\text{Au}_9(\text{PPh}_3)_8^{3+}$ cluster is a key compound in this sense, and e.g., reactions have been described with PPh_3 , I^- , $\text{Ph}_2\text{PCH}_2\text{PPh}_2$, Cl^- , and SCN^- which lead to clusters with 8, 4, 5, and 11 gold atoms, respectively.¹

No detailed electrochemical studies on these gold cluster compounds have been reported, although preliminary results have appeared.^{4,5}

In this paper we present a detailed electrochemical study of the two-electron reduction of the $\text{Au}_9(\text{PPh}_3)_8^{3+}$ cluster which follows a EE reaction path. In addition, evidence will be given for the existence of the paramagnetic gold cluster $\text{Au}_9(\text{PPh}_3)_8^{2+}$.

Experimental Section

Measurements. Electrochemical measurements were made with a three-electrode Bruker E310 instrument or a PAR Polarographic Analyzer Model 174A coupled with a Universal Programmer PAR Model 175. The working electrode was a platinum disk, the auxiliary electrode a platinum plate, and the reference electrode a Ag-AgCl (0.1 M LiCl-acetone) electrode separated from the test solution via a Luggin capillary containing the supporting electrolyte (0.1 M Bu_4NPF_6). The Luggin capillary was positioned as close as possible (within 0.5 mm) to the working electrode to minimize iR drop. No external iR compensation was employed. Normal and differential pulse voltammograms were obtained at a scan rate of 5 mV/s with a pulse frequency of 2.0 pulses s^{-1} ; the differential amplitude was 10 mV. Cyclic voltammograms were

taken with scan rates of 0.05–50 V/s. The recording device was a Kipp BD 30 recorder, while cyclic voltammograms with scan speeds larger than 200 mV/s were displayed on a Tektronix 564B storage oscilloscope or a Nicolet Explorer II Model 206. Controlled potential electrolyses were carried out with a Wenking LB 75M potentiostat and a Birtley electronic integrator. Complete electrolysis of about 25 mg of electroactive material generally required 50 min. The temperature of the electrochemical measurements was 25 ± 1 °C.

AC voltammetry was carried out on a platinum disk, using a PAR 175A instrument coupled via a PAR 174/50 interface with a PAR Model 5204 lock-in amplifier with a built-in oscillator. Frequencies were measured with a HP 5381 frequency counter. The interface was modified in such a way that the amplitude of the applied voltage can be adjusted to every value between 0–30 mV. Measurements were made with an amplitude of 4 mV peak to peak in the frequency range 25–700 Hz, due to the frequency limit of the PAR 174A instrument.

³¹P{¹H} NMR spectra were recorded on a Varian XL-100 FT instrument at a frequency of 40.5 MHz with TMP as the internal reference. Electron spin resonance experiments were carried out on a Varian E12 instrument. All measurements were carried out under a nitrogen atmosphere.

Materials. All the reagents used were of reagent quality. $\text{Au}_9(\text{PPh}_3)_8(\text{PF}_6)_3$ was prepared as described either by the reduction of $\text{Au}(\text{PPh}_3)\text{NO}_3$ with NaBH_4 in ethanol⁶ or by evaporation of metallic gold into an ethanolic solution of PPh_3 and NH_4PF_6 .⁷ $\text{Au}_9(\text{PPh}_3)_8\text{PF}_6$ was obtained from controlled potential electrolyses (–0.60 V) in acetonitrile solutions of about 50 mg of the $\text{Au}_9(\text{PPh}_3)_8^{3+}$ cluster compound. The $\text{Au}_9(\text{PPh}_3)_8^{2+}$ cluster was isolated by repeatedly scraping off the product from the electrode and recrystallizing from CH_2Cl_2 -diethyl ether mixtures.

Diffusion Coefficient. The diffusion coefficient of the $\text{Au}_9(\text{PPh}_3)_8^{3+}$ cluster ($c = 5.2 \times 10^{-4}$ M) was obtained from the analysis of the chronoamperometric $i-t$ transient⁸ according to eq 1. These measurements

$$i t^{1/2} = nFAC(D/\pi)^{1/2} \quad (1)$$

shows a constant value for $i t^{1/2} = 40.4$ A $\text{s}^{1/2}$ in the time range 1.8–4.5

(1) For a recent review, see: Steggerda, J. J.; Bour, J. J.; Van der Velden, J. W. A. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 164.

(2) Demartin, F.; Mannasero, M.; Naldini, J.; Ruggeri, R.; Sansoni, M. *J. Chem. Soc., Chem. Commun.* **1981**, 222.

(3) Chini, P. *J. Organomet. Chem.* **1980**, *200*, 37.

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(7) Vollenbroek, F. A.; Bour, J. J.; Van der Velden, J. W. A. *Recl. Trav. Chim. Pays-Bas* **1980**, *99*, 137.

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Table I. Electrochemical Data for the Reduction of $\text{Au}_9(\text{PPh}_3)_8^{3+}$ in Acetone (0.1 M Bu_4PF_6)^a

Pulse Voltammetry ^b	
$E_{1/2} = -0.371$ V	
slope of the log plot = 54 mV	
$i_d/c = 0.318$ A dm ³ mol ⁻¹	
Differential Pulse Voltammetry ^b	
$E_p = -0.385$ V	
peak width $w_{1/2} = 97$ mV	
$i_p/c = 3.05 \times 10^{-2}$ A dm ³ mol ⁻¹	
Cyclic Voltammetry ^c	
$E_{p,c} = -0.407$ V	
$E_{p,a} = -0.344$ V	
$E_{1/2} = -0.376$ V	

^a Ag-AgCl (LiCl-acetone) reference electrode. ^b Scan rate 5 mV/s; 2 pulses/s. $\Delta E_{\text{pulse}} = 10$ mV. ^c Scan rate 2 V/s.

s. The diffusion constant is $D = 0.64 \times 10^{-5}$ cm² s⁻¹. The area of the electrode was calibrated with $\text{K}_4\text{Fe}(\text{CN})_6$ in 4 M KCl-water in which the diffusion coefficient⁸ is $D = 0.629 \times 10^{-5}$ cm² s⁻¹. Three different concentrations gave $A = 0.284$ cm².

Computational Information. Convolution or semiintegral electroanalyses was applied to linear sweep voltammetry and cyclic voltammetry by using a Minc 11ED computer system directly coupled with the electrochemical unit. A program was written in BASIC by one of us (M. H.L.P.) utilizing the algorithm for the convolution integral $I(t)$, as given by eq 6.7.9 in ref 9. This program was tested and verified by running it on a LSV of the oxidation of $\text{Ni}(\text{S}_2\text{C}_2(\text{CN})_2)_2^{2-}$ in acetone. A plot of $\ln [(I_1 - I)/I]$ vs. E gave a slope of -39.9 mV⁻¹. The theoretical value for a reversible one-electron process for this slope is $-(nF)/RT = -39.8$ mV⁻¹ (293 K). From the measured value of the limiting value of the convolution integral $I_1 = 6.2 \times 10^{-5}$ A s^{1/2} ($c = 7.2 \times 10^{-4}$ mol/dm³), the diffusion coefficient can be calculated according to eq 2, and this turned

$$I_1 = nFACD^{1/2} \quad (2)$$

out to be $D[\text{Ni}(\text{S}_2\text{C}_2(\text{CN})_2)_2^{2-}] = 1.18 \times 10^{-5}$ cm² s⁻¹, which is in agreement with a published value¹⁰ $D = 1.38 \times 10^{-5}$ cm² s⁻¹ for 0.1 M Et_4NClO_4 -acetonitrile solution.

The area of the electrode could also be obtained by convolution sweep voltammetry of $\text{K}_4\text{Fe}(\text{CN})_6$ in 4 M KCl. Three different concentrations (2.32, 4.05, and 5.75 mmol dm⁻³) gave $A = 0.260$ cm².

Results and Discussion

The electrochemical measurements on the $\text{Au}_9(\text{PPh}_3)_8^{3+}$ cluster ion have been made on a platinum electrode vs. a Ag-AgCl (0.1 M LiCl-acetone) reference electrode.

With all the various technique used, pulse and differential pulse voltammetry (PP and DPP) and linear sweep voltammetry (LSV), a single reduction wave was observed at ca. -0.37 V (Table I) in various solvents (acetone, CH_3CN , CH_2Cl_2). Cyclic voltammetry (CV) showed that the charge transfer is a chemically reversible process. A well-resolved anodic peak is observed in the backward scan.

Controlled potential electrolyses in acetone at -0.60 V revealed that two electrons are transferred in this reduction ($n = 1.94$ at 3% of the initial current).

When the controlled potential electrolyses experiments were carried out in acetonitrile solutions at -0.65 V, the current decayed to nearly zero after some time. Inspection of the electrode showed that a dark red microcrystalline substance was precipitated on the platinum electrode. Repeated cleaning of the electrode resulted also in values of $n = 2$.

These data strongly indicated the formation of the unipositive gold cluster compound. Further evidence for this came from the ³¹P[¹H] NMR spectra taken before and after the exhaustive electrolyses. In both cases only one singlet is observed, indicating that after electrolysis only one reduced species is present in the solution. The observed values are in agreement with those noted for the pure compounds: 54.8 ppm for $\text{Au}_9(\text{PPh}_3)_8^{3+}$ and 53.7 ppm for $\text{Au}_9(\text{PPh}_3)_8^+$ in CH_2Cl_2 downfield relative to TMP.

Table II. Cyclic Voltammetric Data^a for the Reduction of $\text{Au}_9(\text{PPh}_3)_8^{3+}$

scan rate, V/s	ΔE_p , ^b mV	$E_{p,c} - E_{p/2,c}$, ^c mV	$10^3 i_p/v^{1/2}$ A s ^{1/2} V ^{-1/2}	i_b/i_f
0.02	55	56	0.111	0.98
0.05	54	55	0.113	0.95
0.1	55	56	0.114	0.94
0.2	57	55	0.114	0.92
0.5	56	55	0.115	0.93
1	61	60	0.114	0.91
2	64	60	0.114	0.94
5	66	61	0.116	0.91
10	73	64	0.114	0.94
20	83	66	0.113	0.95
50	129	71	0.107	0.97

^a In acetone (0.1 M Bu_4NPF_6) with $c = 3.03 \times 10^{-3}$ M at 298 K. ^b Anodic-cathodic peak potential separation. ^c Cyclic voltammetric peak width.

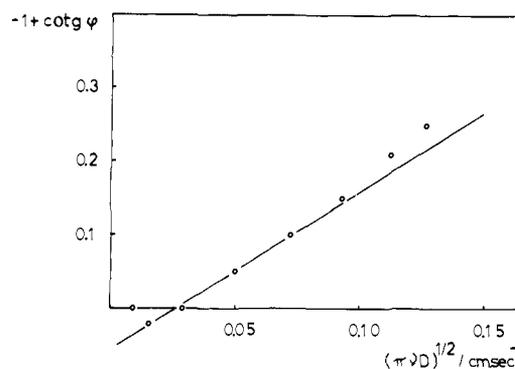


Figure 1. Dependence of the phase angle φ from the frequency $\omega = 2\pi\nu$ for a 5×10^{-4} M solution of $\text{Au}_9(\text{PPh}_3)_8(\text{PF}_6)_3$ in acetone (0.1 M Bu_4NPF_6).

Larger scale electrolysis in acetonitrile thus provides an easy method for the preparation of larger quantities of this cluster compound. The X-ray structure determination of this substance showed it to contain indeed $\text{Au}_9(\text{PPh}_3)_8$ units, the full details of which will be published elsewhere.¹¹

Cyclic and AC Voltammetry. The data of the cyclic voltammetric measurements show that the current function $i_p/v^{1/2}$ as well as the peak current ratio i_b/i_f are constant over a wide range of scan rates (Table II). These so-called diagnostic criteria normally point to a fast and uncomplicated charge-transfer reaction. However, ΔE_p values are distinctly different from the value expected for a reversible two-electron transfer, $2.2RT/nF = 29$ mV. Even for ΔE_p extrapolated to a scan rate value in the reversible region of this transition and an applied correction for uncompensated iR losses with R about 10 Ω , the peak potential difference is still much larger than the expected theoretical value (Table II).

Also other commonly applied criteria in the analyses of recorded $i-E$ curves, i.e., the slope of the plot of E vs. $\log [(i_d - i)/i]$ (in PP) and the peak width at half-height, $w_{1/2}$ (in DPP) show larger values than expected for a reversible two-electron transfer process (Table I).

AC voltammetry was also performed with a platinum disk electrode. The peak current I_p of the recorded voltammograms was proportional to $\omega^{1/2}$ in the frequency range $\omega = 25-700$ Hz. The maximum in the current occurred at $E_p = E_{1/2}$. Furthermore, the potential of maximum $\cot \varphi$ in the plot of $\cot \varphi$ vs. $\omega^{1/2}$ was independent of the frequency and coincide also with $E_{1/2}$. The plot of $(-1 + \cot \varphi)$ vs. $(\pi\nu D)^{1/2}$ ($\omega = 2\pi\nu$) showed linear behavior in the same frequency range (Figure 1). All these observations point to a fast, diffusion-controlled electron transfer.¹² At low

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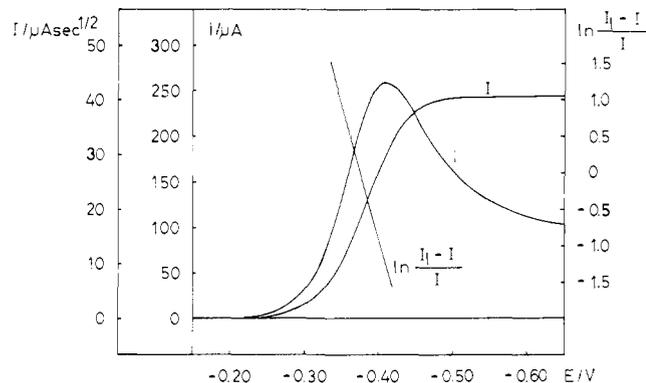
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(12) Smith, D. E. *Electroanal. Chem.* **1966**, *1*, 1.

Table III. Potential Difference $\Delta E_{1/2} = E_{1/2}(1) - E_{1/2}(2)$

method	criterion	$\Delta E_{1/2}$, mV	$-E_{1/2}(1)$, mV	$-E_{1/2}(2)$, mV
differential pulse voltammetry	$w_{1/2} = 97$ mV	41	360	400
cyclic voltammetry ^a	$\Delta E_p = 63$ mV	40	356	396
convolution of LSV ^b	$E_{p,c} - E_{p/2,c} = 60$ mV	41	356	397
	slope of the log plot = 37.6 mV ⁻¹	39	359	399

^a Scan rate 2 V/s. ^b Scan rate 5 V/s.Figure 2. Current, convoluted current, and logarithmic analysis for the linear sweep voltammogram of the reduction of $\text{Au}_9(\text{PPh}_3)_8^{3+}$ in acetone.

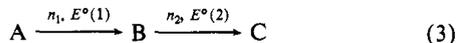
frequencies phase angles larger than 45° were observed, as can be seen from Figure 1. Such values have been attributed to the occurrence of adsorption at the electrode of reactants and/or products.

For the bulky compounds studied here there might be close contact between the electrode and the cluster molecules ($r = 10.0$ Å), and still then the center of the cluster is outside the outer Helmholtz plane. With a sensitive technique like AC voltammetry, such nonspecifically¹³ adsorption may result in the observed magnitude of the phase angles.

The peak width at half-height also show values larger than those expected for a reversible two-electron transfer, e.g., 85 mV at 36 Hz and 90 mV at 477 Hz.

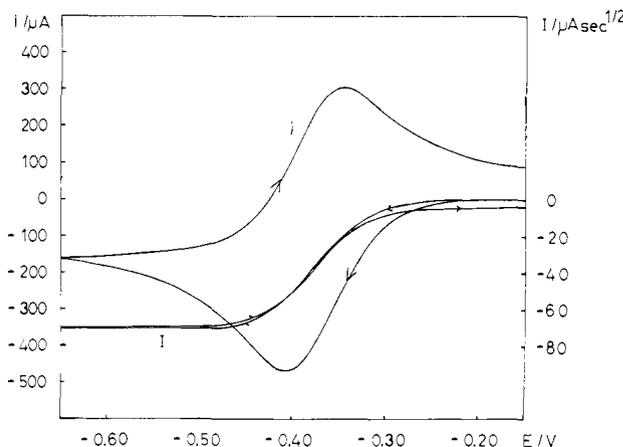
Thus, according to the results thus far discussed a mechanism other than a two-electron transfer must be operating. Hung and Smith¹⁴ have noted that such notably wider AC curves are indicative for the occurrence of an EE mechanism.

E₁E₂C₁ Mechanism. Recently Richardson and Taube¹⁵ developed a method for the determination of $\Delta E^\circ = E^\circ(2) - E^\circ(1)$ for a two-step electrochemical charge transfer as shown in eq 3.



This $\Delta E^\circ = \Delta E_{1/2}$ ¹⁶ value can be obtained from a set of tabulated parameters, such as the peak width in DPP and the peak width $E_p - E_{p/2}$, and peak separation ΔE_p in CV.

The results for the case studied here obtained from the various techniques are given in Table III. Excellent agreement for $\Delta E_{1/2}$ values as well as for now easily to calculate¹⁵ $E_{1/2}$ values are obtained for the different methods. For cyclic voltammetry the measured data at scan rates of about 2–5 V/s were used, because the reduction process remains essentially electrochemical reversible up to 10 V/s. The reversible behavior is confirmed by the con-

Figure 3. Cyclic voltammogram and convolution of 3.0×10^{-4} M $\text{Au}_9(\text{PPh}_3)_8^{3+}$ in acetone (0.1 M Bu_4NPF_6) at a scan rate of 2 V/s.

volution⁹ of the measured cyclic voltammograms. At a scan rate of 2 V/s the forward and backward convoluted $I-E$ curves superimpose reasonably well (Figure 3), which is a decisive criterion for reversibility. At low scan rates some deviations in the convolution pattern are seen, which may indicate a very slow decomposition reaction (Figure 3).

Convolution potential sweep voltammetry^{17,18} has also been shown to be a very useful technique in deciding which reaction mechanism should be assigned to an electron transfer. For the two-step charge transfer of eq 3, Ammar and Savéant^{18,19} have given a detailed analysis. For the present discussion it is sufficient to give the resulting equations of the logarithmic analysis of the convoluted current I for the assumed EE mechanism (eq 4–9).

$$\ln \frac{I_1 - I}{I} = n f (E - E^\circ) + \ln \frac{0.5 \exp(0.5 n f \Delta E^\circ) + \exp(n f (E - E^\circ))}{1 + 0.5 \exp(0.5 n f \Delta E^\circ) \exp(n f (E - E^\circ))} \quad (4)$$

$$E^\circ = 0.5[E^\circ(1) + E^\circ(2)] = 0.5[E_{1/2}(1) + E_{1/2}(2)] \quad (5)$$

$$\Delta E^\circ = \Delta E_{1/2} = E^\circ(2) - E^\circ(1) = E_{1/2}(2) - E_{1/2}(1) \quad (6)$$

$$f = nF/RT \quad (7)$$

$$I_1 = 2nFAC_A D^{1/2} \quad (8)$$

$$S = 4f/[2 + \exp(0.5f\Delta E^\circ)] \quad (9)$$

I_1 is the limiting value of I . The function (eq 4) is characterized by an inflexion at $E = E^\circ$ in which the observed slope S is represented by eq 9.

The results of the convoluted LSV are given in Figure 2, where the slope S delivers $\Delta E^\circ = \Delta E_{1/2} = 39$ mV, a value in good agreement with those found above (Table III). From the observed value of $I_1 = 7.13 \times 10^{-5}$ A s^{1/2} (eq 8) the diffusion coefficient can be calculated $D(\text{Au}_9^{3+}) = 0.64 \times 10^{-5}$ cm²/s, which is the same as that found from chronoamperometry (see Experimental Section).

(13) Reference 9; p 511.

(14) Smith, D. E.; Hung, H. L. *J. Electroanal. Chem.* **1966**, *11*, 237.(15) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278.(16) Neglectable differences are assumed to exist between E° and $E_{1/2}$ for which holds⁹

$$E_{1/2} = E^\circ + \frac{RT}{nF} \ln \frac{D_{\text{red}}^{1/2}}{D_{\text{ox}}^{1/2}}$$

while in this case differences in the diffusion coefficients of the various 3+, 2+, and + clusters will be small.

(17) Imbeaux, J. C.; Savéant, J. M. *J. Electroanal. Chem.* **1973**, *44*, 1969.(18) Oldham, K. B.; Spanier, J. *J. Electroanal. Chem.* **1970**, *26*, 331.(19) Ammar, F.; Savéant, J. M. *J. Electroanal. Chem.* **1973**, *47*, 215.

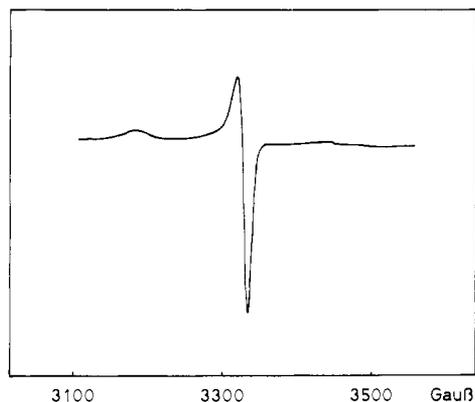
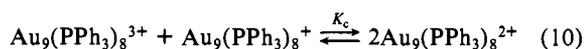


Figure 4. Electron spin resonance spectrum of a frozen sample of a 1:1 molar mixture of $\text{Au}_9(\text{PPh}_3)_8^{3+}$ and $\text{Au}_9(\text{PPh}_3)_8^+$ in CH_2Cl_2 at 20 K.

Thus, conclusive evidence has been found in support of an EE charge transfer.

The conproportionation constant K_c of the conproportionation equilibrium of eq 10 can be calculated from $K_c = \exp$

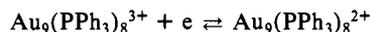


$[n_1 n_2 F \Delta E_{1/2} / RT] = \exp[\Delta E_{1/2} / 25.69] = 4.7$ (at 298 K and with $n_1 = n_2 = 1$). The observed magnitude of K_c indicates that in mixing the Au_9^{3+} and Au_9^+ cluster compounds in a 1:1 molar ratio a fairly large amount of the paramagnetic cluster should be formed. In an experiment, solutions which contained 1 mg of the Au_9^{3+} and Au_9^+ clusters, respectively, in acetone were mixed. Immediately thereafter a sample was placed in an ESR tube and frozen as quickly as possible. The electron paramagnetic resonance spectrum revealed a signal attributed to $\text{Au}_9(\text{PPh}_3)_8^{2+}$. This ESR experiment was also conducted successfully in CH_2Cl_2 (at 20 K) with $g_{\text{av}} = 1.982$ ($g_{\parallel} = 2.011$ and $g_{\perp} = 1.923$) (Figure 4), a value not uncommon for gold complexes.²⁰ The absence of hyperfine structure may be due to fast electron exchange over the nine gold atoms. The 2+ species seems to be stable for at least about 30 min, being the acquisition time for an ^{31}P NMR spectrum, because in a $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum no peaks were seen for such a 1:1 mixture. This implies also that the paramagnetic 2+ ion is in fast equilibrium with the 3+ and + ions.

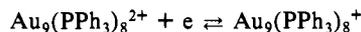
Conclusions

From the results discussed above we conclude that the $\text{Au}_9(\text{PPh}_3)_8^{3+}$ can be reduced electrochemically at a platinum electrode by a two-step charge transfer, accompanied by a fast chemical equilibrium reaction according to the reaction Scheme I. The reaction mechanism will be denoted⁹ by $E_r E_r C_r$.

Scheme I



$$E_{1/2}(1) = -0.36 \text{ V}$$



$$E_{1/2}(2) = -0.40 \text{ V}$$



This two-electron reduction seems to be accompanied by a large molecular reorganization process within the cluster. The molecular structures of the Au_9^{3+} and Au_9^+ cluster as obtained from X-ray structure analyses are shown in Figure 5. Both compounds are seen from the same direction with analogous numbering of the gold atoms. The Au_9^+ cluster is shown in a view directly along the 3-fold axis which comprises the $\text{P}(2)\text{-Au}(2)\text{-Au}(1)\text{-Au}(2')\text{-P}(2')$ moiety. Two triangles of gold atoms indicated with 3 and 3' are perpendicular to this 3-fold axis. The differences

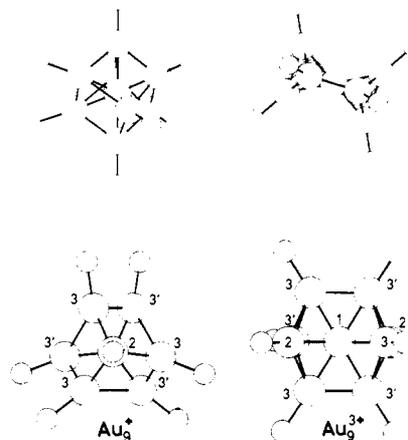


Figure 5. Structures of the cluster ions $\text{Au}_9(\text{PPh}_3)_8^{3+}$ and $\text{Au}_9(\text{PPh}_3)_8^+$. Only the gold atom (large circles) and phosphorous atoms (small circles) are shown.

Table IV. Comparison of the Gold-Gold Distances (Å) in the Cluster Compounds

	$\text{Au}_9(\text{PPh}_3)_8^+$		$\text{Au}_9(\text{PPh}_3)_8^{3+}$		change
	N^a	distance	N^a	distance	
Au(1)-Au(2)	2	2.62	2	2.68	-0.06
Au(1)-Au(3)	6	2.55	4	2.73	-0.18
Au(1)-Au(3')			2	2.68	-0.13
Au(2)-Au(3)	6	2.91	2	2.85	0.06
Au(2)-Au(3')			2	2.89	0.02
			2	2.75	0.16
Au(3)-Au(3')	3	2.69	2	2.85	-0.16
	3	3.35	2	2.89	-0.20
			2	2.79	0.46
			2	2.79	0.56

^a N is the number of times this bond length occurs.

in the positions of the Au(2) atoms in both clusters are apparent. Upon reduction the Au(2) atoms are shifted toward positions above and below the centers of the 3 and 3' triangles, while furthermore these parallel triangles are each twisted in opposite directions around the 3-fold axis with a twist angle of 15°. Concomitant shortenings and elongations of several gold-gold distances (Table IV) ultimately result in a symmetry change from D_{2h} for the 3+ ion to D_3 for the 1+ ion.

It has to be noted that all these changes and differences are observed for the solid state; in solution a different situation might be present. The heterogeneous reduction reaction described here is fast, and also the chemically induced homogeneous interconversions and reactions proceed with large velocities.¹

From CV and AC data given above, a very crude estimation of the (overall) heterogeneous rate constant leads to a value of $k_s > 0.3$ cm/s and consequently to a very small value for the activation energy ($\Delta G^\ddagger < 4.5$ kcal/mol).

Following contemporary much-used theories for electron-transfer processes, the activation free energy due to solvent reorganization is calculated from eq 11, where e is the electronic

$$\Delta G_{\text{out}}^\ddagger = \frac{e^2}{8} \left(\frac{1}{r} - \frac{1}{R} \right) \left(\frac{1}{n^2} - \frac{1}{\epsilon_s} \right) \quad (11)$$

charge, $n^2 = \epsilon_o$ is the optical and ϵ_s is the static dielectric constant, $r = 10.0$ Å is the radius of the spherical cluster, and R is twice the distance from the reacting species in the transition state to the electrode surface (i.e., the distance from the center of the cluster to its "image" in the metal), here about 20 Å. For acetone as the solvent and a one-electron transfer, a value for $\Delta G_{\text{out}}^\ddagger$ of about 1 kcal/mol is obtained, leaving only a few kilocalories for the activation free energy due to inner reorganization. It has recently been argued¹ that fluxional behavior will be normal for

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this class of compounds and that even at low temperatures fast intramolecular movements occur. This explains why the heterogeneous reduction is diffusion controlled even at high scan speeds and only minor molecular rearrangements are needed in solution with very small activation energy.

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Cobalt Metallacycles. 11. On the Transformation of Bis(acetylene)cobalt to Cobaltacyclopentadiene¹

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Abstract: Formation of η^5 -cyclopentadienyl(triphenylphosphine)cobaltacyclopentadienes (**4**) by the reaction of acetylenes with (η^5 -cyclopentadienyl)(triphenylphosphine)(acetylene)cobalt (**1**) has been investigated in detail. Kinetic studies indicate the intermediacy of (η^5 -cyclopentadienyl)bis(acetylene)cobalt (**2**), which cyclizes to coordinatively unsaturated η^5 -cyclopentadienylcobaltacyclopentadiene (**3**) by a spontaneous oxidative coupling reaction. Regioselectivity of the cyclization process is controlled by the steric factor of substituents rather than their electronic factor. The structures and bonding of intermediates **2** and **3** are studied with ab initio molecular orbital calculations. The transition state of the cyclization reaction is postulated to be a low-symmetry C_s conformation derived from an "upright" bis(acetylene)cobalt. This accounts for the observed regioselectivity that the acetylenic carbon bearing a bulky substituent becomes the α -carbon of the metallacycle.

Introduction

There has been much recent interest in metallacyclic compounds, especially those formed from unsaturated ligands such as olefins and acetylenes, principally in connection with the mechanism of transition-metal-catalyzed oligomerization reactions. While many experimental results have been accumulated, there has been little theoretical analysis of the reaction. A recent work by Stockis and Hoffmann deals with the reaction path of bis(olefin)tricarbonyliron to ferracyclopentane interconversion on the basis of extended Hückel molecular-orbital calculations.³ More recently a closely related reaction, the degradation of nickelacyclopentane to ethylene, has also been analyzed by them.⁴

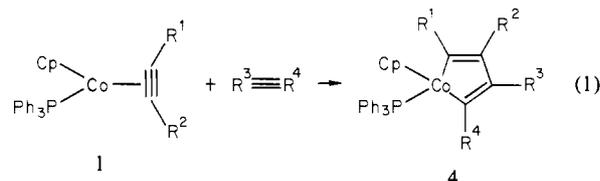
In the course of our investigation of the η^5 -cyclopentadienylcobalt system, we have found that the reaction with acetylene to give cobaltacyclopentadiene is a very facile one. This property of (η^5 - C_5H_5)Co has been utilized by us and other workers for stoichiometric and catalytic preparation of a variety of cyclic organic compounds.⁵

In this paper we focus on the fundamental part of these reactions, i.e., the formation of the cobalt metallacycle from two molecules of acetylene, and elucidate its detailed mechanism with the aid of molecular orbital theory.

Results and Discussion

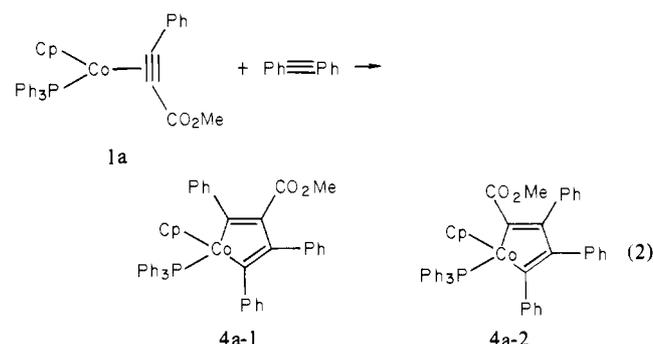
Reaction Route. Previously we reported that the reaction of η^5 -cyclopentadienyl(triphenylphosphine)(acetylene)cobalt (**1**) with

acetylene yielded cobaltacyclopentadiene complexes (**4**) with various substituents (eq 1).⁶ To date over 20 compounds of **4**



$\text{R}^1, \text{R}^2 = \text{Ph}, \text{CO}_2\text{Me}, \text{CN}$
 $\text{R}^3, \text{R}^4 = \text{H}, \text{Me}, \text{Ph}, \text{CO}_2\text{Me}, \text{Fc}$
 $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$
 $\text{Fc} = \text{ferrocenyl}$

have been prepared by this and similar reactions. For example, the reaction of methyl phenylpropiolate complex **1a** with excess diphenylacetylene gives two isomeric cobaltacyclopentadienes (**4a-1** and **4a-2**) in 5:1 ratio (eq 2).



The rate of reaction 2 at room temperature in CD_2Cl_2 was followed by NMR spectra with or without the addition of free

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