Table IV (Continued)

Ru(6)–C(61)–O(61)	178.7 (7)	Ru(7)–C(72)–O(72)	177.3 (9)	Ru(8)–C(82)–O(82)	179.2 (9)	Ru(9)–C(92)–O(92)	178.5 (8)
Ru(6)–C(62)–O(62)	178.7 (8)	Ru(7)–C(73)–O(73)	179.0 (9)	Ru(9)–C(91)–O(91)	178.5 (9)	Ru(9)–C(93)–O(93)	177.1 (8)
Ru(7)–C(71)–O(71)	178.0 (8)	Ru(8)–C(81)–O(81)	178.4 (10)				

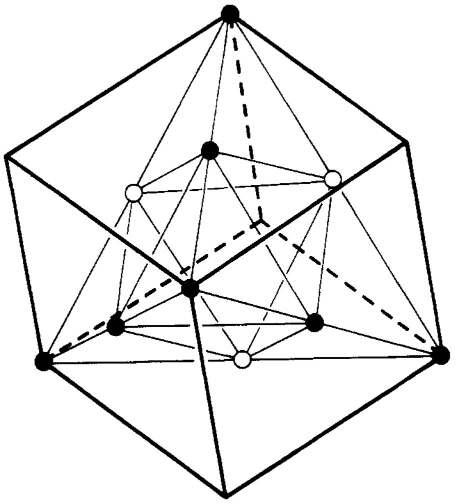

Figure 2. Relationship between the Ru_{10} core and the fcc unit cell.

cluster **3** is the first example in which the ruthenium atom has a cubic close-packed (ccp) metal array. The structure of the metal core of **3** may be seen as a tetracapped octahedron. A carbido atom is placed at the center of the octahedron.

There is a difference between the Ru–Ru bond lengths within the central octahedron (2.834 (1)–2.878 (1) Å) and those from the capping ruthenium atoms (2.751 (1)–2.792 (1) Å). The former relatively long Ru–Ru bond lengths are seen in a wide range of ruthenium clusters, that is 2.8512 (4)–2.8595 (4) Å in $Ru_3(CO)_{12}$,[9] 2.85 (±0.02)–2.90 (±0.10) Å in **1**,[10,11] 2.832 (2)–2.927 (2) Å in $[HRu_6(CO)_{18}]^-$,[12] 2.80–2.89 Å in $[Ru_6(CO)_{18}]^{2-}$,[13] 2.827 (5)–3.034 (5) Å in $Ru_6C(CO)_{17}$,[14] and 2.858 (3)–2.959 (2) Å in $H_2Ru_6(CO)_{18}$.[15] On the other hand, the latter short Ru–Ru bond lengths are reported in those participating with capping ruthenium atoms without or virtually without bridging ligands, that is, 2.778 (1)–2.807 (1) Å in $[Ru_8H_2(CO)_{21}]^{2-}$[7] and 2.787 (1) Å in $[Ru_4H_3(CO)_{12}]^-$ of C_{3v} symmetry.[16] Consequently, those short Ru–Ru bond lengths in **3** may be attributable to the capping structure.

When the structure of **3** is compared with that of **2**, the Ru–Ru bonds are 0.8% shorter than the corresponding Os–Os bonds, and the Ru–carbido bonds are 0.7% shorter than the Os–carbido bonds.[3] These findings are in agreement with the fact that the metallic radius of ruthenium is 0.9% smaller than that of osmium.[17] Similar tendencies are seen in related cases: Ru–Ru bonds of $Ru_3(CO)_{12}$[9] and $[Ru_6(CO)_{18}]^{2-}$[13] are 0.8% and 0.6% shorter than the corresponding bonds of $Os_3(CO)_{12}$[18] and $[Os_6(CO)_{18}]^{2-}$,[19] respectively.

There are two kinds of terminal carbonyl ligands in **3**; two CO's coordinate to each ruthenium atom of the carbido-centered octahedron, and three CO's coordinate to each capping ruthenium atom. Although there are no differences in the bond angles of Ru–C–O (176.4 (8)–179.4 (9)°) among these carbonyl ligands, there is a slight difference in the bond lengths. The C–O bonds coordinating to the capping Ru atoms are 0.02 Å (mean) longer than those to the carbido-centered octahedron.

There is a relatively large difference between **2** and **3** in the bond lengths where carbonyl ligands are concerned. The Ru–CO bonds of **3** are 1.3% longer than the Os–CO bonds of **2**, and the C–O bonds of **3** are, in contrast, 2.7% shorter than those of **2**,[3] which suggests less metal–CO back-bonding interactions in the ruthenium cluster than those in the osmium cluster. A similar trend can be seen in the equatorial CO groups of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ of the same structure.[9,18]

Acknowledgment. We thank Ken-ichi Sakaguchi for help with the X-ray diffraction experiments. The present work was partially supported by a Grant-in-Aid for Scientific Research (No. 62115004) from the Ministry of Education, Science and Culture.

Supplementary Material Available: Complete listings of crystallographic data, atomic coordinates, anisotropic thermal parameters, bond lengths, and bond angles and a packing diagram of the unit cell (18 pages); a listing of structure factors (44 pages). Ordering information is given on any current masthead page.

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Electron-Transfer Series of Gold Clusters: $PtAu_8(PPh_3)_8{}^{2+/+/0}$, $Au_9[P(p\text{-}MeOC_6H_4)_3]_8{}^{3+/2+/+}$, and $Au_9(PPh_3)_8{}^{3+/2+/+}$

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Continuous interest in metal cluster redox chemistry results in large part from the observed structural differences effected by changes in the oxidation states of these compounds.[1-5] Gold–phosphine clusters show a fluxional behavior in solution, even at low temperatures,[6] and they exhibit an interesting electrochemical behavior. We reported the electrochemical behavior in acetone of the gold cluster $Au_9(PPh_3)_8{}^{3+}$, which could be reduced at a platinum electrode in two consecutive one-electron steps.[7] Re-

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Table I. Determination of the Half-Wave Potentials for the Gold Cluster Compounds

	method, criterion					
	DPP	CV^d				
cluster	$w_{1/2}$, mV	ΔE_p, mV	$E_p - E_{p/2}$, mV	$\Delta E_{1/2}$, mV	$-E_{1/2}$ (1), mV	$-E_{1/2}$ (2), mV
		Benzonitrile[a]				
$PtAu_8(PPh_3)_8^{2+}$	194			107	1520	1627
		146		105	1509	1614
			118	94	1507	1601
		Acetonitrile[a]				
$PtAu_8(PPh_3)_8^{2+}$	133			65	1488	1553
		88		62	1449	1511
		Dichloromethane[b]				
$PtAu_8(PPh_3)_8^{2+}$	237			147	1141	1288
		193		145	1143	1288
			166	134	1154	1288
$Au_9(PPh_3)_8^{3+}$	164			84	598	681
		122		87	597	684
			105	83	602	685
$Au_9[(p\text{-}MeOC_6H_4)_3P]_8^{3+}$	64			−7	740	733
		40[e]		−8	735	727
		Acetone[c]				
$PtAu_8(PPh_3)_8^{2+}$	201			113	885	998
		155		113	884	997
			135	108	889	997
$Au_9(PPh_3)_8^{3+}$	89			34	337	371
		59		36	342	378
$Au_9[(p\text{-}MeOC_6H_4)_3P]_8^{3+}$	51			−67	505	438

[a] Potentials vs the Ag/Ag^+ (0.1 M $AgNO_3$) reference electrode. [b] Potentials vs the SSCE reference electrode. [c] Potentials vs the Ag/AgCl reference electrode. [d] With a scan rate of 50 mV/s. [e] With a scan rate of 20 mV/s.

Table II. Current Functions for the Reduction Processes of the Gold Clusters

		PP	DPP	i_p/i_d	
cluster	solvent	i_d/C^a	i_p/C^a	measd[b]	calcd ($\Delta E_{1/2}$)[c]
$PtAu_8(PPh_3)_8^{2+}$	dichloromethane	0.778	0.0378	0.0486	0.0492 (147)
	acetone	0.846	0.0428	0.0506	0.0511 (113)
$Au_9(PPh_3)_8^{3+}$	dichloromethane	0.791	0.0442	0.0559	0.0575 (84)
	acetone	0.764	0.0745	0.0975	0.0988 (34)
$Au_9[(p\text{-}MeOC_6H_4)_3P]_8^{3+}$	dichloromethane	0.553	0.0922	0.1667	0.1334 (−7)
	acetone	0.696	0.1220	0.1752	0.1694 (−67)

[a] Current functions in A dm^3 mol^{-1}. [b] Ratio of the measured current functions. [c] Ratio of the current functions as calculated from DPP curve simulations from ref 12 and, in parentheses, the corresponding differences in half-wave potentials, $\Delta E_{1/2}$, in mV.

Table III. Half-Wave Potentials[a] and Comproportion Constants (25 °C)

cluster	solvent	$E_{1/2}(1)$, V	$E_{1/2}(2)$, V	K_c[b]	ϵ[c]
$PtAu_8(PPh_3)_8^{2+}$	dichloromethane	−1.57	−1.72	310	9.1
	acetone	−1.51	−1.62	81	21
	benzonitrile	−1.55	−1.65	64	25
	acetonitrile	−1.53	−1.59	12.5	37
$Au_9(PPh_3)_8^{3+}$	dichloromethane	−1.03	−1.11	26	9.1
	acetone	−0.96	−0.99	3.8	21
$Au_9[(p\text{-}MeOC_6H_4)P]_8^{3+}$	dichloromethane	−1.17	−1.16	0.76	9.1
	acetone	−1.13	−1.06	0.074	21

[a] Potentials vs $Fe(C_5H_5)_2^{+,0}$ redox couple. [b] Comproportionation constant calculated from $\Delta E_{1/2}$ values measured by DPP. [c] Dielectric constant of the solvent.

garding the assembled data and the fluxionality of this cluster, an EE reduction path was proposed rather than an ECE mechanism.[3]

Recent investigations on gold cluster compounds in this laboratory have dealt with the preparation, characterization, and molecular structure determination of a mixed-metal cluster,[8] $PtAu_8(PPh_3)_8^{2+}$. In this cluster the platinum atom occupies a central position with the gold atoms arranged around it in a so-called centered crown configuration, as evidenced by an X-ray crystal structure determination and by ^{31}P NMR spectroscopy.[8] An analogous structure has been reported[9,10] for $Au_9[P(p\text{-}MeOC_6H_4)_3]_8^{3+}$.

We report here the results of an electrochemical study of the $PtAu_8(PPh_3)_8^{2+}$ and $Au_9[P(p\text{-}MeOC_6H_4)_3]_8^{3+}$ cluster ions. In various solvents both ions are reduced by the stepwise transfer of two single electrons, thus showing an EE reduction mechanism.

Results

The electrochemical redox behavior of the cluster compounds $PtAu_8(PPh_3)_8^{2+}$, $Au_9[P(p\text{-}MeOC_6H_4)_3]_8^{3+}$ and $Au_9(PPh_3)_8^{3+}$ was

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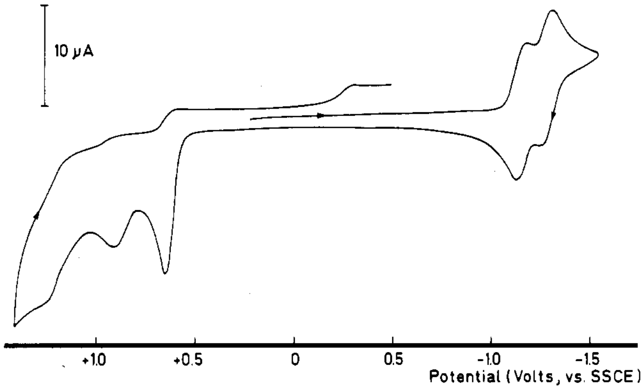

Figure 1. Cyclic voltammogram of $PtAu_8(PPh_3)_8^{2+}$ in CH_2Cl_2 (0.1 M Bu_4PF_6) vs a SSCE reference electrode with v = 200 mV/s.

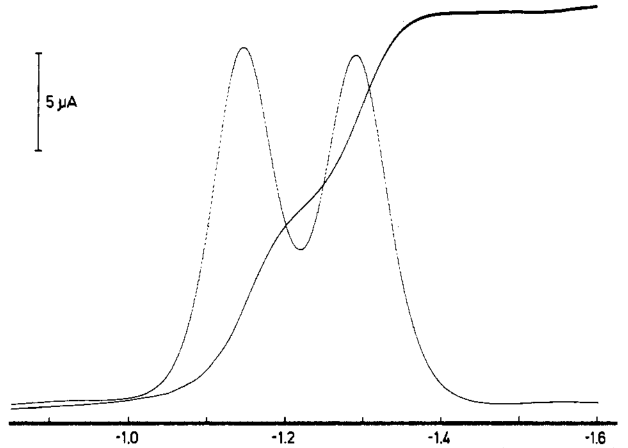

Figure 2. Pulse and differential-pulse voltammograms of $PtAu_8(PPh_3)_8^{2+}$ in CH_2Cl_2.

studied in various solvents (dichloromethane, acetone, acetonitrile, and benzonitrile containing 0.1 M Bu_4NPF_6) by using normal-pulse (PP), differential-pulse (DPP), and cyclic voltammetric (CV) techniques.

The oxidation behavior of the $PtAu_8(PPh_3)_8^{2+}$ and $Au_9(PPh_3)_8^{3+}$ clusters is rather complicated; the irreversible processes lead most probably to a decomposition of the clusters (Figure 1). Therefore this study has been limited to the reduction processes.

Reduction of $PtAu_8(PPh_3)_8^{2+}$. This cluster could be reversibly reduced in two closely spaced one-electron reactions (Figure 2). Tables I–III summarize the data from the electrochemical measurements. The chemical reversible character of these reductions was established by cyclic voltammetry as well-shaped reoxidation waves were noted in the backward scans (Figure 1).

Controlled-potential electrolyses in benzonitrile, in acetone, and in acetonitrile revealed that two electrons are transferred in this reduction (n = 2.0, 2.1, and 2.0 for these solvents, respectively). The color of the benzonitrile solution changed from orange-yellow to dark green after the transfer of approximately one electron, and finally a red-brown solution resulted. In acetonitrile a violet product, most probably the neutral cluster $PtAu_8(PPh_3)_8$ precipitated on the platinum electrode and the electrode was cleaned repeatedly. Attempts to purify and characterize this material have not been successful thus far. In CH_2Cl_2 solutions, no reproducible results were obtained thus far, because of the reaction of the intermediates or products with this solvent. Gold–phosphine clusters have shown also some reactivity toward this solvent.[6,11]

For the determination of the half-wave potentials of such closely spaced electron transfers a procedure has been followed outlined by Richardson and Taube.[12] From parameters extracted from the recorded voltammograms, like the half-widths ($w_{1/2}$ in DPP and $E_p - E_{p/2}$ in CV) and the peak potential difference (ΔE_p in CV), combined with a set of tabulated parameters, the differences in half-wave potentials, $\Delta E_{1/2} = E_{1/2}(2) - \mathrm{E}_{1/2}(1)$, and from these the half-wave potentials themselves were obtained. The results of this computations are given in Table I.

Reduction of $Au_9[P(p\text{-}MeOC_6H_4)_3]_8^{3+}$. This cluster ion showed a single wave in CV and DPP at −0.50 V in acetone. In the backward scan of the cyclic voltammograms a somewhat broadened anodic wave was observed and i_b/i_f ratios reached only values of 0.85. This points toward some decomposition of the formed products.

Controlled-potential coulometry in benzonitrile at a potential lower than the reduction half-wave potential (at −1.2 V) resulted in a value of n = 1.8.

The observation of a single wave in which two electrons are transferred indicates that when a EE mechanism is also operative for this cluster the difference in half-wave potentials for the consecutive reduction steps should be small or even negative. Because no complete chemical reversibility is attained the above used procedure for the determination of the half-wave potentials can strictly not be applied. Because of the fast electrochemical kinetics generally shown by these clusters and the good agreement found for the measured and expected current ratios in acetone (Table II, vide infra) we still applied this procedure. The thus found negative value for $\Delta E_{1/2}$(−67 mV) should be handled cautiously. It signifies that the addition of the second electron is a thermodynamically more favorable process than the transfer of the first one.

Further evidence that these clusters are reduced in two consecutive one-electron steps is gained in considering the measured current functions (i_d/C in PP and i_p/C in DPP) (see Table II).

For two consecutive one-electron steps the peak currents vary considerably with the $\Delta E_{1/2}$ value, as shown by Richardson and Taube[12] with DPP curve simulations. The calculated current ratios i_p/i_d ($\Delta i_{max}/i_d$ in the notation of ref 12) are assembled in Table II together with the measured i_p/i_d values and the corresponding $\Delta E_{1/2}$'s. A good agreement is found between the observed and calculated current ratios. While earlier was shown that $Au_9(PPh_3)_8^{3+}$ can be reduced in two consecutive one-electron steps,[7] these results give further evidence that also for $PtAu_8(PPh_3)_8^{2+}$ and $Au_9[P(p\text{-}MeOC_6H_4)_3]_8^{3+}$ an EE mechanism is operating. A similar mechanism is assumed to proceed with the reduction of $Au_9[P(p\text{-}MeOC_6H_4)_3]_8^{3+}$ because the decomposition of the formed products is ascribed to a side reaction with some impurity. The earlier reported observation that $Au_9[P(p\text{-}MeOC_6H_4)_3]_8^{3+}$ undergoes a one-electron reduction is thus questionable.[13]

ESR Measurements. The $\Delta E_{1/2}$ value for the $PtAu_8(PPh_3)_8^{2+/+/0}$ redox series warrants a sufficiently large concentration of the paramagnetic +1 ion in solution for the observation of a ESR signal. The +1 species was electrochemically generated in acetone solution from the +2 cluster with the passage of 1.0 faraday/mol of cluster. A sample from this solution was transferred to an ESR tube and immediately cooled. The electrolysis was continued, and $PtAu_8(PPh_3)_8$ was prepared by passing another equivalent of electrons. To trace if the comproportionation reaction (eq 3) occurs, a sample of the last solution was taken and an approximate equivalent amount of $PtAu_8(PPh_3)_8^{2+}$ was added, dissolved in the same solvent. This sample was also placed in an ESR tube and immediately cooled.

From both samples identical ESR spectra were obtained with signals at $g_\perp$ = 1.91 and $g_\parallel$ = 1.67 (g_{av} = 1.76) attributed to $PtAu_8(PPh_3)_8^+$. Further studies concerning the ESR spectra of gold clusters[7] are in progress.

Discussion

The results give conclusive evidence that the gold cluster ions can be reduced electrochemically by an EE charge transfer mechanism according to eq 1 and 2. The close agreement between

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$$PtAu_8(PPh_3)_8^{2+} + e^- \rightleftharpoons PtAu_8(PPh_3)_8^{+} + e^- \rightleftharpoons PtAu_8(PPh_3)_8 \quad (1)$$

$$Au_9[P(p\text{-}MeOC_6H_4)_3]_8^{3+} + e^- \rightleftharpoons Au_9[P(p\text{-}MeOC_6H_4)_3]_8^{2+} + e^- \rightleftharpoons Au_9[P(p\text{-}MeOC_6H_4)_3]_8^{+} \quad (2)$$

the parameters calculated for this mechanism and the measured data, both voltage and current functions (Table II), makes the occurrence of another mechanism very unlikely. An intermediate chemical step caused by structural changes is not likely because of the fluxionality in solution shown by these clusters.

The redox potentials for these clusters are almost solvent independent as shown by their nearly constant values vs the Fc/Fc^+ reference (Table III). As this Fc/Fc^+ redox couple is generally believed to be without specific solute-solvent interactions,[14] the same is true for the cluster ions.

The occurrence of the comproportionation equilibrium of eq 3 was demonstrated by the ESR experiment, and we assume that the comproportionation of eq 4 also occurs. The comproportionation constants, K_c calculated with eq 5 for the equilibria of

$$PtAu_8(PPh_3)_8^{2+} + PtAu_8(PPh_3)_8^{0} \rightleftharpoons 2PtAu_8(PPh_3)_8^{+} \quad (3)$$

$$Au_9[P(p\text{-}MeOC_6H_4)_3]_8^{3+} + Au_9[P(p\text{-}MeOC_6H_4)_3]_8^{+} \rightleftharpoons 2Au_9[P(p\text{-}MeOC_6H_4)_3]_8^{2+} \quad (4)$$

$$K_c = \exp[n_1 n_2 F(\Delta E_{1/2})/RT] = \exp[\Delta E_{1/2}/25.69] \quad \text{(at 298 K and with } n_1 = n_2 = 1) \quad (5)$$

eq 3 and 4, are clearly solvent dependent (Table III). Their values increase with decreasing dielectric constants, while no dependence on acceptor or donor numbers was observed. Thus K_c is like the $E_{1/2}$'s predominantly determined by the solvent polarization, and contributions from specific solute-solvent interactions are of minor or no importance. This is not an unexpected result. Earlier we reached the same conclusion for the reaction entropies of the redox reactions for the $Au_9(PPh_3)_8^{3+/2+/+}$ couples. Only Coulombic interactions between the cluster ions and the solvent determine these ΔS_{rc} values as shown by the agreement between the Born prediction and the experimental result for the ratio of there successive values.[15]

One of the striking results of this study is the rather large difference of about 0.5 V between the redox potentials of $Au_9(PPh_3)_8^{3+}$ and $PtAu_8(PPh_3)_8^{2+}$. The difference in positive charges between the two cluster ions leads to a difference of only 0.14 V between the redox potentials ($E°(3+/2+) - E°(2+/+)$) as can be estimated from the differences in the free enthalpy changes by using the Born model.[16] SCC-EHMO calculations made clear that this difference can be ascribed for the larger part to a shift to a higher energy level of the LUMO in $PtAu_8(PPh_3)_8^{2+}$ as compared with that for $Au_9(PPh_3)_8^{3+}$ and a concomitant increase of the electron density on the platinum atom.[17]

This electronic effect is also the reason for the differences in chemical reactivity of these clusters toward small molecules.[11] In CH_2Cl_2 solutions $Au_9(PPh_3)_8^{3+}$ does not react with CO, whereas $PtAu_8(PPh_3)_8^{2+}$ reacts with CO and delivers pure samples of $(CO)PtAu_8(PPh_3)_8^{2+}$.

The difference in redox potentials of 0.15 V between $Au_9(PPh_3)_8^{3+}$ and $Au_9[P(p\text{-}MeOC_6H_4)_3]_8^{3+}$, can also be ascribed to the somewhat increased electron density on the latter cluster. The electron-releasing effect of the methoxy groups increases the electron density on the Au_9 core and $Au_9[P(p\text{-}MeOC_6H_4)_3]_8^{3+}$ is indeed reduced at a lower potential. This electronic factor seems important for the stability of the Au_9 clusters. The electronic charge is influenced by the substituents on the aryl groups of the phosphines. With phosphines like $P(p\text{-}ClC_6H_4)_3$ and also $P(p\text{-}BrC_6H_4)(C_6H_4)_2$ the preparation of a cluster with nine gold atoms failed thus far and only samples containing mainly Au_8P_8 clusters were obtained.[18]

Experimental Section

Measurements. Electrochemical measurements were made as described previously[7] by using a PAR Model 173 potentiostat equipped with a PAR Model 176 I/E converter coupled to a PAR Model 175 universal programmer. Platinum working and auxiliary electrodes were used. In dichloromethane solutions a SSCE reference electrode was used, in acetone solutions a Ag/AgCl(0.1 M LiCl in acetone) reference electrode was used, and in acetonitrile and benzonitrile a Ag/Ag^+ (0.1 M $AgNO_3$) reference electrode was used. The half-wave potentials for 10^{-3} M solutions of the ferrocene/ferrocenium redox couple were measured under identical experimental conditions: $E_{1/2} = 0.62$ V (acetone) vs Ag/AgCl; $E_{1/2} = 0.43$ V (CH_2Cl_2) vs SSCE; $E_{1/2} = 0.04$ V (CH_3CN, C_6H_5CN) vs Ag/Ag^+. Coulometric measurements were made at a potential 0.1 V more negative than the second CV reduction peak with a precision for n of ±5%. Electron spin resonance experiments were carried out on a Bruker ESP 300 spectrometer. All measurements were carried out under a nitrogen atmosphere.

Materials. The cluster compounds $PtAu_8(PPh_3)_8(NO_3)_2$[8], $Au_9(PPh_3)_8(NO_3)_3$[11] were prepared as described.

$Au_9[P(p\text{-}MeOC_6H_4)_3]_8(NO_3)_3$ was prepared by following an analogous procedure as described.[9,10] $(p\text{-}MeOC_6H_4)_3PAuNO_3$ suspended in ethanol was reduced with an equivalent amount of $NaBH_4$ dissolved in ethanol.

Anal. Calcd for $C_{168}H_{168}N_3O_{33}P_8Au_9$: C, 42.4; H, 3.5; N, 0.9. Found: C, 41.5; H, 3.4; N, 0.9.

$Au_9[P(p\text{-}MeOC_6H_4)_3]_8(PF_6)_3$ was obtained from the metathesis reaction of the analogous nitrate cluster with NH_4PF_6 in ethanol. This product was used for the measurements to avoid solubility problems.

$(p\text{-}MeOC_6H_4)_3PAuCl$ was prepared as described.[19,20] $^{31}P\{^1H\}$ NMR data (in ppm with respect to trimethyl phosphate) measured in CH_2Cl_2): $(p\text{-}MeOC_6H_4)_3P$, 12.46; $(p\text{-}MeOC_6H_4)_3PAuCl$, −26.9; $Au_9[P(p\text{-}MeOC_6H_4)_3]_8(PF_6)_3$, −52.0.

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Kinetics of the Reduction of Cobalt(III) Amine Complexes by 1-Hydroxy-1-methylethyl Radicals

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The pentaaquoorganochromium complexes $(H_2O)_5CrR^{2+}$ can serve as storage depots for aliphatic free radicals.[2-4] The controlled homolysis of $(H_2O)_5CrC(CH_3)_2OH^{2+}$ has been used as a source of 1-hydroxy-1-methylethyl radicals in our previous work,[5] including the study of the reduction of several Co(III) amine

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