STUDY OF THE REACTIVITY OF THE CLUSTER [Pd(AuPPh3)8](NO3)2

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The reactivity of [Pd(AuPPh3)8](NO3)2 (I) toward small molecules, such as hydrogen, oxygen, carbon monoxide, carbon dioxide, and ethylene, as well as the catalytic behaviour of I with respect to some reactions involving these molecules, have been studied using IR, ^{1}H NMR, and ^{31}P NMR spectroscopy. It has been found that triphenylphosphine is catalytically oxidized to triphenylphosphine oxide by molecular oxygen in methanol and chloroform solutions containing cluster I. The IR spectral data obtained indicate that the peroxo and carbonato complexes might be formed in the course of the reactions of I with oxygen and carbon dioxide/oxygen mixtures, respectively. The formation of the cluster [(CO)Pd(AuPPh3)8](NO3)2, as a result of nucleophilic addition of carbon monoxide to I, has been observed by ^{31}P NMR spectroscopy.

Keywords: palladium-gold cluster compound; reactivity; catalytic properties; spectroscopic methods.

INTRODUCTION

Studies of ligand stabilized metal clusters increased considerably in the last two decades. Great progress has been achieved in the field of mixed metal-gold cluster compounds. These compounds have gained a lot of attention among chemists and physicists due to their fascinating geometries, unique fluxional behaviour, catalytic potential, and interesting chemical reactivity. Originally, the studies of metal clusters dealt primarily with their synthesis and structure determination. Recently, efforts have turned towards a systematic study of the chemical reactivity and catalytic properties of this class of compounds.

Mixed transition metal-gold cluster compounds are important due not only to their structural properties, but also to their potential as homogeneous catalysts and the relevance to catalysis by supported bimetallic alloys. Transition metals have long been used commercially as catalysts in a wide variety of important processes. However, the mechanism of their action is not yet well clarified, especially in the case of bimetallic systems. It is known, but not understood how that the addition of gold to heterogeneous Pt, Pd, Ru, Ag, Ir, and Os catalysts often produces beneficial effects on their activity and selectivity, whereas gold metal itself is a very poor catalyst[1-6]. Clusters of considerable size might mimic heterogeneous catalysts and might function as molecular models forming a bridge between the molecular and solid-state levels. They can provide a possible route to explain how reactions occur on the surface of bimetallic catalysts and to understand the role of gold in the modification of the catalytic properties of other metals.

A large number of transition metal-gold cluster compounds have been synthesized containing metals such as Pd, Pt, Ru, Rh, V, Cr, Mn, W, Fe, Re, Co, Ir, Os, and Ag[3,7-9], but only a few of them have shown catalytic behaviour under homogeneous conditions[10-13]. It has been found that the gold adducts [(H)3Ru4(AuPPh3)(CO)12][10] and [AuRu(H)2(CO)(PPh3)4]PF6[11] show significantly higher rates of catalytic activity than their parent Ru complexes for the isomerization of 1-pentene and 1-hexene, respectively. The surprising catalytic activity of Pt-Au cluster compounds for H2-D2 equilibration reaction in both homogeneous and heterogeneous (gas-solid reaction without solvent) conditions has been recently reported[12]. As far as we know, none of the mixed metal-gold clusters examined up to now show appreciable catalytic activity for hydrogenation of alkenes, alkynes, or nitroaromatics under mild homogeneous conditions. It has been found[13] that [Pt(AuPPh3)8](NO3)2 catalyzes the hydrogenation of ethylene to ethane in the solid state and in methanol solutions, but the rates are extremely slow. The cluster [Pt(AuPPh3)8](NO3)2 has also been recently shown to be a good catalyst in the solid state for the hydrogenation of oxygen[13].

The report on the synthesis and characterization, including a single-crystal X-ray crystallographic analysis, of the first cluster compound containing an Au-Pd bond, [Pd(AuPPh3)8](NO3)2, was published in 1989[7]. Since then, several novel clusters of this type, such as [(CO)Pd(AuPPh3)8](NO3)2, [(PPh3)Pd(AuPPh3)6](NO3)2, [P(OCH3)3Pd(AuPPh3)6(AuP(OCH3)3)2](NO3)2, and some halide derivatives have been synthesized and well characterized[7,8,9]. However, there is very little information in the literature regarding their reactivity and catalytic behaviour. Palladium is a very important metal in catalysis. A number of commercial processes such as the isomerization of n-heptane[14] and vinyl acetate synthesis from ethylene and acetic acid[15] use Pd-Au alloys as catalysts[1,16].

Studies of the chemical properties of Pd-Au cluster compounds, particularly their catalytic potential, are of a great interest to understand the role of gold in bimetallic catalysts.

The objective of our work was to investigate the reactivity of the palladium-gold cluster [Pd(AuPPh3)8](NO3)2 (1) toward small molecules such as ethylene, carbon monoxide, carbon dioxide, oxygen, and hydrogen and to examine the catalytic potential of 1 in some reactions involving these molecules. Cluster 1 is well studied and has a Pd-centered, crown-shaped geometry in the solid state[7], essentially the same as the structure of [Pt(AuPPh3)8](NO3)2[17]. This structure is stabilized through multicenter electron-deficient bonds between gold atoms. The 16/18-electron counting rule has proved to be very useful in predicting the structure and reactivity of M-Au and Au cluster compounds[17-23].

EXPERIMENTAL

[Pd(AuPPh₃)₈](NO₃)₂ was synthesized according to Ito *et al.*[7] through the reaction of a CH_2Cl_2 solution of $Pd(PPh_3)_4$[24] and 8 equiv. of $Au(PPh_3)NO_3$ with a MeOH solution of 2 equiv. of $NaBH_4$ at room temperature. After the reaction was quenched with water, a dark purple solid was isolated and purified by recrystallization with acetone and then with methanol-diethyl ether.

^{31}P NMR spectra were recorded on a Bruker AC-200 spectrometer at 81.02 MHz. Chemical shifts were measured with respect to TMP (trimethyl phosphate) as internal standard with positive shifts in ppm, downfield. ^1H NMR spectra were recorded on a Bruker AC-200 spectrometer at 200.13 MHz and reported in ppm relative to internal standard tetramethylsilane. Infrared spectra were recorded on a Perkin Elmer-1750 Infrared Fourier Transform Spectrometer. All spectral data were obtained at room temperature.

RESULTS AND DISCUSSION

Behaviour of [Pd(AuPPh₃)₈](NO₃)₂ in acetic acid solutions

It is well known that palladium complexes and clusters catalyze various liquid-phase reactions involving alkenes, carbon monoxide, hydrogen, *etc*. Acetic or trifluoroacetic acids are often effectively used as solvents in successful processes, such as oxidative acetoxylation of alkenes into vinyl, allyl, or glycol acetates[25-27] and alkene hydrocarbonylation resulting in dialkylketones[28]. In acetic acid solution, the substrate oxidation by molecular oxygen occurs, due to the palladium species formed in oxidation reactions and readily reoxidized by reversible oxidants. Our intention was to extend earlier investigations of palladium mononuclear complexes and homonuclear clusters to mixed Pd-Au cluster compounds.

It has been found that solutions of cluster 1 in acetic acid containing cyclohexene or 1-octene slowly consume oxygen at room temperature. The oxygen consumption has also been observed in the absence of alkenes. Initially bright orange solutions turned pale yellow. Oxygen was consumed in more than stoichiometric amounts with respect to palladium. Therefore, triphenylphosphine and perhaps alkenes seem to be catalytically oxidized by molecular oxygen under these conditions.

The stability of the cluster compound in acetic acid solutions has been studied by ^{31}P NMR spectroscopy. The ^{31}P NMR spectrum of 1 (CH_2Cl_2) showed a singlet resonance at d 48.6, due to the fast dynamic behaviour of the [M(AuPPh₃)₈](NO₃)₂ (M=Pt, Pd) clusters in solutions at room temperature. The colour of the solution of 1 in acetic acid changed from deep orange to pale yellow a few minutes after the mixture preparation and the ^{31}P NMR spectrum of this pale yellow solution, consisted of two singlets at d 31.8 and 25.8. The latter resonance, which is relatively more intense, can be assigned to $Au(PPh_3)NO_3$. The singlet at d 31.8 might be due to the $Pd(PPh_3)_4$. In conclusion, the cluster 1 is unstable in acetic acid solutions and undergoes a rapid decomposition into complexes of smaller nuclearity. The catalytic activity of 1 in the oxidation of triphenylphosphine and, perhaps, alkenes can be attributed to mononuclear complexes. Further studies on the reactivity of the cluster 1 should be carried out using other solvents such as chloroform, dichloromethane, or methanol.

Interaction of [Pd(AuPPh₃)₈](NO₃)₂ with oxygen

The reactivity of [Pd(AuPPh₃)₈](NO₃)₂ with molecular oxygen was studied using IR and ^{31}P NMR spectroscopy. No changes in the ^{31}P NMR spectrum of the dichloromethane solution of 1 were found when oxygen was bubbled (15 minutes) through the solution. So, ^{31}P NMR spectroscopy showed no evidence for the formation of the adduct of 1 with molecular oxygen.

A stirred dichloromethane solution of 1 ($10^{-3}M$) was kept for 2.5 h under 1 atm of oxygen at room temperature, and the solvent was then removed under vacuum. The IR spectrum of the solid (recorded in film using chloroform as a solvent) was considerably different in the number and positions of the absorption bands when compared to the spectrum of the starting cluster. In the IR spectrum of 1 several bands were observed within the range of vibrational frequencies under study (Table 1, entry 1; Fig. 1). The assignment of these bands to certain groups was made on the basis of literature data. The bands at 3055, 1630, 1098, 1029, 748, and 693 cm⁻¹ were attributed to PPh₃ ligands. There is some doubt about the attribution of two bands of medium intensity at 1436 and 1479 cm⁻¹. They were observed in all IR experiments with 1 and AuPPh₃NO₃

Table 1. IR spectroscopic data.

Entry	Compound	Treatment[a]	Absorption band (cm⁻¹)
1	[Pd(AuPPh₃)₈](NO₃)₂	no	due to PPh₃ 1384 v(NO₂) uncoordinated NO₃
2	Au(PPh₃)NO₃	no	due to PPh₃ 1379 v(NO₂) uncoordinated NO₃ 1502 v(N=O) coordinated NO₃ 1273 v(N=O) coordinated NO₃ 978 v(N-O) coordinated NO₃
3	[Pd(AuPPh₃)₈(NO₃)₂	O₂	due to PPh₃ 1308 v(NO₂) uncoordinated NO₃ 1261 v(N=O) coordinated NO₃ 800 v (O-O) peroxo complex
4	[Pd(AuPPh₃)₈(NO₃)₂	CO₂/O₂ 1/1	due to PPh₃ 1718 v(C=O) coordinated CO₃ 1369 v(NO₂) uncoordinated NO₃ 1262 v(N=O) coordinated NO₃ 800 v(O-O) peroxo complex

[a] A stirred dichloromethane solution of 1 ($10^{-3}M$) was placed for 2.5 h under 1 atm of oxygen or carbon dioxide/oxigen mixture at room temperature then the solvent was removed under vacuum. The IR spectra of solids obtained were recorded in films using chloroform as a solvent.
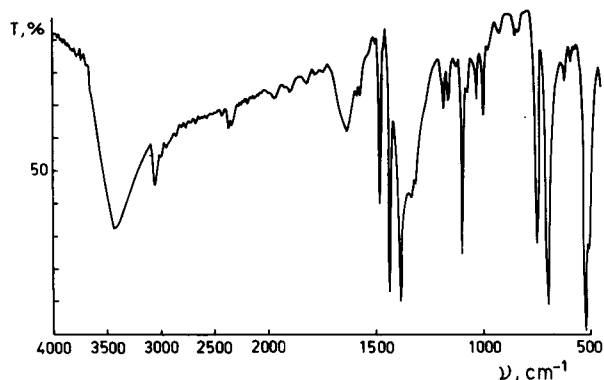
Figure 1. IR spectrum of [Pd(AuPPh₃)₈](NO₃)₂ (KBr).

Figura 3. IR spectrum of Au(PPh₃)NO₃ (using chloroform as a solvent).

before and after any treatment with O₂. They also seem to belong to PPh₃ ligands. The strong band at 1384 cm⁻¹ is characteristic of the free nitrate group.

Treatment of cluster 1 with oxygen, as described above, led to a change in the relative intensities of bands and to the appearance of a new strong absorption at 1261 and 800 cm⁻¹ (Table 1, entry 3; Fig. 2). An increase in intensity of the absorption in the 1000-1100 cm⁻¹ range (presumably due to vibrations of the P-Ph bond) was observed. The absorption at 1261 cm⁻¹ seems to be due to the coordinated nitrate group. The absorption band at 800 cm⁻¹ could be caused either by an out-of-plane deformation of the coordinated NO₃ group or by an O-O stretching vibration in the metal peroxo complex. But usually the IR spectra of nitrate complexes show bands around 780-800 cm⁻¹ which are much less intense, when compared to the absorption bands in the 1250-1500 cm⁻¹ range. As an example, the spectrum of Au(PPh₃)NO₃ shows the absorption of free as well as of coordinated NO₃⁻ (Table 1, entry 2; Fig. 3). On the other hand, the infrared stretch n(O-O) for metal peroxo complexes is known to be in the 750-920 cm⁻¹ range, and in particular for palladium and platinum peroxides in 800-890 cm⁻¹ range[29]. We therefore tentatively assign the band at 800 cm⁻¹ to the peroxo complex, formed as a result of the reaction of cluster 1 with molecular oxygen.

It should be mentioned that in the IR spectrum of the solid under study, no band was found at 1502 cm⁻¹. This band is characteristic of one of the expected products of cluster 1 degradation, Au(PPh₃)NO₃. Moreover, the ³¹P NMR spectrum of the dichloromethane solution of 1 stirred for 2.5 h at room temperature under CO₂/O₂=1/1 atmosphere consisted of only one singlet at δ 48.8 assigned to the starting cluster. Therefore, the decomposition of 1 in appreciable amounts is unlikely to have occurred
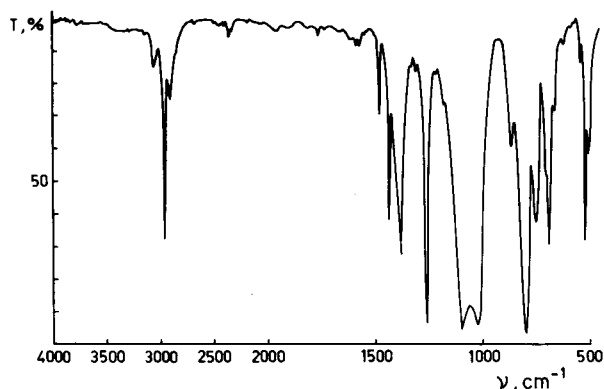

Figure 2. IR spectrum of the solid obtained by stirring a dichloromehane solution of [Pd(AuPPh₃)₈](NO₃)₂ (10⁻³M) for 2.5 h under 1 atm of oxigen at room temperature followed by solvent removal under vacuum (using chloroform as a solvent).

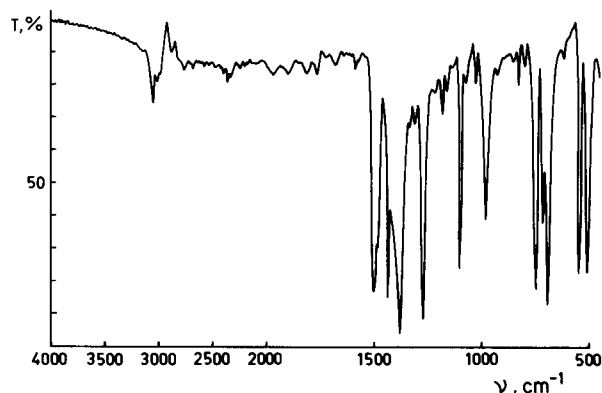as a result of the described procedure.

Thus, exposure of a dichloromethane solution of 1 to 1 atm of oxygen with stirring leads to the formation of a new compound (or mixture of compounds), which is presumably an adduct of the starting cluster with oxygen. The IR spectrum indicates the presence of uncoordinated as well as coordinated nitrate groups. Also, due to the appearance of a strong band at 800 cm⁻¹ the presence of the peroxo ligand can be suggested. However, the absence of appreciable changes in the ³¹P NMR spectrum is not yet well understood. Further investigations to elucidate the composition and structure of the solid obtained are in progress.

Interaction of [Pd(AuPPh₃)₈](NO₃)₂ with carbon dioxide/ oxygen mixtures

The existence of carbonato complexes (PPh₃)₂MCO₃ for M=Pd and Pt has been demonstrated[30]. They have been prepared by the action of CO₂/O₂ mixtures on (PPh₃)₃Pt and (PPh₃)₄Pd. In the complete absense of oxygen or air , carbon dioxide does not react with (PPh₃)₃Pt. In the presence of oxygen, however, the carbonate complex (PPh₃)₂PtCO₃ is formed in diethyl ether, acetone, alcohol, dichloromethane, or benzene solutions at 25°C and 1 atmosphere according to the equation:

$$(PPh_3)_3Pt + O_2 + CO_2 \rightarrow (PPh_3)_2PtCO_3 + Ph_3PO \tag{1}$$
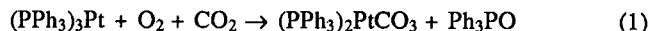
A similar reaction has been observed using (PPh₃)₄Pd in benzene or dichloromethane solutions, which produces the compound (PPh₃)₂PdCO₃. The carbonate complex was isolated and showed a strong absorption at 1670 cm⁻¹ (1680 cm⁻¹ for M = Pd, for comparison), characteristic of the coordinated carbonate ligand[29,30]. Thus, the activation of molecular oxygen and co-oxidation of Pt(0) to Pt(II) [or Pd(0) to Pd(II)] and PPh₃ to OPPh₃ takes place.

The behaviour of cluster 1 under a CO₂/O₂ atmosphere has been studied. No changes in the ³¹P NMR spectra of dichloromethane solutions of 1 were detected after oxygen, carbon dioxide, or their mixture were bubbled through the solutions for 10-15 min. Treatment of the solution of cluster 1 for a longer period of time (2.5 hours) in CH₂Cl₂ with stirring under CO₂/O₂ atmosphere at room temperature was also attempted. The solvent was then removed under vacuum and the IR spectrum of the solid recorded in solution using chloroform as a solvent. The spectrum displayed three new bands at 1718, 1262, and 801 cm⁻¹· in addition to those of the starting cluster (Table 1, entry 4; Fig 4). The bands at 1262 and 801 cm⁻¹ were also observed after the treatment of 1 with oxygen alone and could be attributed to the coordinated nitrate and peroxo groups, respectively. A strong absorption at 1718 cm⁻¹ that was not observed in the absence of carbon dioxide could correspond to the carbonate group coordinated to the palladium atom[29,30]. After a shorter treatment (20-30 min), when methanol was used
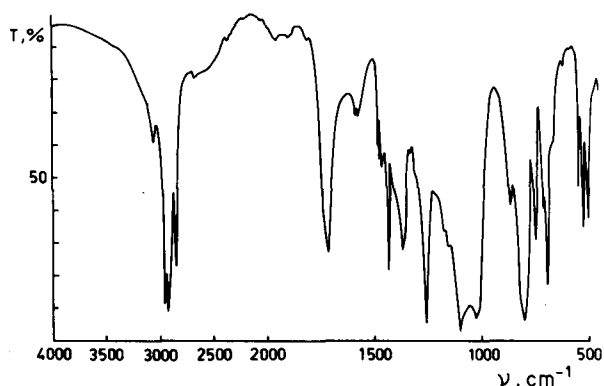
Figure 4. IR spectrum of the solid obtained by stirring a dichloromethane solution of [Pd(AuPPh₃)₈](NO₃)₂ (10⁻³M) for 2.5 h under 1 atm of oxygen/carbon dioxide=1/1 mixture at room temperature, followed by solvent removal under vacuum (using chloroform as a solvent).

as a solvent, no bands attributed to the coordinated CO_3 group were detected. As mentioned above, the ^{31}P NMR spectrum of a dichloromethane solution of 1 stirred for 2.5 h at room temperature under $CO_2/O_2=1/1$ atmosphere consisted of only one singlet at δ 48.8 assigned to the starting cluster 1. This result gives no additional evidence for the formation of a new cluster compound with a carbonate or a peroxo ligand, but indicates that the cluster did not suffer decomposition in appreciable amounts.

Based on the data obtained, the formation of a new cluster compound (or mixture of compounds) as a result of interaction of 1 with the CO_2/O_2 gas mixture is suggested. It appears to contain both coordinated and uncoordinated nitrate groups and the carbonate group coordinated to palladium atom.

Study of the reactions of [Pd(AuPPh₃)₈](NO₃)₂ with hydrogen, ethylene, carbon mono- and dioxides, oxygen, and their mixtures by NMR spectroscopy

The ^{31}P NMR spectra of dichloromethane and chloroform solutions of 1 treated with various gases and gas mixtures were recorded and analyzed in order to see if new cluster compounds could be identified. As mononuclear palladium compounds are catalysts for the reactions of oxidation, hydrogenation, and hydrocarbonylation of ethylene, we have explored a possible catalytic activity of cluster 1 in these reactions.

No changes in the ^{31}P NMR spectra or solution colour were observed after oxygen, carbon dioxide, hydrogen, ethylene, or their mixtures were bubbled for 10-15 min through the solutions of 1. The ^1H NMR spectra of the CDCl₃ solutions were also recorded. The chemical shift for the ethylene protons was the same as that in the absence of 1 (δ 5.37), indicating that there is no formation of a π-ethylene palladium complex in appreciable concentration. The ^1H NMR spectra of the CDCl₃ solutions of 1 treated with an ethylene/oxygen mixture showed no evidence for the formation of any oxidation products from ethylene.

It was discovered[13] that [Pt(AuPPh₃)₈](NO₃)₂ reacts rapidly and reversibly at room temperature and atmospheric pressure with hydrogen, forming the hydride complexes. This cluster is an excellent H₂-D₂ equilibration catalyst[12] and also catalyzes the hydrogenation of ethylene in solutions[13], although at an extremely slow rate. However, we failed to obtain any spectroscopic data in favour of the formation of hydride complexes from the analogous palladium cluster, [Pd(AuPPh₃)₈](NO₃)₂. No trace amounts of ethane in a CDCl₃ solution of 1 treated with an ethylene/hydrogen mixture were observed by ^1H NMR spectroscopy, so the hydrogenation of ethylene in the presence of 1 could not be detected. Perhaps the reaction rate is so slow that the amounts of ethane produced under these

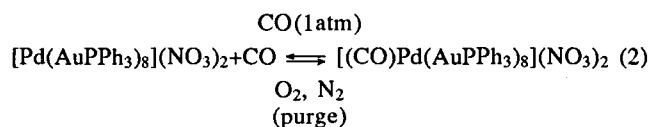conditions are undetectable, as it was previously observed with the analogous platinum cluster[12].

Under 1 atm of CO the colour of the solution of 1 in CH₂Cl₂ changed immediately from purple to dark brown and the original ^{31}P resonance of 1 (δ 48.6) was replaced by a new, narrow line at δ 43.7. This new singlet could be attributed to the carbonyl adduct of 1, [(CO)Pd(AuPPh₃)₈](NO₃)₂, containing one CO ligand bonded to the Pd atom. This compound has been synthesized and reported by Ito et al[8]. [^{31}P NMR (CH₂Cl₂, 25°C): δ 44.5 (s)]; similarly to the carbonyl adduct, the parent cluster 1 shows fluxional behaviour in solution, at room temperature, and its ^{31}P NMR spectrum consists of only one singlet, indicating the equivalency of all phosphine sites.

It has been reported[31] that [(CO)Pd(AuPPh₃)₈](NO₃)₂ is stable in solution only under 1 atm of CO and that the solution should be kept under these conditions as this ligand is labile and can be lost from the compound forming 1. Indeed, the original colour and spectrum of 1 reappeared immediately when either nitrogen or oxygen were bubbled through the solution (Table 1, entry 11). When ethylene was used to purge the tube, however, both singlets at δ 48.6 and 43.3 were observed and their intensity ratio was dependent on time. A decrease in intensity of the resonance at δ 43.3 was observed, whereas the intensity of the resonance at δ 48.6 increased with time. After 1 h, a 0.25:1 relative intensity was reached.

As the hydrocarbonylation of ethylene is known[28] to be catalyzed by palladium mononuclear complexes, the reactivity of 1 in this reaction has been studied. The CDCl₃ solution of 1 was treated with a $C_2H_4/CO/H_2=2/1/1$ mixture and the ^1H and ^{31}P NMR spectra were recorded after 2.5 h. Only one ^{31}P resonance at δ43.7, attributed to the carbonyl adduct [(CO)Pd(AuPPh₃)₈](NO₃)₂, was observed. No signals in the ^1H NMR spectrum which could be assigned to the expected products of ethylene hydrocarbonylation were found.

In conclusion, we have no NMR spectroscopic evidence for the formation of adducts between cluster 1 and either oxygen, hydrogen, ethylene, or carbon dioxide. Cluster 1 also showed no catalytic activity for the oxidation, hydrogenation, or hydrocarbonylation of ethylene in chloroform solutions. Steric hindrance at the Pd atom and/or the lack of ligand dissociation obviously prevent the reactions.

The 16 electron cluster [Pd(AuPPh₃)₈](NO₃)₂ undergoes carbon monoxide addition to yield the 18 electron compound according to equation (2).

$$[Pd(AuPPh_3)_8](NO_3)_2 + CO \underset{\substack{O_2, N_2 \\ (purge)}}{\overset{\substack{CO(1atm)}}{\rightleftharpoons}} [(CO)Pd(AuPPh_3)_8](NO_3)_2 \quad (2)$$

This nucleophilic addition reaction (2) has been followed by ^{31}P NMR spectroscopy. This reaction is reversible and associated with a colour change. Carbon monoxide ligand can be readily and fully removed by nitrogen or oxygen purge but, remarkably, under an ethylene atmosphere, the carbonyl adduct is much more stable. We observed [(CO)Pd(AuPPh₃)₈](NO₃)₂ by ^{31}P NMR spectroscopy for 4 h after the solution had been intensively purged twice with ethylene.

Oxidation of triphenylphosphine by molecular oxygen in the presence of [Pd(AuPPh₃)₈](NO₃)₂

On the basis of spectral data analysis it might be suggested that cluster 1 forms an adduct with molecular oxygen. We have explored a possible catalytic activity of 1 in oxidation processes, in which cluster 1 could serve as an activator of molecular oxygen. Triphenylphosphine was used as the substrate.

The ^{31}P NMR spectrum of a CH₂Cl₂ solution of PPh₃ consisted of one singlet at δ -8.4 (Table 2, entry 1). No new

lines or essential changes were observed for at least 4 h under 1 atm of oxygen in the absence of 1 (Table 2, entry 2). There is no appreciable oxidation of PPh₃ under these reaction conditions in the absence of a catalyst.

The ^{31}P NMR spectrum of the CDCl₃ solution of 1 (10^{-3}M) and PPh₃ (10^{-1}M) under 1 atm of oxygen was observed to be time dependent and showed, initially, a singlet at δ 48.2 belonging to 1 and a broad line tentatively assigned to PPh₃ (Table 2, entry 5). The chemical shift of the broad line was dependent on reaction time and varied from δ -7.7 to + 4.5. After 4h a new narrow line appeared at δ 26.6 whose relative intensity increased with time. A similar result was obtained when methanol was used as solvent (Table 2, entry 6) except for the position of the new narrow line (δ 30.7 ppm).

A possible explanation for the chemical shift variation of the line from δ -7.7 to +4.5 could be the following. It seems to be an average spectrum that arises from fast (on the NMR time scale) exchange between free PPh₃ molecules and those bound to gold or palladium atoms. The starting cluster 1 is unlikely to participate in any interchange process, because no broadening and/or shift of the ^{31}P resonance at δ 48.2 was observed. Moreover, it was found that the fluxional behaviour of [M(AuPPh₃)₈]$^{+2}$ cluster compounds in solution is due to intramolecular rather than intermolecular exchange of phosphine ligands or gold phosphine groups[32,33] as the ^{31}P NMR spectra of [M(AuPPh₃)₈]$^{+2}$ do not undergo any change upon addition of extra ligand[32].

Alternatively, complexes of smaller nuclearity, products of cluster degradation, could be involved in an exchange process with free PPh₃. Actually, the ^{31}P NMR spectrum of a CHCl₃ solution of Au(PPh₃)NO₃ (10^{-2}M) and PPh₃ (10^{-1}M) consisted of only one broad line at δ 1.9, whereas in the absence of PPh₃ a narrow line at δ 24.6 was observed (Table 2, entries 3, 4). Thus, the decomposition of 1 with formation of Au(PPh₃)NO₃ could cause a downfield shift of the ^{31}P resonance of PPh₃. An increase in the Au(PPh₃)NO₃ concentration with time led to a further downfield shift of the resonance.

The new lines at δ 26.6 in CDCl₃ and at δ 30.7 in CH₃OH could be attributed to triphenylphosphine oxide formed as a result of PPh₃ oxidation by molecular oxygen. According to the literature, the chemical shift of phosphorous in OPPh₃ is in the range of δ 23.0-27.0 from H₃PO₄ (*i.e.*, d

20.6-29.4 with respect to trimethyl phosphate as internal standard) depending on the solvent and solution composition[34].

The ^{1}H NMR spectrum of the solution after reaction in CDCl₃ showed the multiplet at δ 7.26-7.48 that was observed in the spectra of both PPh₃ and OPPh₃ and the multiplet at δ 7.55-7.65 observed in the ^{1}H NMR spectrum of OPPh₃ but not for PPh₃ [35]. Therefore, ^{1}H NMR spectroscopy showed additional evidence for the presence of OPPh₃ in the reaction solution.

The slow catalytic oxidation of triphenylphosphine to triphenylphosphine oxide by molecular oxygen therefore takes place in chloroform and methanol solutions containing 1 and, according to ^{31}P NMR spectroscopy, this process is accompanied by partial cluster degradation. We suppose that cluster 1 might catalyze the oxidation of PPh₃ by molecular oxygen, but an alternative explanation of the observed catalytic effect could be the action of Pd-Au clusters of smaller nuclearity or mononuclear palladium complexes.

CONCLUSIONS

The palladium-gold mixed cluster [Pd(AuPPh₃)₈](NO₃)₂ has been studied with respect to its catalytic potential and reactivity with small molecules, especially those relevant to the homogeneous and surface catalysis of palladium and gold. The results of the IR spectroscopic study might indicate formation of peroxo and carbonato complexes in the course of the reactions of 1 with oxygen and carbon dioxide-oxygen mixture, respectively. No spectroscopic evidence was obtained for the formation of adducts between cluster 1 and either hydrogen or ethylene. Cluster 1 also did not show any catalytic activity for the oxidation, hydrogenation, and hydrocarbonylation of ethylene in chloroform solutions, although this cluster undergoes carbon monoxide addition giving the 18 electron compound [(CO)Pd(AuPPh₃)₈] (NO₃)₂. Triphenylphosphine wasx found to be catalytically oxidized into triphenylphosphine oxide by molecular oxygen in methanol and chloroform solutions containing 1. This process is accompanied by partial cluster fragmentation.

An exploration of the catalytic behaviour of 1 does not look promising. Steric hindrance at the Pd atom and/or difficulties of ligand dissociation might be preventing the reactions

Table 2. ^{31}P NMR spectroscopy data.

Entry	Solution composition	Treatment[a]	Time after treatment, (h)	Chemical shifts δ, (ppm)
1	PPh₃ CH₂Cl₂	-		-8.4 (s)
2	PPh₃ CH₂Cl₂	O₂	4	-8.1 (s)
3	Au(PPh₃)NO₃- CHCl₃	10^{-2}M	-	24.6 (s)
4	Au(PPh₃)NO₃	10^{-2}M	-	1.9 (br.s)
	PPh₃ CHCl₃	10^{-1}M		
5	[Pd(AuPPh₃)₈](NO₃)₂	10^{-3}M	O₂	0.2	48.2(s),-7.7(s)
	PPh₃	10^{-1}M		0.4	48.2(s),-7.3(br.s)
	CDCl₃			1.5	48.2(s),-6.6(br.s)
				4.0	48.2(s), 26.6(s), -5.8(br.s)
				14.0	48.2(s), 26.6(s), -5.7(br.s)
6	[Pd(AuPPh₃)₈](NO₃)₂	10^{-3}M	O₂	0.3	48.8(s), -6.9(s)
	PPh₃	10^{-1}M		19	48.7(s), 30.7(s), -4.3(br.s)
	CH₃OH				
				25	48.7(s), 30.7(s), -3.1(br.s)

[a] gas bubbling for 10-15 min.

with ethylene and other molecules. Space filling models show that the Pd-Au sites are effectively blocked by the large PPh$_3$ ligands. One of the goals of our further investigations is to synthesize clusters with smaller ligands (trialkyl phosphines or isonitriles) and use them for catalytic purposes. Other studies in progress include reactions with [(PPh$_3$)Pd(AuPPh$_3$)$_6$](NO$_3$)$_2$ and Pd-Au clusters that contain Hg or Ag as a third metal. Preliminary results raise the expectation that these compounds possess a rich chemistry.

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