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Reactivity of $(NBu_4)[Pt(C_6F_5)_2(acac)]$ toward Electrophilic Metal Centers: Metal−Metal *vs* Metal−C^γ(acac) Bond Formation. Crystal Structure of $[PtAg(C_6F_5)_2(acac)(CH_2Cl_2)]_2$, a Complex Containing a μ^2-acac-*O,O′* Bridging Ligand and a Coordinated Dichloromethane

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The reaction between $(NBu_4)[Pt(C_6F_5)_2(acac)]$ and $AgClO_4$ (1:1 molar ratio) in CH_2Cl_2 at room temperature gives the neutral tetranuclear complex $[PtAg(C_6F_5)_2(acac)]_2$ (**1**) in a good yield. The structure, which has been determined by single-crystal X-ray diffraction methods, shows two anionic fragments $[Pt(C_6F_5)_2(acac)]^-$ linked by two Ag^+ atoms, each silver center being bonded to a Pt atom of one fragment and to an oxygen atom of the acac ligand of the other fragment. Noteworthy structural features are the O-acac coordination of the silver atom (instead of the more usual C^γ coordination) and the unexpected presence of a dichloromethane molecule coordinated to the silver center. The reaction of **1** with tht (tht = SC_4H_8, tetrahydrothiophene) or PPh_3 gives the dinuclear complexes $[PtAg(C_6F_5)_2(acac)(L)]$ (L = tht (**2**), PPh_3 (**3**)) by cleavage of the O−Ag bond; alternatively, complexes **2** and **3** can be one-pot synthesized by reaction of $(NBu_4)[Pt(C_6F_5)_2(acac)]$ and $O_3ClOAgL$ (L = tht, PPh_3). Their structural characterization points to the presence of donor−acceptor Pt→Ag bonds. Different behavior is observed in the reaction of $(NBu_4)[Pt(C_6F_5)_2(acac)]$ with $O_3ClOAuPPh_3$, giving the dinuclear complex $[PtAu(\mu\text{-acac})(C_6F_5)_2(PPh_3)]$ (**4**) in which, as can be seen from its spectroscopic data, the gold atom is bonded to C^γ of the acac ligand.

Introduction

The synthesis of polynuclear Pt−Ag complexes by using (perhalophenyl)platinate substrates and silver complexes or silver salts is well established, and a great variety of stoichiometries and structures have been obtained in the last few years.[1] However, although attempts to synthesize similar Pd−Ag complexes have been carried out, we have not been successful. In the reaction between the (perhalophenyl)palladate substrates and the $[AgL]^+$ fragment, due to the higher lability of the palladium complexes which display a stronger arylating capability, AgC_6X_5 is formed, precluding the formation of the polynuclear Pd−Ag derivatives.[2]

In an attempt to prepare complexes containing Pd−Ag bonds we have recently studied the reactions between $(NBu_4)[M(C_6F_5)_2(acac)]$ (M = Pd, Pt) and $AgClO_4$ since, with these metalate complexes which contain a chelating ligand and a lower number of C_6F_5 groups, a decrease of the number of undesirable reaction pathways would be expected. In fact, the reactions in a 2:1 (M:Ag) molar ratio render the trinuclear species $(NBu_4)[M_2Ag(C_6F_5)_4(acac)_2]$ (M = Pd, Pt) which, surprisingly, display very different structures (see Figure 1).[3] The platinum derivative is formed through Pt−Ag bonds (Figure 1A), while the palladium one does not show any

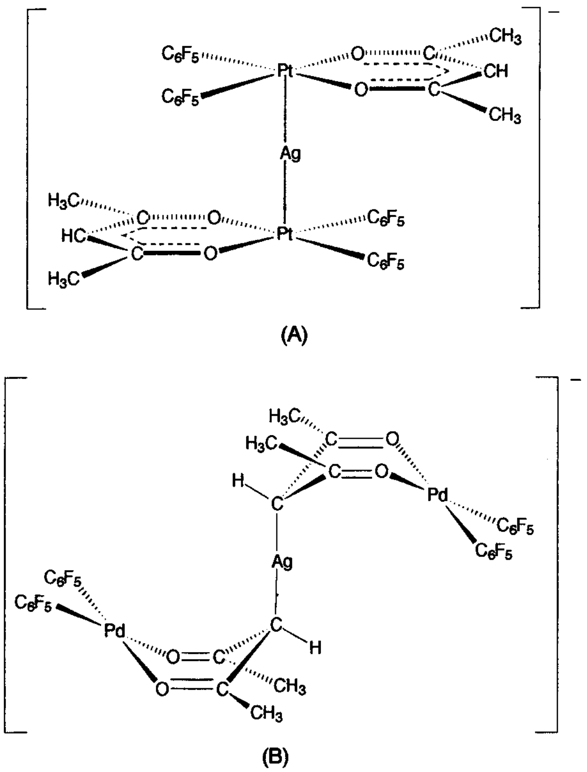

Figure 1. Schematic representation of (A) $[Pt_2Ag(C_6F_5)_4(acac)_2]^-$ and (B) $[Pd_2Ag(C_6F_5)_4(acac)_2]^-$.

[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1996.

(1) Usón, R.; Forniés, J. *Inorg. Chim. Acta* **1992**, *198−200*, 165.

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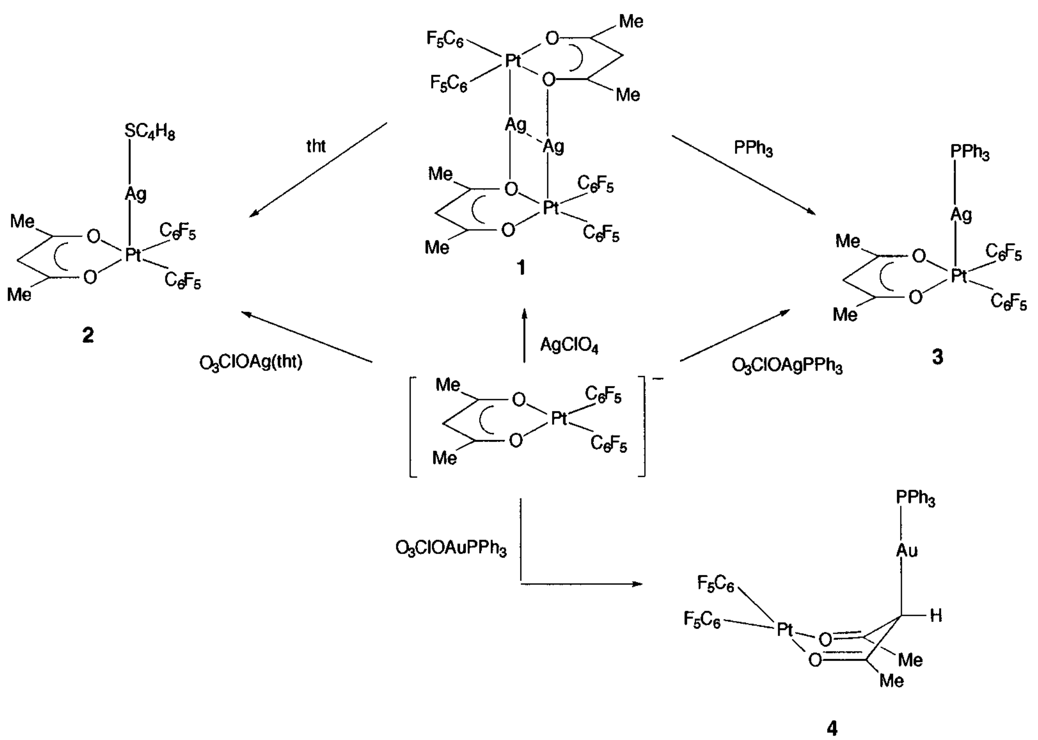
Scheme 1. Reactions Performed for the Synthesis of Complexes 1−4



Pd−Ag bond, the silver center being connected to the $[Pd(C_6F_5)_2(acac)]^-$ moiety through Ag−C^γ bonds, with the acetylacetonate acting as a bridging ligand (Figure 1B). These results not only show the different basicities of the palladium and the platinum metal centers but also indicate that in the $[Pt(C_6F_5)_2(acac)]^-$ fragment at least both the Pt center and the C^γ atom of the acetylacetonate could act as basic centers and that by reaction of $(NBu_4)[Pt(C_6F_5)_2(acac)]$ and $AgClO_4$, in adequate molar ratios, complexes of higher nuclearity with both the Pt and the C^γ atoms bonded to silver could be obtained.

In this paper we study the reaction between $(NBu_4)[Pt(C_6F_5)_2(acac)]$ and $AgClO_4$ in a 1:1 molar ratio which renders a tetranuclear derivative. In addition we have also studied the reactions of $(NBu_4)[Pt(C_6F_5)_2(acac)]$ with $O_3ClOMPPh_3$ (M = Ag, Au) which result in the formation of binuclear Pt/M species which also display different structures.

Results and Discussion

Reactions between $(NBu_4)[Pt(C_6F_5)_2(acac)]$ and $AgClO_4$ or $O_3ClOAgL$ (L= tht, PPh_3). The reaction of $(NBu_4)[Pt(C_6F_5)_2(acac)]$ with the equimolecular amount of $AgClO_4$ in CH_2Cl_2 at room temperature results in the formation of a tetranuclear complex of stoichiometry $[Pt_2Ag_2(C_6F_5)_4(acac)_2]$ (**1**). The structure of **1** (X-ray diffraction; see Figure 2), which will be discussed in detail later, indicates that, as expected, each silver center is connected to two $Pt(C_6F_5)_2(acac)$ moieties. It is therefore reasonable to assume that the reaction of this tetranuclear complex **1** with neutral monodentate ligands in the adequate molar ratio will result in the formation of species of lower nuclearity. Thus, **1** reacts with S- or P-donor ligands, such as tht (SC_4H_8, tetrahydrothiophene) or PPh_3 in a 1:2 molar ratio, producing the corresponding binuclear complexes $[PtAg(C_6F_5)_2(acac)(tht)]$ (**2**) or $[PtAg(C_6F_5)_2(acac)(PPh_3)]$ (**3**) as a result of the symmetrical cleavage of the tetranuclear unit and coordination of the ligand L to the silver center (Scheme 1). Complexes **2** and **3** can also be obtained directly by reacting $(NBu_4)[Pt(C_6F_5)_2(acac)]$ with the corresponding $O_3ClOAgL$ (L = tht, PPh_3) derivative in CH_2Cl_2 at room temperature, although in lower yields. These data suggest that **2** and **3** are the result of the binding of the $[AgL]^+$ fragment to the $[Pt(C_6F_5)_2(acac)]^-$ moiety through Pt−Ag bonds (see Scheme 1). Complexes **1**−**3** are nonconducting in CH_2Cl_2 but behave as 1:1 electrolytes in acetone,[4] indicating that the donor solvent is able to cleave both the Pt−Ag and Ag−O bonds forming the ionic species $[Pt(C_6F_5)_2(acac)]^-$ and $[Ag(acetone)_x]^+$ or $[Ag(PPh_3)(acetone)_{x'}]^+$.

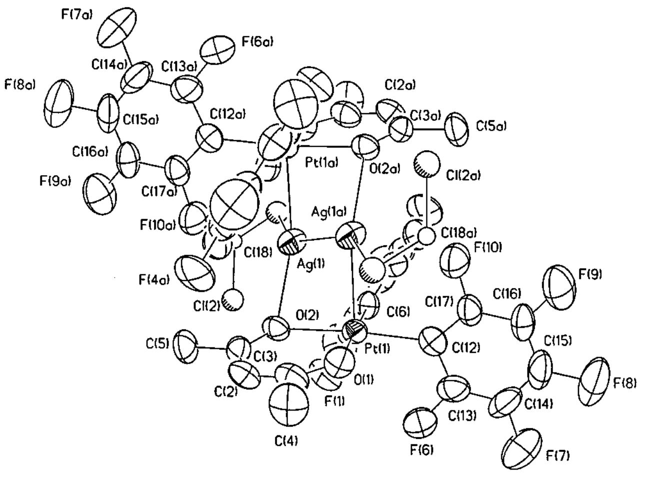


Figure 2. Molecular structure of complex **1**. Thermal ellipsoids represent 50% probability contours.

Experimental details, analytical results and spectroscopic data for complexes **1**−**3** are given in the Experimental Section. The structure of **1** has been established by X-ray diffraction methods. The structural assign-

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Scheme 2

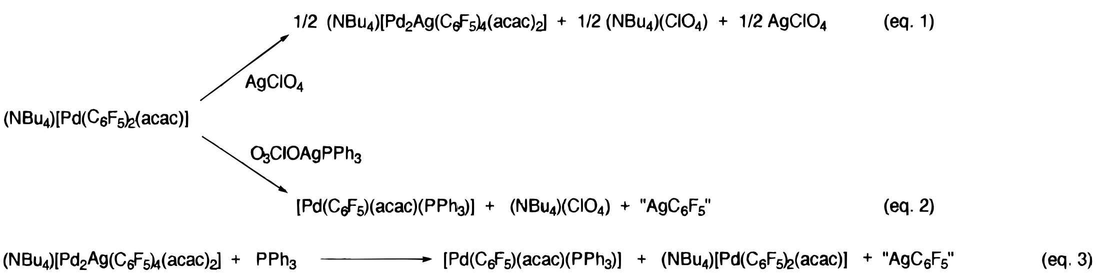

Table 1. Crystallographic Data for Complex 1

complex	$Pt_2Ag_2(C_6F_5)_4(acac)_2(CH_2Cl_2)_2$
formula	$Pt_2Ag_2C_{36}H_{18}F_{20}O_4Cl_4$
M	1642.23
color	yellow blocks
cyst size (mm)	0.4 × 0.6 × 0.7
cryst system	monoclinic
space group	$P2_1/n$
a (Å)	10.072(2)
b (Å)	12.932(3)
c (Å)	17.049(3)
β (deg)	93.74(3)
V (Å^3)	2215.92
T (K)	293
Z	2
D_{calc} (g/cm^3)	2.46
F(000)	1496.00
μ (mm^{-1})	7.53
2θ range (deg)	4.0−50.0
no. of unique data	3883
no. of data with $F > 4.0\sigma(F)$	3000
R	0.0465
wR	0.0645
$w^{-1} = 1/(\sigma^2(F) + g(F^2))$	$g = 0.0018$
max D/S	0.001
scan type	$\omega-\theta$
largest diff peak (e Å^{-3})	1.45
largest diff hole (e Å^{-3})	−1.39
transm factors	
max	0.0685
min	0.0367
no. of refined params	292

ments of **2** and **3** have been carried out on the basis of their spectroscopic data.

Attempts to prepare similar palladium complexes failed in all cases. Equations 1−3 in Scheme 2 summarize the reactions attempted: (a) By reaction of $(NBu_4)[Pd(C_6F_5)_2(acac)]$ with $AgClO_4$ (1:1 molar ratio, CH_2Cl_2, room temperature) the trinuclear complex $(NBu_4)[Pd_2Ag(C_6F_5)_4(acac)_2]$, which we had prepared on previous occasions[3] (Figure 1B), was obtained together with $(NBu_4)(ClO_4)$ and unreacted $AgClO_4$ (eq 1). (b) The reaction between $(NBu_4)[Pd(C_6F_5)_2(acac)]$ and $O_3ClOAgPPh_3$ (1:1 molar ratio, CH_2Cl_2, room temperature) gave $[Pd(C_6F_5)(acac)(PPh_3)]$ together with $(NBu_4)(ClO_4)$ and deposition of silver. This seems to be an arylation process in which the AgC_6F_5 or $C_6F_5AgPPh_3$ formed decomposes to silver under the reaction conditions (eq 2). (c) Finally, the reaction between $(NBu_4)[Pd_2Ag(C_6F_5)_4(acac)_2]$ and PPh_3 renders a mixture of $(NBu_4)[Pd(C_6F_5)_2(acac)]$ and $[Pd(C_6F_5)(acac)(PPh_3)]$ (eq 3), the formation of which can easily be understood by assuming that the PPh_3 initially produces the cleavage of the trinuclear compound, giving $(NBu_4)[Pd(C_6F_5)_2(acac)]$ and $[PdAg(C_6F_5)_2(acac)(PPh_3)]$, the latter decomposing with a similar transarylation pathway to that the described in eq 2.

Reaction between $(NBu_4)[Pt(C_6F_5)_2(acac)]$ and $O_3ClOAuL$ (L = tht, PPh_3). The behavior of $(NBu_4)[Pt(C_6F_5)_2(acac)]$ toward $AgClO_4$ or $O_3ClOAgL$ prompted us to study the reaction of this platinum anionic compound with the gold derivatives $O_3ClOAuL$ (L = PPh_3, tht). The reaction of $(NBu_4)[Pt(C_6F_5)_2(acac)]$ with a solution of freshly prepared $O_3ClOAuPPh_3$ (1:1 molar ratio, CH_2Cl_2, room temperature) allows the dinuclear derivative $[PtAu(\mu\text{-acac})(C_6F_5)_2(PPh_3)]$ (**4**) (see Scheme 1) to be obtained, as expected. However, in spite of the analogous stoichiometry of $[PtAg(C_6F_5)_2(acac)(PPh_3)]$ (**3**) and complex **4**, some interesting differences in the structural data (which are discussed later) indicate that in **4** the cation $[AuPPh_3]^+$ is connected to the platinum substrate by a C^γ−Au bond (see Scheme 1). This different behavior in the coordination mode of $[Pt(C_6F_5)_2(acac)]^-$ unity toward $[AuPPh_3]^+$ when compared to $[AgPPh_3]^+$ is in keeping with the high tendency of the Au(I) center to form Au−C bonds.[5,6] Complex **4** is nonconducting in CH_2Cl_2, and its acetone solution presents a conductivity which is lower than the expected for a 1:1 electrolyte. These facts indicate that the Au−C bonds are preserved in a noncoordinating solvent although in acetone these Au−C bonds are partially dissociated. We have also studied the reaction of $(NBu_4)[Pt(C_6F_5)_2(acac)]$ with $O_3ClOAu(tht)$ (1:1 molar ratio) with the aim of preparing a tetranuclear derivative similar to **1** by displacing both $OClO_3^-$ and tht ligands from the gold center. Unfortunately, all attempts (even those carried at low temperature) resulted in the decomposition and formation of a gold mirror.

X-ray Crystal Structure of $[Pt_2Ag_2(C_6F_5)_4(acac)_2(CH_2Cl_2)_2]$. A drawing of the molecule is shown in Figure 2. Experimental details concerning data collection and structure solution and refinement are given in Table 1 and in the Experimental Section. Selected bond distances (Å) and angles (deg) are given in Table 2. As it can be seen, the tetrametallic compound is formed by two anionic fragments $[Pt(C_6F_5)_2(acac)]^-$ and two silver ions. Each silver atom is bonded to a platinum center of one of the anionic fragments and to an oxygen atom of the acetylacetonato ligand of the other fragment. Moreover, a dichloromethane molecule is also coordinated to each silver center as a monodentate ligand.

The Pt−Ag distance [Pt(1)−Ag(1a) = 2.758(1) Å] is slightly longer than that found in $(NBu_4)[Pt_2Ag(C_6F_5)_4(acac)_2]$,[3] although it is within the usual range found in other complexes containing Pt−Ag bonds.[1] The Pt−Ag bond forms an angle of 9.82(2)° to the perpendicular of

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Table 2. Selected Bond Lengths (Å) and Angles (deg)

Pt(1)-Ag(1)	3.072(1)	Pt(1)-O(1)	2.052(8)
Pt(1)-O(2)	2.072(8)	Pt(1)-C(6)	2.014(11)
Pt(1)-C(12)	2.012(12)	Pt(1)-Ag(1A)	2.758(1)
Ag(1)-O(2)	2.405(7)	Ag(1)-Cl(1)	2.776(8)
Ag(1)-Pt(1A)	2.758(1)	Ag(1)-Ag(1A)	2.920(2)
O(1)-C(1)	1.281(16)	O(2)-C(3)	1.297(13)
C(1)-C(2)	1.396(19)	C(1)-C(4)	1.478(18)
C(2)-C(3)	1.381(16)	C(3)-C(5)	1.491(17)
C(18)-Cl(1)	1.608(33)	C(18)-Cl(2)	1.715(32)

Ag(1)-Pt(1)-O(1)	120.0(2)	Ag(1)-Pt(1)-O(2)	51.4(2)
O(1)-Pt(1)-O(2)	90.3(3)	Ag(1)-Pt(1)-C(6)	60.4(3)
O(1)-Pt(1)-C(6)	178.8(4)	O(2)-Pt(1)-C(6)	89.2(4)
Ag(1)-Pt(1)-C(12)	132.3(3)	O(1)-Pt(1)-C(12)	90.4(4)
O(2)-Pt(1)-C(12)	174.5(4)	C(6)-Pt(1)-C(12)	90.0(4)
Ag(1)-Pt(1)-Ag(1A)	59.8(1)	O(1)-Pt(1)-Ag(1A)	81.1(2)
O(2)-Pt(1)-Ag(1A)	91.5(2)	C(6)-Pt(1)-Ag(1A)	100.0(3)
C(12)-Pt(1)-Ag(1A)	94.0(3)	Pt(1)-Ag(1)-O(2)	42.3(2)
Pt(1)-Ag(1)-Cl(1)	133.4(2)	O(2)-Ag(1)-Cl(1)	124.1(2)
Pt(1)-Ag(1)-Pt(1A)	120.2(1)	O(2)-Ag(1)-Pt(1A)	131.7(2)
Cl(1)-Ag(1)-Pt(1A)	99.2(2)	Pt(1)-Ag(1)-Ag(1A)	54.7(1)
O(2)-Ag(1)-Ag(1A)	81.4(2)	Cl(1)-Ag(1)-Ag(1A)	150.9(2)
Pt(1A)-Ag(1)-Ag(1A)	65.4(1)	Pt(1)-O(1)-C(1)	125.2(8)
Pt(1)-O(2)-Ag(1)	86.3(2)	Pt(1)-O(2)-C(3)	124.5(7)
Ag(1)-O(2)-C(3)	132.2(7)	O(1)-C(1)-C(2)	125.4(11)
O(1)-C(1)-C(4)	115.7(12)	C(2)-C(1)-C(4)	118.9(12)
C(1)-C(2)-C(3)	128.4(11)	O(2)-C(3)-C(2)	124.9(11)
O(2)-C(3)-C(5)	115.9(10)	C(2)-C(3)-C(5)	119.2(11)
Pt(1)-C(6)-C(7)	119.2(8)	Pt(1)-C(6)-C(11)	128.0(8)
Pt(1)-C(12)-C(13)	116.4(9)	Pt(1)-C(12)-C(17)	130.3(9)
Cl(1)-C(18)-Cl(2)	112.5(18)	Ag(1)-Cl(1)-C(18)	113.0(12)

the platinum coordination plane.[7] However, no metal–metal-bonding interaction seems to be present between the silver atom bonded to the acetylacetonato group and the platinum center which is also bonded to this chelating ligand [Pt(1)–Ag(1) = 3.072(1) Å]. In addition, each silver center is bonded to one acetylacetonato ligand although not through the C^{γ} atom, which is usually the donor atom,[3,8] but through one of the oxygen atoms, which becomes three-coordinated. The acac group remains essentially planar, showing that no substantial structural changes have taken place in the acetylacetonato–Pt ring after silver coordination.[7] This contrasts with the structure of $(NBu_4)[Pd_2Ag(C_6F_5)_4(\mu^2\text{-}acac)_2]$, which displays a nonplanar acetylacetonato–palladium ring with a boat conformation due to the presence of the C^{γ}–Ag bond.[3] The dihedral angle between the best least-square planes defined by Pt(1)–O(1)–O(2)–C(6)–C(12) and O(1)–O(2)–C(1)–C(3) is 12.22(2)°.

The Ag(1)–O(2) distance [2.405(7) Å] is similar, within experimental error, to that found in $[AgNi(acac)_3{\cdot}2AgNO_3{\cdot}H_2O]$[9] [2.46(7) Å]. As a result of the O-coordination of the Ag^+ center, one should expect slightly longer Pt–O distances for the oxygen atoms which are also bonded to the silver center [O(2)] than for the others, although no significant differences, within experimental errors, are observed.

The distance between both silver atoms [Ag(1)–Ag(1a) = 2.920(2) Å] is slightly longer than that found in the metallic silver (2.8894 Å)[10] and falls within the range of distances found for other complexes with silver–silver interactions (2.82 - 2.99 Å).[11–13]

It is somewhat surprising that the silver center is bonded to one of the O atoms of the acac ligand instead of to the C^{γ} atom, in spite of the well-known ability of this ligand to involve the C^{γ} atom in coordination.[14,15] In fact, in a similar situation for $(NBu_4)[Pd_2Ag(C_6F_5)_4(acac)_2]$[3] the silver center is bonded to the C^{γ} and not to the O atom (Figure 1B). This peculiar coordination mode shown in **1** could be explained if we take into account that the bonding of Ag to Pt and to O favors the proximity of both Ag atoms, which could in this way be involved in a Ag–Ag interaction.

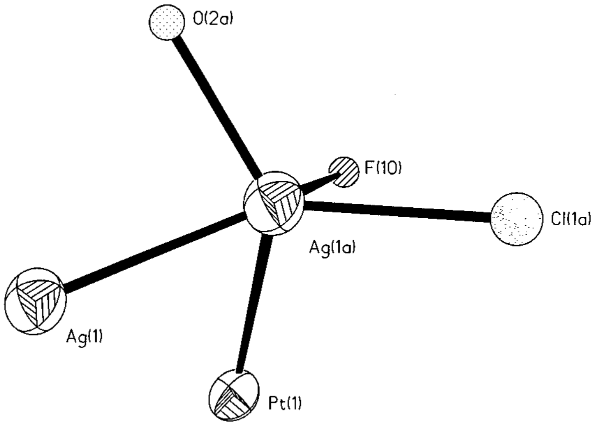

Figure 3. Environment of the silver atom in **1**.

It is also noteworthy that a molecule of dichloromethane is coordinated to each silver center through one of the chlorine atoms; *i.e.*, the dichloromethane (a typical noncoordinating solvent) is acting as a monodentate ligand. The Ag(1)–Cl(1) distance [2.776(8) Å] is within the range of distances found in the literature for the few Ag–chloroalkane complexes[16,17] which contain significantly covalent Ag–Cl bonds. The Ag(1)–Cl(1)–C(18) angle is 113.0(12)°, which is slightly higher than the Ag–Cl–C angles found in complexes containing both bidentate[16] or monodentate[17] chlorocarbon ligands.

Finally, as is usual in most of these pentafluorophenyl Pt–Ag complexes,[1] one of the pentafluorophenyl rings is oriented so as to produce a short *o*-F···Ag contact [Ag(1a)···F(10): 2.655(2) Å, $\rho = 1.34$] which is in the low end of the range for other complexes of this type.[1] As a result of all these interactions, the silver center is five coordinated and its environment is represented in Figure 3.

Spectroscopic Studies for Complexes 1–4. Two IR-active absorptions, the ν_{st}(CO, acac)[18a] (about 1600 cm^{-1}) and the Π(CH)[18b] (out-of-plane bending mode)

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Table 3. Relevant IR (ν, cm^{-1}) and $^{13}C\{^1H\}$ NMR (δ, ppm) Data

compd	ν_{st}(CO)	Π(CH)	$\delta(C^\gamma)$	δ(CO)
$(NBu_4)[Pt(C_6F_5)_2(acac)]$	1580	780	101.34	183.16
$(NBu_4)[Pd(C_6F_5)_2(acac)]$	1587	770	99.40	185.86
$(NBu_4)[Pt_2Ag(C_6F_5)_4(acac)_2]$ (**A**)	1570	795	101.89	185.39
$(NBu_4)[Pd_2Ag(C_6F_5)_4(acac)_2]$ (**B**)	1600		84.05	193.51
$[Pt_2Ag_2(C_6F_5)_4(acac)_2]$ (**1**)	1581	*a*	88.72	192.61
$[PtAg(C_6F_5)_2(acac)(tht)]$ (**2**)	1564	800	101.14	186.20
$[PtAg(C_6F_5)_2(acac)(PPh_3)]$ (**3**)	1565	790	102.68	186.24
$[PtAu(C_6F_5)_2(acac)(PPh_3)]$ (**4**)	1610		95.83	197.97

[a] See text.

(about 800 cm^{-1}) of the acac ligand in these complexes provide important structural information concerning the coordination mode of M^+ or ML^+ cations to the platinum fragment. Table 3 shows the ν_{st}(CO, acac) and the Π(CH) absorptions for **1**−**4**, together with the corresponding absorptions for the platinum starting materials. In addition, the absorptions of $(NBu_4)[Pt_2Ag(C_6F_5)_4(acac)_2]$ (**A**) (Figure 1A) and $(NBu_4)[Pd_2Ag(C_6F_5)_4(acac)_2]$ (**B**) (Figure 1B), which were prepared on a previous occasion,[3] and which were characterized by X-ray diffraction methods, are also given in Table 3. As can be seen, **A** (which contains Pt−Ag bonds) shows the Π(CH) absorption at about 800 cm^{-1}, while we observe a decrease of the wavenumber of ν(CO) compared to the corresponding absorptions in the starting material $(NBu_4)[Pt(C_6F_5)_2(acac)]$. Since ν(CO) and Π(CH) of **2** and **3** behave in a similar way, it can be inferred that bonding between the anionic and the cationic fragments in these complexes is through Pt−Ag bonds (see Scheme 1). For complex **B**, which contains C^γ−Ag bonds instead of the Pd−Ag ones (Figure 1B), an increase of the absorption due to ν(CO) and the disappearance of the Π(CH) (a change of the hybridization of the C^γ atom from sp^2 to sp^3 takes place) can be observed and this behavior is similar to that observed for ν(CO) and Π(CH) in **4**, showing that in the latter the $[AuPPh_3]^+$ fragment is connected to the platinum one through a C^γ−Au bond. For complex **1**, which contains Pt−Ag and Ag−O bonds, no change in the ν(CO) is observed. The Π(CH) absorption, which should appear at about 800 cm^{-1}, is not observed, probably because it is overlapped by the nearest internal absorptions of the C_6F_5 groups,[19] since this Π(CH) absorption has to be IR active due to the planarity of the acac ring (X-ray structure).

The ^1H NMR spectra of complexes **1**−**4** at room temperature reveal two singlets, one corresponding to the $C^\gamma H$ and the other to the CH_3 protons of the acac group. In addition, resonances of the tht ligand (two broad multiplets) were found for complex **2** and a set of multiplets (7−8 ppm) indicates the presence of Ph groups in complexes **3** and **4**. The $^{31}P\{^1H\}$ NMR spectrum of **3** shows the presence of a resonance as a doublet of doublets due to the coupling of the ^{31}P nucleus with the two active silver isotopes. A singlet resonance at 33.46 ppm is observed in the $^{31}P\{^1H\}$ NMR spectrum of **4**.

The ^{19}F NMR spectra of **1**−**3** at room temperature show three sets of signals which correspond to F_{ortho}, F_{para}, and F_{meta}, with a typical AA′MM′X spin system. Both the ^1H and the ^{19}F NMR spectra of **1** at room temperature do not reflect the solid-state structure, indicating that dissociative processes are probably taking place in the NMR time scale. The ^{19}F NMR spectra of **1**−**3**, at room temperature, undergo a systematic change upon addition of $(NBu_4)[Pt(C_6F_5)_2(acac)]$. The pattern remains similar but the chemical shifts of all resonances are changed, and those due to F_{para} suffer more significant modifications than the others. No signals of free $[Pt(C_6F_5)_2(acac)]^-$ are observed. All these facts indicate that in the CD_2Cl_2 solutions of **1**−**3** partial dissociative processes involving $[Pt(C_6F_5)_2(acac)]^-$ are operating at room temperature.

The ^{19}F NMR spectra of complexes **2** and **3** remain unaltered at low temperature (CD_2Cl_2, −90 °C). However the ^{19}F NMR spectrum of **1** under the same conditions shows that the resonance corresponding to the ortho-F is split into two resonances while only one resonance of F_{para} is observed. This means at low temperature (a) that at least the species $[Pt(C_6F_5)_2(acac)]^-$ is not participating in the dissociative process, (b) that **1** is not present in solution since two inequivalent C_6F_5 and CH_3 groups would be observed, and (c) that the species in solution should present, on the NMR time scale, a mirror plane containing the Pt, Ag, and C^γ atoms. However, the species present in solution cannot be unambiguously established with these spectroscopic data.

The ^{19}F NMR spectrum of **4**, at room temperature, reveals the usual pattern of three resonances (AA′MM′X spin system) showing that both pentafluorophenyl groups and both halves of each C_6F_5 group behave as equivalents. A CD_2Cl_2 solution of **4** behaves as **1** upon addition of $(NBu_4)[Pt(C_6F_5)_2(acac)]$ so that a reasonable explanation could be partial dissociation. At low temperature (CD_2Cl_2, −90 °C) the signal corresponding to F_{ortho} splits into two resonances showing that the dissociative process is not taking place under these conditions.

The $^{13}C\{^1H\}$ NMR spectrum (see Table 3) of **1** shows, at room temperature, an important upfield shift of the C^γ and a downfield shift of the carbonyl resonances with respect to $(NBu_4)[Pt(C_6F_5)_2(acac)]$. Similar behavior has been observed previously in $(NBu_4)[Pd_2Ag(C_6F_5)_4(acac)_2]$ when compared to the starting compound $(NBu_4)[Pd(C_6F_5)_2(acac)]$. In this case, these shifts were understood to be a result of the higher keto character of the acac ligand in the trinuclear complex compared to that of the mononuclear one due to the C^γ−Ag interaction (Figure 1B). Therefore, the $^{13}C\{^1H\}$ NMR spectrum of **1** seems to indicate that species with C^γ−Ag interactions must be present in solution. For complex **4** the Au−C^γ interaction could account for the similar shifts observed (upfield shift for C^γ and downfield shift for the carbonyl). However, no displacement of these signals was observed for **2** and **3**, thus indicating, as expected, that the acac ring does not interact with the silver atom. Similar behavior has been observed previously in $(NBu_4)[Pt_2Ag(C_6F_5)_4(acac)_2]$ when it was compared with the starting compound $(NBu_4)[Pt(C_6F_5)_2(acac)]$.[3]

The mass spectra of complexes **1**−**4** provide additional information about their behavior in solution. Thus, in no case was the molecular peak observed in these spectra and peaks corresponding to species such as $[Pt(C_6F_5)_2(acac)]^-$ (in all spectra), $[Pt_2Ag(C_6F_5)_4(acac)_2]^-$ (in **1**−**3**), $[Pt_2Au(C_6F_5)_4(acac)_2]^-$ (in **4**), or even $[Pt_3Ag_2(C_6F_5)_6(acac)_3]^-$ were observed in the negative FAB

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(19) Usón, R.; Forniés, J. *Adv. Organomet. Chem.* **1988**, *28*, 219 and references therein.

spectra. In addition, peaks corresponding to species such as $[Ag(PPh_3)]^+$ or $[Ag(PPh_3)_2]^+$ (for **3**) and $[Au(PPh_3)]^+$ or $[Au(PPh_3)_2]^+$ (for **4**) were observed in the positive FAB spectra. The presence of these species in solution is in keeping with the existence of partial dissociative processes, as we have postulated on the basis of the NMR data.

Conclusion

The work reported in this paper has shown the polydentate character of the anionic platinate complex $(NBu_4)[Pt(C_6F_5)_2(acac)]$ which can act as a metallo ligand toward electrophilic substrates. With silver derivatives, bimetallic complexes containing Pt−Ag bonds are obtained and, using an adequate molar ratio of the reactants, a tetrametallic complex containing both Pt−Ag and Ag−O(acac) bonds is formed. In reaction with gold derivatives only the C^{γ}(acac) atom acts as a base, forming Au−C bonds. The X-ray structure of the tetranuclear derivative shows two unusual features: Ag−O(acac) coordination as a result of the silver−silver interaction and coordination of a molecule of dichloromethane to each silver center.

Experimental Section

Solvents were dried and distilled under nitrogen prior to use: diethyl ether over benzophenone ketyl, dichloromethane over P_2O_5, and *n*-hexane over sodium. Elemental analyses were carried out on a Perkin-Elmer 240-B microanalyzer. Molar conductances were carried out on a Philips PW9509 conductivity meter in acetone and dichloromethane solutions (5×10^{-4} M). IR spectra (4000−200 cm^{-1}) were recorded on a Perkin-Elmer 883 infrared spectrophotometer in Nujol mulls between polyethylene sheets. NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 at room temperature (otherwise specified) on Varian Unity 300 and on Bruker ARX 300 spectrometers. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to the residual protons of the solvent as an internal standard, ^{19}F to $CFCl_3$ and $^{31}P\{^1H\}$ to H_3PO_4 (85%). Mass spectra were recorded on a V.G. Autospec. $(NBu_4)[M(C_6F_5)_2(acac)]$[20] (M = Pd, Pt), $O_3ClOAgL$[21] (L = PPh_3, tht), and $ClAuPPh_3$[22] were prepared according to published methods. **Safety note**: *Perchlorate salts of metal complexes with organic ligands are potentially explosive! Only small amounts of these materials should be prepared, and they should be handled with great caution.*

$[Pt_2Ag_2(C_6F_5)_4(acac)_2]$ (1). To a solution of $(NBu_4)[Pt(C_6F_5)_2(acac)]$ (0.216 g, 0.248 mmol) in 25 mL of CH_2Cl_2 was added $AgClO_4$ (0.052 g, 0.248 mmol) and the mixture was stirred at room temperature for 3 h. The solution was then evaporated to dryness, and the residue was treated with 30 mL of Et_2O and stirred continuously. A white solid of $(NBu_4)(ClO_4)$ remained insoluble and was filtered off. The resulting solution was evaporated to dryness and the yellow residue was stirred with *n*-hexane, giving **1** (0.158 g, 87% yield) as a yellow solid. Anal. Calc for $C_{34}H_{14}Ag_2F_{20}O_4Pt_2$: C, 27.73; H, 0.96. Found: C, 28.11; H, 1.07. Λ_M (Ω^{-1} cm^2 mol^{-1}): 3.5 (CH_2Cl_2), 90.8 (acetone). IR (cm^{-1}): 1508, 1066, 958 (vs, C_6F_5), 815, 806 (s, X-sensitive C_6F_5[19]). ^1H NMR: δ 5.77 (s, 1H, CH, acac), 2.14 (s, 6H, CH_3, acac). ^{19}F NMR: δ −121.50 (d, 2F, F_{ortho}, $^3J_{Pt-F_o}$ = 496 Hz), −157.98 (t, 1F, F_{para}), −162.30 (m, 2F, F_{meta}). $^{13}C\{^1H\}$ NMR: δ 149.90 ($^1J_{F-C}$ = 225 Hz), 138.79 ($^1J_{F-C}$ = 243 Hz), 136.58 ($^1J_{F-C}$ = 250 Hz) (C_6F_5), 28.56 (CH_3, acac).

$[PtAg(C_6F_5)_2(acac)(tht)]$ (2). Method a. To a solution of $(NBu_4)[Pt(C_6F_5)_2(acac)]$ (0.250 g, 0.287 mmol) in 25 mL of CH_2Cl_2 was added $O_3ClOAg(tht)$ (0.085 g, 0.287 mmol), and the mixture was stirred at room temperature for 30 min with exclusion of light. The resulting colorless solution was evaporated to dryness, and Et_2O (20 mL) was added. The insoluble $(NBu_4)(ClO_4)$ was separated, the solution was evaporated to dryness, and the oily residue was treated with *n*-hexane (20 mL) and stirried continuously, giving **2** (0.191 g, 81% yield) as a white solid.

Method b. $[Pt_2Ag_2(C_6F_5)_4(acac)_2]$ (**1**) (0.100 g, 0.068 mmol) was dissolved in 15 mL of Et_2O, and tht (12 μL, 0.136 mmol) was added. The solution was stirred at room temperature for 30 min with exclusion of light and then evaporated to dryness. Addition of *n*-hexane (20 mL) and continuous stirring gave **2** (0.080 g, 71% yield). Anal. Calc for $C_{21}H_{15}AgF_{10}O_2PtS$: C, 30.59; H, 1.83; S, 3.89. Found: C, 30.71; H, 1.70; S, 4.12. Λ_M (Ω^{-1} cm^2 mol^{-1}): 2.70 (CH_2Cl_2), 101.3 (acetone). IR (cm^{-1}): 1502, 1062, 960 (vs, C_6F_5), 1275 (w, tht), 811, 802 (s, X-sensitive C_6F_5[19]). ^1H NMR: δ 5.40 (s, 1H, CH, acac), 3.02 (m, 4H, α-CH_2, tht), 2.00 (m, 4H, β-CH_2, tht), 1.82 (s, 6H, CH_3, acac). ^{19}F NMR: δ −120.76 (d, 2F, F_{ortho}, $^3J_{Pt-F_o}$ = 499 Hz), −162.35 (t, 1F, F_{para}), −164.89 (m, 2F, F_{meta}). $^{13}C\{^1H\}$ NMR: δ 150.08 ($^1J_{F-C}$ = 216 Hz), 137.50 ($^1J_{F-C}$ = 242 Hz), 135.93 ($^1J_{F-C}$ = 250 Hz) (C_6F_5), 36.32 (α-CH_2, tht), 31.38 (β-CH_2, tht), 27.60 (CH_3, acac).

$[PtAg(C_6F_5)_2(acac)(PPh_3)]$ (3). Method a. To a solution of $(NBu_4)[Pt(C_6F_5)_2(acac)]$ (0.300 g, 0.344 mmol) in 25 mL of CH_2Cl_2 was added $O_3ClOAgPPh_3$ (0.161 g, 0.344 mmol), and the resulting solution was stirred at room temperature for 1 h, with exclusion of light. Complex **3** (0.244 g, 71% yield) was isolated as a white powder following the same workup as that described for complex **2** in method a.

Method b. To a solution of $[Pt_2Ag_2(C_6F_5)_4(acac)_2]$ (**1**) (0.100 g, 0.069 mmol) in 15 mL of Et_2O was added PPh_3 (0.036 g, 0.136 mmol), and the resulting solution was stirred at room temperature for 30 min with exclusion of light. Following the same workup as that described for complex **2** in method b, **3** was isolated (0.075 g, 56% yield). Anal. Calc for $C_{35}H_{22}AgF_{10}O_2PPt$: C, 42.10; H, 2.22. Found: C, 42.07; H, 2.03. Λ_M (Ω^{-1} cm^2 mol^{-1}): 3.52 (CH_2Cl_2), 89.0 (acetone). IR (cm^{-1}): 1505, 1063, 959 (vs, C_6F_5), 812, 802 (s, X-sensitive C_6F_5[19]), 541, 517, 503 (s, PPh_3). ^1H NMR: δ 8.0−7.0 (m, 15 H, Ph), 5.45 (s, 1H, CH, acac), 1.84 (s, 6H, CH_3, acac). ^{19}F NMR: δ −121.10 (d, 2F, F_{ortho}, $^3J_{Pt-F_o}$ = 470 Hz), −161.70 (t, 1F, F_{para}), −164.50 (m, 2F, F_{meta}). $^{31}P\{^1H\}$ NMR: δ 12.26 (dd, $^1J_{^{109}Ag-P}$ = 784.8 Hz, $^1J_{^{107}Ag-P}$ = 680.6 Hz). $^{13}C\{^1H\}$ NMR: δ 150.20 ($^1J_{F-C}$ = 220 Hz), 137.86 ($^1J_{F-C}$ = 242 Hz), 136.28 ($^1J_{F-C}$ = 252 Hz) (C_6F_5), 134.14 ($^2J_{P-C}$ = 16 Hz), 131.96, 129.82 ($^3J_{P-C}$ = 10 Hz), 129.43 ($^1J_{P-C}$ = 65 Hz) (PPh_3), 27.71 (CH_3, acac).

$[PtAu(\mu\text{-acac})(C_6F_5)_2(PPh_3)]$ (4). To a solution of 0.345 mmol of $O_3ClOAuPPh_3$ in 25 mL of CH_2Cl_2 (prepared from 0.170 g of $ClAuPPh_3$ and 0.072 g of $AgClO_4$) was added $(NBu_4)[Pt(C_6F_5)_2(acac)]$ (0.270 g, 0.310 mmol), and the colorless solution was stirred at room temperature for 30 min. The resulting solution was evaporated to dryness, and the residue was treated with Et_2O (30 mL). After separation of the insoluble $(NBu_4)(ClO_4)$, the ether solution was evaporated to dryness and the residue was treated with *n*-hexane (25 mL) yielding **4** (0.156 g, 50%). Anal. Calc for $C_{35}H_{22}AuF_{10}O_2PPt$: C, 38.65; H, 2.04. Found: C, 38.37; H, 1.86. Λ_M (Ω^{-1} cm^2 mol^{-1}): 9.77 (CH_2Cl_2), 24.08 (acetone). IR (cm^{-1}): 1500, 1060, 958 (vs, C_6F_5), 811, 800 (s, X-sensitive C_6F_5[19]), 540, 505 (s, PPh_3). ^1H NMR: δ 8.0−7.0 (m, 15 H, Ph), 5.23 (s, 1H, CH, acac), 2.17 (s, 6H, CH_3, acac). ^{19}F NMR: δ −119.75 (d, 2F, F_{ortho}, $^3J_{Pt-F_o}$ = 478 Hz), −163.50 (t, 1F, F_{para}), −165.96 (m, 2F, F_{meta}). $^{31}P\{^1H\}$ NMR: δ 33.46. $^{13}C\{^1H\}$ NMR: δ 150.53 ($^1J_{F-C}$ = 229 Hz), 137.18 ($^1J_{F-C}$ = 242 Hz), 136.05 ($^1J_{F-C}$ = 241 Hz) (C_6F_5), 134.58 ($^2J_{P-C}$ = 14 Hz), 132.72, 129.86 ($^3J_{P-C}$ = 11 Hz), 128.39 ($^1J_{P-C}$ = 61 Hz) (PPh_3), 29.13 (CH_3, acac).

Preparation of Crystals for X-ray Structure Determination. Suitable crystals for X-ray purposes were obtained

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by slow diffusion of *n*-hexane into a CH_2Cl_2 solution of complex **1** (typically 40−60 mg of **1** in 2 mL of CH_2Cl_2) at −18 °C.

X-ray Structure Analysis. Diffraction data were collected on a Siemens/STOE-AED2 diffractometer with graphite-monochromated Mo Kα radiation and were corrected for Lorentz and polarization effects. The refined cell constants and the most relevant data for this complex are collected in Table 1. The SHELXTL PLUS[23] crystallographic software package was used. A total of 4323 reflections were collected in the range of $4° < 2\theta < 50°$ (*hkl*: 0 to 12, 0 to 15, −20 to 20) using $\omega-\theta$ scans. Absorption correction was based on ψ-scan solutions (heavy metal atom) (maximum and minimum transmission factors: 0.0685 and 0.0367, respectively). The structure was solved by the Patterson method and refined to $R = 0.0465$ and $wR = 0.0645$ [3000 reflections with $F > 4.0\sigma(F)$ and 292 variables]. The hydrogen atoms were not located. All atoms (except for the solvent) were refined with anisotropic displacement parameters. The highest peak on the final difference Fourier map corresponds to 1.45 e Å^{-3} (largest difference hole −1.39 e Å^{-3}), and it is located close to the uncoordinated chlorine atom of the CH_2Cl_2 molecule. However, attempts to refine it as disordered CH_2Cl_2 failed. Selected bond distances and bond angles are given in Table 2.

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Supporting Information Available: Tables of atomic coordinates and *U* values, complete bond distances and angles, and anisotropic thermal parameters for **1** (4 pages). Ordering information is given on any current masthead page.

OM950878C

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[23] Siemens Analytical X-Ray Instruments, Inc., SHELXTL PLUS Software Package, Release 4.11/V, Madison, WI, 1990.