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Synthesis and Reactivity of Bridging and Terminal Hydrosulfido Palladium and Platinum Complexes. Crystal Structures of $[NBu_4]_2[\{Pt(C_6F_5)_2(\mu\text{-}SH)\}_2]$, $[Pt(C_6F_5)_2(PPh_3)\{S(H)AgPPh_3\}]$, and $[Pt(C_6F_5)_2(PPh_3)\{S(AuPPh_3)_2\}]$

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The reactions of the hydroxo complexes $[M_2R_4(\mu\text{-}OH)_2]^{2-}$ (M = Pd, R = C_6F_5, C_6Cl_5; M = Pt, R = C_6F_5), $[\{PdR(PPh_3)(\mu\text{-}OH)\}_2]$ (R = C_6F_5, C_6Cl_5), and $[\{Pt(C_6F_5)_2\}_2(\mu\text{-}OH)(\mu\text{-}pz)]^{2-}$ (pz = pyrazolate) with H_2S yield the corresponding hydrosulfido complexes $[M_2(C_6F_5)_4(\mu\text{-}SH)_2]^{2-}$, $[\{PdR(PPh_3)(\mu\text{-}SH)\}_2]$, and $[\{Pt(C_6F_5)_2\}_2(\mu\text{-}SH)(\mu\text{-}pz)]^{2-}$, respectively. The monomeric hydrosulfido complexes $[M(C_6F_5)_2(SH)(PPh_3)]^-$ (M = Pd, Pt) have been prepared by reactions of the corresponding binuclear hydrosulfido complexes $[M_2(C_6F_5)_4(\mu\text{-}SH)_2]^{2-}$ with PPh_3 in the molar ratio 1:2, and they can be used as metalloligands toward $Ag(PPh_3)^+$ to form the heterodinuclear complex $[(C_6F_5)_2(PPh_3)\{S(H)AgPPh_3\}]$, and toward $Au(PPh_3)^+$ yielding the heterotrinuclear complexes $[M(C_6F_5)_2(PPh_3)\{S(AuPPh_3)_2\}]$. The crystal structures of $[NBu_4]_2[\{Pt(C_6F_5)_2(\mu\text{-}SH)\}_2]$, $[Pt(C_6F_5)_2(PPh_3)\{S(H)AgPPh_3\}]$, and $[Pt(C_6F_5)_2(PPh_3)\{S(AuPPh_3)_2\}]$ have been established by X-ray diffraction and show no short metal−metal interactions between the metallic centers.

Introduction

There is much current interest in the chemistry of transition metal hydrosulfido complexes, mainly because these are useful in understanding many catalytic processes, such as hydrogenation and hydrodesulfuration.[1,2] However, these species are still quite rare, and hydrosulfido palladium or platinum complexes are very poorly represented. Only some terminal hydrosulfido compounds of the types $[ML_2(SH)_2]$ (M = Pd or Pt; L_2 = 2 PPh_3, 2 PEt_3, 2 P^iBu_3, or diphos),[3−5] $[PtH(SH)L_2]$ (L_2 = 2 PPh_3, 2 PEt_3),[6,7] [PtH(SH)(triphos)],[8] or [PtR(SH)(dcpe)] (dcpe = $Cy_2PC_2H_4PCy_2$, R = Me, Ph, CH_2tBu)[9] have been reported and, to the best of our knowledge, no examples of bridging hydrosulfido palladium or platinum are known so far. A tetranuclear palladium cluster with sulfide ligands, $[\{Pd(\eta^3\text{-}C_4H_7)\}_4S_2]$, synthesized from the reaction of $[Pd(\eta^3\text{-}C_4H_7)_2]$ and H_2S,[10] has been shown to serve as a homogeneous catalyst.[11]

The μ-hydroxo complexes of palladium and platinum of the types $[M_2R_4(\mu\text{-}OH)_2]^{2-}$ (M = Pd, R = C_6F_5, C_6Cl_5; M = Pt, R = C_6F_5),[12,13] $[\{PdR(PPh_3)(\mu\text{-}OH)\}_2]$ (R = C_6F_5, C_6Cl_5; L = PPh_3),[14] and $[\{Pt(C_6F_5)_2\}_2(\mu\text{-}OH)(\mu\text{-}pz)]^{2-}$ (pz = pyrazolate)[15] have been shown to be excellent precursors in synthetic work.[17−19] We report now their reactions with H_2S gas to give the first bridging hydrosulfido palladium and platinum complexes. The mononuclear hydrosulfido complexes $[M(C_6F_5)_2(SH)(PPh_3)]^-$ (M = Pd, Pt), prepared from the corresponding dimers by addition of PPh_3 in the molar ratio 1:2, can be used as metalloligands toward $M'(PPh_3)^+$ (M′ = Ag or Au), yielding heterobinuclear or heterotrinuclear complexes. In the heterotrinuclear complexes $[M(C_6F_5)_2(PPh_3)\{S(AuPPh_3)_2\}]$, it is possible to envisage the isolobal analogy existing between the hydrogen atom and the $AuPR_3$ fragment. Some of these

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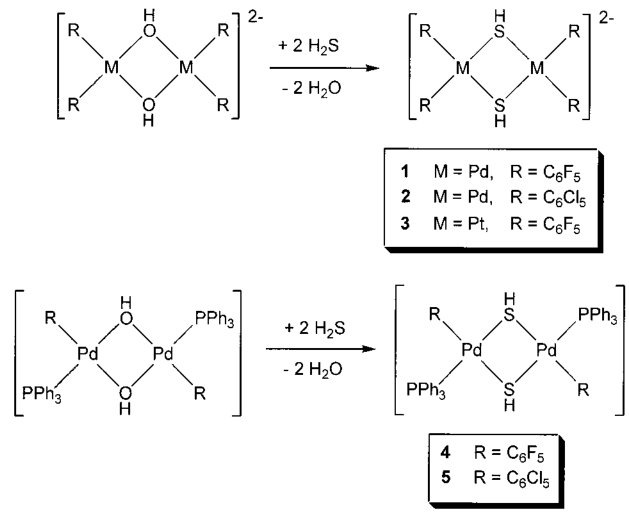
Scheme 1



polynuclear complexes have been characterized by X-ray diffraction, and the crystal structure of a binuclear hydrosulfido platinum complex is reported for the first time.

Results and Discussion

***μ*-Hydrosulfido Palladium and Platinum Complexes [$M_2(C_6F_5)_4(\mu\text{-}SH)_2]^{2-}$, [$\{Pd(R)(PPh_3)(\mu\text{-}SH)\}_2$], and [$\{Pt(C_6F_5)_2\}_2(\mu\text{-}SH)(\mu\text{-}pz)]^{2-}$.** The di-*μ*-hydroxo palladium and platinum complexes $[NBu_4]_2[\{M(R)_2(\mu\text{-}OH)\}_2]$ (M = Pd, R = C_6F_5, C_6Cl_5; M = Pt, R = C_6F_5) and $[\{Pd(R)(PPh_3)(\mu\text{-}OH)\}_2]$ (R = C_6F_5, C_6Cl_5; L = PPh_3) react with H_2S to yield the corresponding binuclear di-*μ*-hydrosulfido complexes $[NBu_4]_2[\{M(R)_2(\mu\text{-}OH)\}_2]$ and $[\{Pd(R)(PPh_3)(\mu\text{-}SH)\}_2]$ **1**−**5** (Scheme 1) with the concomitant formation of H_2O.

Complexes **1**−**5** have been characterized on the basis of partial elemental analyses and spectroscopic data. The IR-active band corresponding to the ν(SH) mode, which usually appears in the range 2300−2600 cm^{-1}, is not observed; its weakness is a common feature of most SH complexes. The IR spectra show the bands attributed to the C_6F_5 (1630, 1490, 1460, 1050, and 950 cm^{-1})[20] or C_6Cl_5 (1315, 1285, 1220, and 670 cm^{-1})[21] groups. Morever, a split absorption, located at ca. 800 cm^{-1} in the spectra of the bis(pentafluorophenyl) derivatives or at ca. 830 cm^{-1} for the bis(pentachlorophenyl)derivatives, has been previously used for structural elucidation.[22] It is derived from the so-called halogen-sensitive mode in C_6F_5 and C_6Cl_5 halogen molecules, and in square-planar MR_2L_2 (R = C_6F_5, C_6Cl_5) complexes, it is related to the skeletal symmetry of the entire molecule[22] and behaves like a ν(M−C) which is characteristic of the *cis*-MR_2 fragment (C_{2v} symmetry). Complexes **1**−**3** behave as 1:2 electrolytes in acetone solution,[23] in accordance with the formulas given.

All the complexes exhibit a high field resonance (δ −2 to −1.2) in their ^1H NMR spectra due to the SH ligand. This SH signal appears in most other late transition metal complexes in the range δ −4 to +2.[24] Upon addition of D_2O to an NMR sample of **1** in acetone-d_6, the SH signal disappears from its previous position (δ −2.03) and a new signal at δ 3.7 arises (for HOD). The ^1H NMR spectra of **1**−**3** also show the signals assigned to the protons of the NBu_4 group. The resonance at δ −1.19 ppm in the ^1H NMR of complex **3** is flanked by ^{195}Pt satellites ($I = 1/2$, natural abundance 33.8%; $^2J_{PtH} = 37.2$ Hz). The ^{19}F NMR data of complex **4** and the $^{31}P\{^1H\}$ NMR data of complexes **4** and **5** show unambiguously that they exist in chloroform solution as only one isomer. Since the ^1H spectra of **4** and **5** exhibit a unique high-field resonance for the SH groups, consisting of a doublet arising from coupling to ^{31}P of the phosphine trans to SH, it should exist as the anti isomer, as it also occurs with the hydroxo precursor complex.[11] The ^{19}F NMR spectrum of complex **4** shows two broad resonances in the *o*-F region, together with one sharp triplet for the *p*-F atoms, suggesting restricted rotation of the perfluorophenyl rings around the Pd−C bond. The ^{19}F NMR spectrum of **4** at −50 °C shows two sharp doublets in the *o*-F region (δ −114.4, d, $J_{om} = 33.6$ and δ −117.0, d, $J_{om} = 31.9$). It is noteworthy that the dinuclear palladium complex with bridging sulfide ligands $[Pd_2(dppe)_2(\mu\text{-}S)_2]$ has been very recently successfully prepared from $[Pd(dppe)Cl_2]$ and an excess of $Na_2S{\cdot}9H_2O$, though it easily evolves into the trimetallic species $[Pd_3(dppe)_2(\mu_3\text{-}S)_2]Cl_2$.[25]

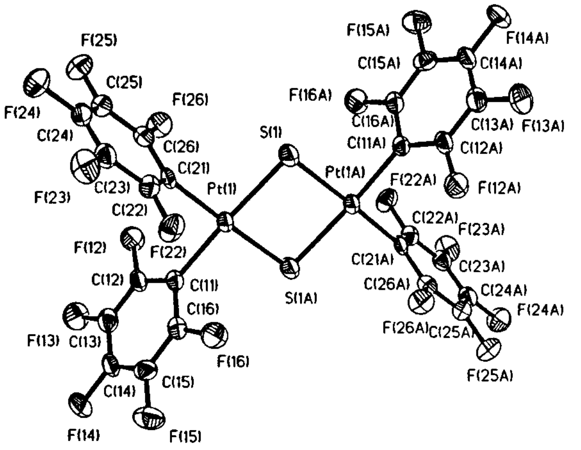


Figure 1. ORTEP diagram of **3**.

Table 1. Selected Distances (Å) and Bond Angles (deg) for Complex **3**[a]

Bond Distances		Bond Angles	
Pt(1)−C(11)	2.009 (5)	C(11)−Pt(1)−C(21)	90.4(2)
Pt(1)−C(21)	2.014(5)	C(11)−Pt(1)−S(1)#1	91.37(13)
Pt(1)−S(1)#1	2.3591(15)	C(21)−Pt(1)−S(1)#1	178.22(15)
Pt(1)−S(1)	2.3577(15)	C(11)−Pt(1)−S(1)	175.72(15)
Pt(1)···Pt(1)#	3.494(1)	C(21)−Pt(1)−S(1)	93.82(15)
		S(1)#1−Pt(1)−S(1)	84.43(6)

[a] Symmetry transformations used to generate equivalent atoms: # 1 − *x* + 1, −*y* + 1, −*z*.

The crystal structure of **3** has been established by X-ray diffraction. A view of complex **3** is given in Figure 1. Selected bond distances and angles are presented in Table 1. The complex is a centrosymmetric dinuclear unit where two hydrosulfido anions bridge two $Pt(C_6F_5)_2$ fragments through the sulfur atoms. Coordination at each of the platinum centers is essentially square planar, the largest deviation from the best plane through the atoms defining the coordination plane is 0.005(2) Å, and the largest deviation from the ideal angles is for C(11)−Pt(1)−S(1), which shows a value of 175.7(2)°. The Pt····Pt distance is 3.494(1) Å, showing no significant metal−metal interaction. The two C_6F_5 rings on each Pt are planar and rotated 88.7(2)° with respect to each other.

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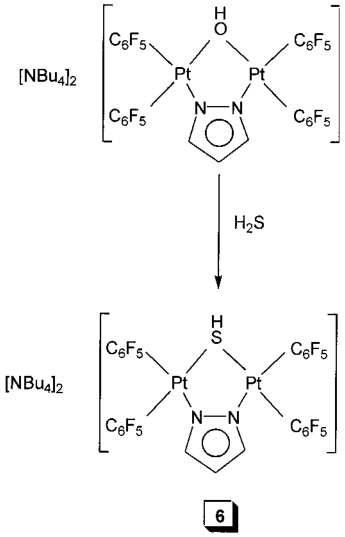
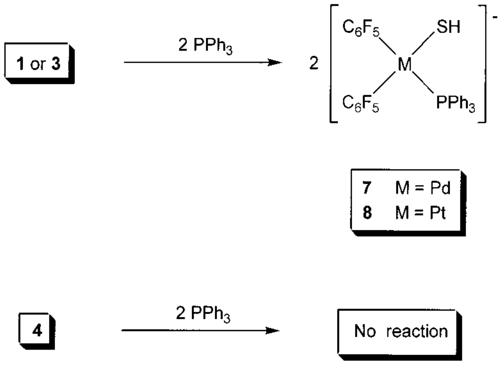
Scheme 2



Scheme 3

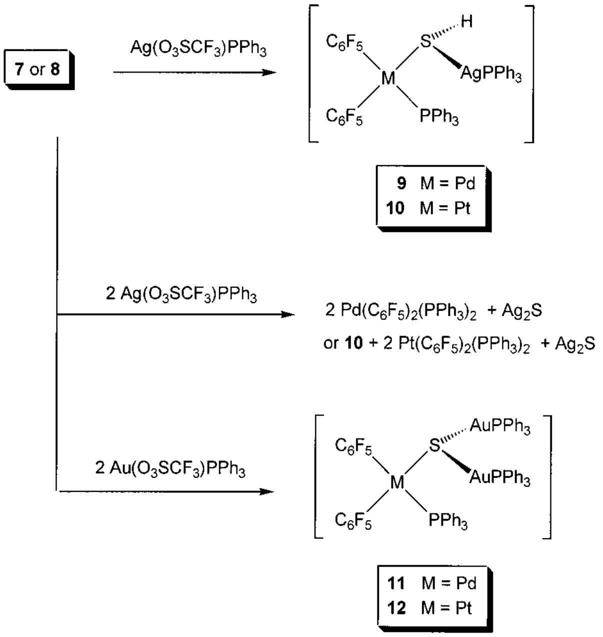


The mixed μ-hydroxo-μ-pyrazolate complex $[\{Pt(C_6F_5)_2\}_2(\mu\text{-}OH)(\mu\text{-}pz)]^{2-}$ reacts in methanol with H_2S to yield the heterobridged μ-hydrosulfido-μ-pyrazolate complex $[\{Pt(C_6F_5)_2\}_2(\mu\text{-}SH)(\mu\text{-}pz)]^{2-}$ **6** (Scheme 2). This reaction implies protonation of the hydroxo group and replacement by μ-SH. The microanalytical data and molar conductance in acetone solution is in agreement with the proposed formula.

The ^1H NMR spectrum of **6** shows one resonance at δ 5.69 (H^4) and one resonance at δ 6.99 (H^3 and H^5), with relative intensities of 1:2, which is consistent with the presence of a bridging pyrazolate ligand.[12] It should be noted that the μ-SH resonance at δ -1.19 in **3** moves to a lower field (δ -0.45 ppm) in the μ-hydrosulfido-μ-pyrazolate complex **6**, a result that can be attributed to the increased electron delocalization in the bridging system when one μ-SH group is substituted by the pyrazolate ligand.[9,12] The ^{19}F NMR spectrum of **6** is in accordance with the presence of two pairs of nonequivalent C_6F_5 groups freely rotating around the Pt−C bonds, one trans to S and one trans to N, with two resonances in the *o*-fluorine region (flanked by ^{195}Pt satellites; $^2J_{PtH} = 40.6$ Hz) and two resonances both in the *p*- and *m*-fluorine regions.

Monomeric Palladium and Platinum Complexes $[M(C_6F_5)_2(SH)(PPh_3)]^-$. The di-$\mu$-hydrosulfido complexes $[M_2(C_6F_5)_4(\mu\text{-}SH)_2]^{2-}$ **1** and **3** react with PPh_3 (1:2 molar ratio) to yield the corresponding hydrosulfido monomeric complexes $[M(C_6F_5)_2(SH)(PPh_3)]^-$ (M = Pd **7**, Pt **8**) (Scheme 3). The microanalytical data are in agreement with the proposed formulas. Measurements of the molar conductivities in acetone indicate that complexes **7** and **8** behave as 1:1 electrolytes.[23] The presence of two

Scheme 4



absorptions assignable to the X-sensitive mode of the C_6F_5 groups[20] suggests that they are on cis positions.[22] The absorptions in the 500 cm^{-1} region due to the PPh_3 ligand show the typical pattern for this ligand bound to Pd or Pt.

The ^{19}F NMR spectra of **7** and **8** show the presence of two different sets of resonances, each with an intensity ratio 2:1:2 ($2F_o$:$1F_p$:$2F_m$), revealing the presence of two different pentafluorophenyl groups, one trans to S and one trans to P (a multiplet resonance for the *o*-F atoms being observed due to coupling to ^{31}P). A singlet resonance is observed in the ^{31}P NMR spectra of **7** and **8** at δ 28.7 and 22.0, respectively, flanked by ^{195}Pt satellites ($^3J_{PtFo} = 2677$ Hz) in complex **8**. The ^1H NMR spectra of **7** and **8** exhibit, in each case, a high field resonance for the SH group consisting of a doublet at δ -2.26 and -2.03, respectively, arising from coupling to ^{31}P of the phosphine ($^3J_{PH} = 12.9$ Hz), and flanked by ^{195}Pt satellites ($^2J_{PtH} = 50.8$ Hz) in complex **8**. This resonance is observed at a higher field than in the corresponding dimeric precursors **1** and **3**, respectively.

No reaction was observed when complex **4** was treated with PPh_3 (1:2 molar ratio) in refluxing acetone for 3 h (see experimental).

$[M(C_6F_5)_2(PPh_3)\{S(H)AgPPh_3\}]$ and $[M(C_6F_5)_2(PPh_3)\{S(AuPPh_3)_2\}]$. The recently reported reaction of the related dimeric hydrosulfido gold complex $NBu_4[\{Au(C_6F_5)_3\}_2SH]$ with $[Au(OClO_3)(PPh_3)]$ or $[Ag(O_3SCF_3)(PPh_3)]$ in the presence of Na_2CO_3 , yielding sulfur-centered gold complexes $NBu_4[\{Au(C_6F_5)_3\}_2SR]$ (R = $AuPPh_3$, $AgPPh_3$),[26] prompted us to try the reaction of $[M(C_6F_5)_2(SH)(PPh_3)]^-$ **7** (M = Pd) and **8** (M = Pt) with the $[M'PPh_3]^+$ (M′ = Ag or Au) moiety to check whether they can behave as mononuclear metalloligands.

Complexes **7** and **8** react with $[Ag(O_3SCF_3)(PPh_3)]$ in a 1:1 ratio affording the heterobinuclear complexes $[M(C_6F_5)_2(PPh_3)\{S(H)AgPPh_3\}]$ **9** or **10** (Scheme 4). Both complexes are nonconducting in acetone solution.

The ^{19}F NMR spectra of **9** and **10** are in accordance with the presence of two pairs of non equivalent C_6F_5 groups freely rotating around the M−C bonds (M = Pd or Pt), one trans to S and one trans to P. The $^{31}P\{^1H\}$ NMR spectra of **9** and **10**

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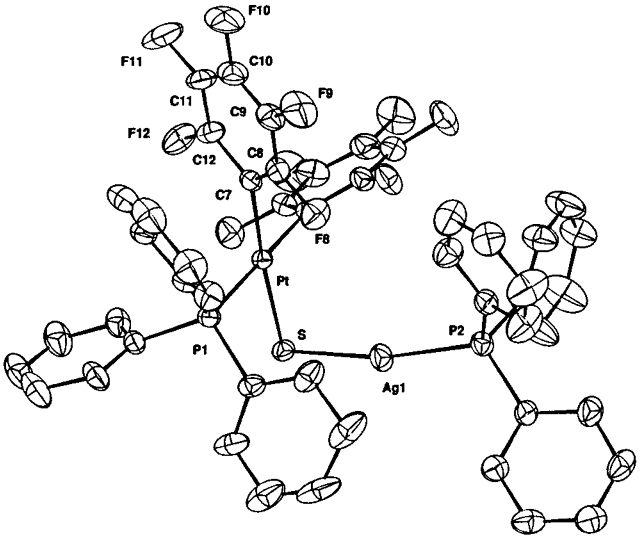

Figure 2. ORTEP diagram of **10**.

Table 2. Selected Distances (Å) and Bond Angles (deg) for Complex **10**

Bond Distances		Bond Angles	
Pt(1)−C(7)	2.037 (5)	P(2)−Ag(1)−S(1)	167.05 (6)
Pt(1)−C(1)	2.059(5)	C(7)−Pt(1) −C(1)	89.06 (19)
Pt(1)−P(1)	2.2860 (14)	C(7)−Pt(1)−P(1)	92.96 (14)
Pt(1)−S(1)	2.3617 (12)	C(7)−Pt(1)−S(1)	176.72 (15)
Ag(1)−P(2)	2.3869 (15)	C(1)−Pt(1)−P(1)	176.73 (16)
S(1)−Ag(1)	2.4142 (14)	C(1)−Pt−S(1)	89.35 (14)
Pt(1)···Ag(1)	3.366(1)	P(1)−Pt(1)−S(1)	88.76 (5)
		Pt(1)−S(1)−Ag(1)	89.64(5)

show the presence of two chemically nonequivalent phosphorus atoms, with relative intensities of 1:1, one of which is bound to palladium (for **9**) or platinum (for **10**), as revealed by the presence for **10** of the characteristic ^{195}Pt satellites (δ 16.5 ppm, $^1J_{PtP} = 2467$ Hz), and the other phosphorus atom is bound to silver (δ 13.8 and 12.0 ppm for **9** and **10**, respectively); its resonance appears as a broad signal at room temperature that sharpens at −50 °C into two doublets because of the coupling with the silver nuclei ^{107}Ag and ^{109}Ag (^1J (^{107}Ag,^{31}P) = 570 Hz, ^1J (^{109}Ag,^{31}P) = 657 Hz). The broadening observed at room temperature for this signal can be ascribed to an operative dynamic process, possibly involving dissociation of the PPh_3 ligand as is frequently observed in the coordination chemistry of silver.[27] The ^{1}H NMR spectra of **9** and **10** exhibit, in each case, a high field resonance for the SH group consisting of a doublet at δ −1.05 and −0.84, respectively, arising from coupling to ^{31}P of the phosphine bound to Pd or Pt ($^3J_{PH} \approx 12.6$ Hz), and flanked by ^{195}Pt satellites ($^2J_{PtH} = 42.4$ Hz) in complex **10**.

The crystal structure of $[Pt(C_6F_5)_2(PPh_3)\{S(H)AgPPh_3\}]$ **10** has been established by single-crystal X-ray diffraction. A view of complex **10** is given in Figure 2 , and selected bond distances and bond angles are presented in Table 2. Compound **10** is a heterodinuclear species in which the Pt^{II} and Ag^{I} centers are linked by the bridging S atom of the hydridosulfido ligand. The Pt atom is in a nearly square-planar environment, whereas the geometry around Ag deviates from linearity; the angle P(2)−Ag(1)−S(1) is 167.05 (6)°. In the related complex $[Pt(C_6F_5)_2(PPh_3)(C_5H_4NS)AgPPh_3]$, in which the Pt^{II} and Ag^{I} centers are linked by the bridging S atom of the pyridine-2-thiolato ligand,[28] the geometry around Ag can be considered to be quasi-linear 175.71(9)°. The Pt(1)−S(1) distance in complex **10** (2.3617 (12) Å) is very similar to that found in $[Pt(C_6F_5)_2(PPh_3)(C_5H_4NS)AgPPh_3]$.[28] The Ag(1)····Pt(1) distance (3.366(1) Å) is too long to be considered a bonding interaction. The Pt(1)−S(1)−Ag(1) angle is very small, showing a value of 89.64 (5)°.

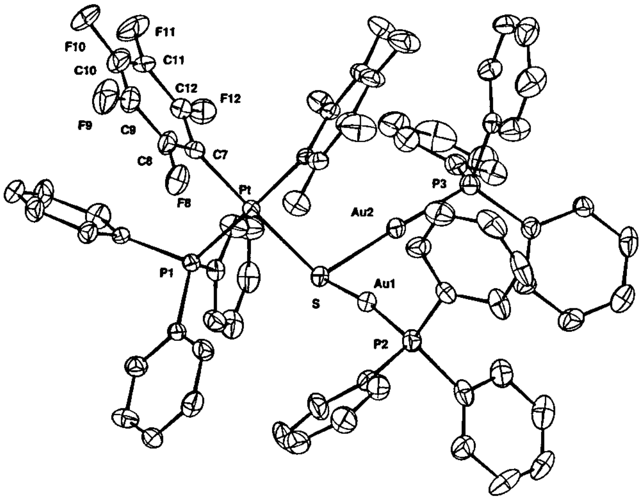

Figure 3. ORTEP diagram of **12**.

Owing to the isolobal analogy between the hydrogen atom and the $AgPR_3$ fragment, we also tried the treatment of complexes **7** or **8** with $[Ag(O_3SCF_3)(PPh_3)]$ in a 1:2 ratio in order to get the trinuclear complexes $[M(C_6F_5)_2(PPh_3)\{S(AgPPh_3)_2\}]$ (M = Pd or Pt). However, we obtained the mononuclear complex $[Pd(C_6F_5)_2(PPh_3)_2]$ (as shown by microanalysis and ^{31}P NMR data)[29] and Ag_2S (for **7**) or mixtures containing the heterobinuclear complex $[Pt(C_6F_5)_2(PPh_3)\{S(H)AgPPh_3\}]$ **10** together with $[Pt(C_6F_5)_2(PPh_3)_2]$ and Ag_2S (for **8**) (Scheme 4). As mentioned above, the reaction of the related hydrosulfido gold complex $NBu_4[\{Au(C_6F_5)_3\}_2SH]$ with $[Ag(O_3SCF_3)(PPh_3)]$ yields the sulfur-centered heterotrinuclear complex $NBu_4[\{Au(C_6F_5)_3\}_2S(AgPPh_3)]$.[26]

On the other hand, treatment of complexes **7** or **8** with $[Au(O_3SCF_3)(PPh_3)]$ in a 1:2 ratio produces the heterotrinuclear complexes $[M(C_6F_5)_2(PPh_3)\{S(AuPPh_3)_2\}]$ **11** or **12** (Scheme 4).

The ^{31}P{^{1}H} NMR spectra of the trinuclear complexes **11** and **12** show the presence of two different resonances, with relative intensities of 1:2, one of which is assigned to the P bound to palladium (for **11**) or to platinum (for **12**, $^1J_{PtP} = 2518$), and the other resonance is assigned to the phosphorus atoms bonded to the two gold metal centers, which is observed at higher frequency.

The crystal structure of $[Pt(C_6F_5)_2(PPh_3)\{S(AuPPh_3)_2\}]$ has been established by X-ray diffraction. A view of complex **12** is given in Figure 3. Selected bond distances and bond angles are presented in Table 3. Compound **12** is a heterotrinuclear species in which the Pt^{II} and Au^{I} centers are linked by the bridging S atom of the hydridosulfido ligand, and **12** shows a distorted trigonal-pyramidal geometry, with the sulfur at the vertex lying 1.033 Å out of the plane of the three metallic centers with no short metal−metal interactions between them. Some polynuclear gold complexes with bridging sulfido ligands show weak metal−metal interactions between the closed-shell d^{10} metal centers, termed aurophilic attractions,[30] that cannot be explained in terms

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Table 3. Selected Distances (Å) and Bond Angles (deg) for Complex **12**

Bond Distances		Bond Angles	
Pt(1)−C(7)	2.022(11)	C(7)−Pt(1)−C(1)	86.15 (4)
Pt(1)−C(1)	2.045 (11)	C(7)−Pt(1)−P(1)	94.0 (3)
Pt(1)−P(1)	2.278 (3)	C(7)−Pt(1)−S(1)	177.15 (3)
Pt(1)−S(1)	2.371(3)	C(1)−Pt(1)−P(1)	175.2 (3)
Au(1)−P(2)	2.259(4)	C(1)−Pt(1)−S(1)	93.7 (3)
S(1)−Au(1)	2.314 (3)	P(1)−Pt(1)−S(1)	86.3 (10)
Au(2)−P(3)	2.256 (3)	P(2)−Au(1)−S(1)	170.55(11)
S(1)−Au(2)	2.304 (3)	P(3)−Au(2)−S(1)	176.81(12)
Pt(1)···Au(1)	3.883(1)	Au(2)−S(1)−Au(1)	86.52 (12)
Pt(1)···Au(2)	3.712(1)	Au(2)−S(1)−Pt(1)	105.27(12)
Au(1)···Au(2)	3.164(1)	Au(1)−S(1)−Pt(1)	112.1 (12)

of the classical theory of chemical bonding, but only in theoretical studies when considered as a correlation effect, strengthened by relativistic effects.[31] The Pt atom is in a nearly square-planar environment. The Pt(1)−S(1) distance (2.371(3) Å) is very similar to that found in complex **10** and in other related complexes.[28] The coordination of the Au centers to the S and P atoms can be considered as quasi-linear (P(3)−Au(2)−S(1) = 176.81 (12)° and P(2)−Au(1)−S(1) = 170.55 (11)°).

Treatment of complexes **7** or **8** with $[Au(O_3SCF_3)(PPh_3)]$ in a 1:1 ratio produces mixtures containing the heterotrinuclear complexes $[M(C_6F_5)_2(PPh_3)\{S(AuPPh_3)_2\}]$ **11** or **12** and the starting material, but the formation of the binuclear complexes $[M(C_6F_5)_2(PPh_3)\{S(H)AuPPh_3\}]$ was not observed.

Experimental Section

Instrumental Measurements. C, H, and N analyses were performed with a Carlo Erba model EA 1108 microanalyzer. Decomposition temperatures were determined with a Mettler TG-50 thermobalance at a heating rate of 5 °C min^{-1} and with the solid samples under nitrogen flow (100 mL min^{-1}). Molar conductivities were measured in acetone solution ($c \approx 5 \times 10^{-4}$ mol L^{-1}) with a Crison 525 conductimeter. The NMR spectra were recorded on a Bruker AC 200E or Varian Unity 300 spectrometer, using $SiMe_4$ and $CFCl_3$ as the standard, respectively. In the ^{1}H NMR spectra of the ionic compounds, the signal of the NBu_4^+ cation has been omitted. Infrared spectra were recorded on a Perkin-Elmer 1430 spectrophotometer using Nujol mulls between polyethylene sheets.

Materials. The starting complexes $[NBu_4]_2[\{M(R)_2(\mu\text{-}OH)\}_2]$ (M= Pd, R = C_6F_5 or C_6Cl_5; Pt, R = C_6F_5),[12−14] $[\{Pd(R)(PPh_3)(\mu\text{-}OH)\}_2]$ (R = C_6F_5 or C_6Cl_5),[15] $[NBu_4]_2[\{Pt(C_6F_5)_2\}_2(\mu\text{-}OH)(\mu\text{-}pz)]$,[16] and $[M'(O_3SCF_3)(PPh_3)]$ (M′ = Ag, Au)[25] were prepared by procedures described elsewhere. Solvents were dried by the usual methods. H_2S gas was generated by treating FeS with commercial 96% H_2SO_4.

***CAUTION*:** *H_2S is extremely toxic, and all the preparations involving its use should be carried out in a well-ventilated fume hood!*

Preparation of Complexes $[NBu_4]_2[\{Pd(R)_2(\mu\text{-}SH)\}_2]$ (R = C_6F_5 1 and C_6Cl_5 2). H_2S was bubbled, at room temperature, through a solution of $[NBu_4]_2[\{Pd(R)_2(\mu\text{-}OH)\}_2]$ (R = C_6F_5 or C_6Cl_5) (0.071 mmol) in methanol (for **1**) or acetone (for **2**) (15 cm^3) for 15 min. The solvent was partially evaporated under reduced pressure. Addition of water caused the precipitation of a brown solid, which was collected by filtration, washed with water, and air dried.

Complex **1**: Yield: 90%. Anal. Calcd for $C_{56}H_{74}F_{20}N_2Pd_2S_2$: C, 47.0; H, 5.2; N, 2.0; S, 4.5. Found: C, 46.7; H, 5.4; N, 2.1; S, 4.8. Mp: 148 °C. Dec Λ_M: 240 S cm^2 mol^{-1}. IR (Nujol, cm^{-1}) 780, 770 (Pd−C_6F_5). ^{1}H NMR ($CDCl_3$) δ −2.03 (s, 2H, SH). ^{19}F NMR ($CDCl_3$) δ −111.1 (d, 8F$_o$, J_{om}= 27.4), −166.7 (m, 8F$_m$ + 4F$_p$). Complex **2**: Yield: 68%. Anal. Calcd for $C_{56}H_{74}Cl_{20}N_2Pd_2S_2$: C, 38.2; H, 4.2; N, 1.6; S, 3.7. Found: C, 38.4; H, 4.2; N, 1.8; S, 3.9. Mp: 175 °C. Dec Λ_M: 178 S cm^2 mol^{-1}. IR (Nujol, cm^{-1}) 825, 800 (Pd−C_6Cl_5). ^{1}H NMR ($CDCl_3$) δ −1.85 (s, 2H, SH).

Preparation of Complex $[NBu_4]_2[\{Pt(C_6F_5)_2(\mu\text{-}SH)\}_2]$ (3). $[NBu_4]_2[\{Pt(C_6F_5)_2(\mu\text{-}OH)\}_2]$ (0.10 g, 0.063 mmol) in methanol (15 cm^3) was reacted with H_2S at reflux temperature for 30 min. The solvent was partially evaporated under reduced pressure. Addition of water caused the precipitation of a brown solid, which was collected by filtration and air dried.

Complex **3**: Yield: 89%. Anal. Calcd for $C_{56}H_{74}F_{20}N_2Pt_2S_2$: C, 41.8; H, 4.6; N, 1.7; S, 4.0. Found: C, 41.4; H, 4.6; N, 1.7; S, 4.3. Mp: 190 °C. Dec Λ_M: 204 S cm^2 mol^{-1}. IR (Nujol, cm^{-1}) 795, 785 (Pd−C_6F_5). ^{1}H NMR ($CDCl_3$) δ −1.19 (s, 2H, SH, J_{PtH} = 37.2).^{19}F NMR ($CDCl_3$) δ −116.5 (d, 8F$_o$, J_{PtFo} = 469, J_{om} = 25.9), −167.7 (m, 8F$_m$), −168.2 (t, 4F$_p$, J_{mp} = 20.0).

Preparation of Complexes $[\{Pd(R)(PPh_3)(\mu\text{-}SH)\}_2]$ (R = C_6F_5 4 and C_6Cl_5 5). H_2S was bubbled, at room temperature, through a solution of $[\{Pd(R)(PPh_3)(\mu\text{-}OH)\}_2]$ (R = C_6F_5 or C_6Cl_5) (0.071 mmol) in acetone (for **4**) or dichloromethane (for **5**) (15 cm^3) for 15 min. The solvent was removed under vacuum, and the residue was treated with methanol. The brown solid was filtered off, washed with water then hexane, and air dried.

Complex **4**: Yield: 90%. Anal. Calcd for $C_{48}H_{32}F_{10}P_2Pd_2S_2$: C, 50.7; H, 2.8; S, 5.6. Found: C, 51.0; H, 2.9; S, 5.4. Mp: 170 °C. Dec IR (Nujol, cm^{-1}) 780 (Pd−C_6F_5). ^{1}H NMR ($CDCl_3$) δ 7.3 (m, 30H, Ph), −1.29 (d, 2H, SH, J_{PH} = 2.2).^{19}F NMR ($CDCl_3$) δ −114.9 (br, 2F$_o$), −116.3 (br, 2F$_o$), −161.6 (t, 2F$_p$, J_{mp} = 21.4), −161.3 (br, 4F$_m$). ^{31}P NMR ($CDCl_3$) δ 25.5 (s). Complex **5**: Yield: 74%. Anal. Calcd for $C_{48}H_{32}Cl_{10}P_2Pd_2S_2$: C, 44.3; H, 2.5; S, 4.9. Found: C, 44.7; H, 2.9; S, 4.7. Mp: 186 °C. Dec IR (Nujol, cm^{-1}) 830 (Pd−C_6Cl_5). ^{1}H NMR ($CDCl_3$) δ 7.4 (m, 30H, Ph), −1.38 (d, 2H, SH, J_{PH} = 2.2). ^{31}P NMR ($CDCl_3$) δ 24.9 (s).

Preparation of Complex $[NBu_4]_2[\{Pt(C_6F_5)_2\}_2(\mu\text{-}SH)(\mu\text{-}pz)]$ (6). $[NBu_4]_2[\{Pt(C_6F_5)_2\}_2(\mu\text{-}OH)(\mu\text{-}pz)]$ (0.1 g, 0.061 mmol) in methanol (15 cm^3) was reacted with H_2S at reflux temperature for 30 min. The solvent was removed under reduced pressure, and the residue was treated with 2-propanol. The greenish solid was filtered off and air dried.

Complex **6**: Yield: 73%. Anal. Calcd for $C_{59}H_{76}F_{20}N_4Pt_2S_2$: C, 43.1; H, 4.7; N, 3.4; S, 2.0. Found: C, 42.8; H, 4.9; N, 3.4; S, 2.3. Mp: 248 °C. Dec Λ_M: 224 S cm^2 mol^{-1}. IR (Nujol, cm^{-1}) 795, 780 (Pt−C_6F_5). ^{1}H NMR ($CDCl_3$) δ 6.99 (br, 2H, 3- and 5-H of pz), 5.69 (br, 1H, 4-H of pz), −0.45 (s, 1H, SH, J_{PtH} = 40.6).^{19}F NMR ($CDCl_3$) δ −115.7 (d, 4F$_o$, J_{PtFo} = 452, J_{om} = 29.1), −116.1 (d, 4F$_o$, J_{PtFo} = 480, J_{om} = 22.5), −166.8 (m, 4F$_m$ + 2F$_p$), −168.1 (m, 4F$_m$ + 2F$_p$).

Preparation of Complex $[NBu_4][Pd(C_6F_5)_2(SH)(PPh_3)]$ (7). To a solution of **1** (0.1 g, 0.069 mmol) in methanol (10 cm^3) was added PPh_3 (0.139 mmol). The solution was stirred under reflux for 1 h. The solvent was partially evaporated under reduced pressure. Addition of water caused the precipitation of a brownish solid, which was collected by filtration and air dried.

Complex **7**: Yield: 79%. Anal. Calcd for $C_{46}H_{52}F_{10}NPPdS$: C, 56.5; H, 5.4; N, 1.4; S, 3.3. Found: C, 56.8; H, 5.3; N, 1.3; S, 3.2. Mp: 230 °C. Dec Λ_M: 97 S cm^2 mol^{-1}. IR (Nujol, cm^{-1}) 775, 760 (Pd−C_6F_5), 530, 510, 494 (PPh_3). ^{1}H NMR ($CDCl_3$) δ 7.72 (m, 6H, H$_o$ of Ph), 7.34 (m, 9H, H$_m$ and H$_p$ of Ph), −2.26 (d, 1H, SH, J_{PH} = 12.9). ^{19}F NMR ($CDCl_3$) δ −111.2 (m, 2F$_o$), −113.0 (d, 2F$_o$, J_{om} =30.8), −165.8 (m, 2F$_m$), −166.4 (m, 2F$_m$ + 2F$_p$). ^{31}P NMR ($CDCl_3$) δ 28.7 (s).

Preparation of Complex $[NBu_4][Pt(C_6F_5)_2(SH)(PPh_3)]$ (8). To a suspension of **3** (0.1 g, 0.062 mmol) in 2-propanol (10 cm^3) was added PPh_3 (0.124 mmol). The suspension was stirred under reflux for 8 h. The solvent was removed under reduced pressure, and the residue was treated with dichloromethane/hexane. The brownish solid was filtered off and air dried.

Complex **8**: Yield: 72%. Anal. Calcd for $C_{46}H_{52}F_{10}NPPtS$: C, 51.8; H, 4.9; N, 1.3; S, 3.0. Found: C, 51.6; H, 5.1; N, 1.3; S, 3.2. Mp: 204 °C. Dec Λ_M: 97 S cm^2 mol^{-1}. IR (Nujol, cm^{-1}) 790, 775 (Pt−C_6F_5) 524, 512, 492 (PPh_3). ^{1}H NMR ($CDCl_3$) δ 7.74 (m, 6H, H$_o$ of Ph), 7.32 (m, 9H, H$_m$ and H$_p$ of Ph), −2.03 (d, 1H, SH, J_{PH} = 12.9, J_{PtH} = 50.8). ^{19}F NMR ($CDCl_3$) δ −114.6 (m, 2F$_o$, J_{PtFo} = 395), −116.0 (d, 2F$_o$, J_{PtFo} = 395, J_{om} = 30.8), −166.8 (m, 2F$_m$ + 1F$_p$), −168.1 (m, 2F$_m$ + 1F$_p$). ^{31}P NMR ($CDCl_3$) δ 22.0 (s, J_{PtFo} = 2677).

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Table 4. Crystal Structure Determination Details

	3	**10**	**12**
formula	$C_{56}H_{74}F_{20}N_2Pt_2S_2$	$C_{48}H_{31}AgF_{10}P_2PtS$	$C_{66}H_{45}Au_2F_{10}P_3PtS\cdot 0.25CH_2Cl_2$
fw	1609.47	1194.69	1763.24
space group	P 2(1)/c	$P\bar{1}$	C 2/c
a (Å)	12.7811(9)	13.9502(2)	62.6035(9)
b (Å)	12.4547(8)	14.1938(2)	13.0329(2)
c (Å)	19.558(2)	15.1239(2)	32.0828(5)
α (deg)	90	83.44	90
β (deg)	103.706(5)	74.8860(10)	104.7030(10)
γ (deg)	90	70.3330(10)	90
V(Å^3)	3024.7(4)	2721.24(7)	25319.3(7)
Z	2	2	16
D_{calc} (g cm^{-1})	1.767	1.458	1.850
λ (Å)	0.71073	0.71073	0.71073
μ(mm^{-1})	4.789	3.087	7.027
temp (K)	173(2)	293(2)	293(2)
data/restraints/parameters	5294/3/402	12865/0/568	22862/63/1524
GOF[a]	0.995	0.759	1.081
final R indices [$I > 2\sigma(I)$]: R1,[b] wR2[c]	0.0343, 0.0880	0.0412, 0.1106	0.0619, 0.1374
R indices (all data): R1,[b] wR2[c]	0.0430, 0.0927	0.0594, 0.1248	0.1079, 0.1594

[a] GOF $= [\Sigma(w(F_o^2 - F_c^2)^2)/(n - p)]^{1/2}$ where n is the reflections number and p the refined parameters number. [b] R1 $= \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] wR2 $=[\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$.

Reaction of Complex 4 with PPh_3. To a solution of **4** (0.08 g, 0.070 mmol) in acetone (10 cm^3) was added PPh_3 (0.140 mmol). The reaction mixture was stirred under reflux for 3 h. The solvent was partially evaporated under reduced pressure. The addition of water and methanol caused the precipitation of a brown solid, which was filtered off and air dried. NMR data showed that **4** was recovered unchanged.

Preparation of Complex [Pd(C_6F_5)$_2$(PPh_3){S(H)AgPPh_3}] (9). To a solution of **7** (0.12 g, 0.123 mmol) in CH_2Cl_2 (20 mL) was added [Ag(O_3SCF_3)(PPh_3)] (63.67 mg, 0.123 mmol). The mixture was stirred at room temperature for 5 min and then filtered through a small column packed with florisil. The solvent was partially evaporated under reduced pressure. The addition of hexane caused the precipitation of a white solid, which was collected by filtration and air dried. No analytically pure sample was obtained because it contains a small portion of a persistent impurity.

Complex **9**: IR (Nujol cm^{-1}) 782−772 (Pd−C_6F_5), 530, 522, 508, 490 (PPh_3). ^{1}H NMR ($CDCl_3$) δ 7.58−7.12 (m, 30H, Ph), −1.05 (d, 1H, SH, J_{PH} = 12.6). ^{19}F NMR ($CDCl_3$) δ −111.6 (d, 2F$_o$, J_{om} = 36.1), −115.7 (d, 2F$_o$, J_{om} = 29.6), −161.8 (t, 1F$_p$, J_{mp} = 19.5), −163.1 (m, 2F$_m$), −166.6 (t, 1F$_p$, J_{mp} = 19.8), −164.5 (m, 2F$_m$). ^{31}P NMR ($CDCl_3$) δ 24.3 (s, 1P, Pd−PPh$_3$), 13.8 (br, 1P, Ag−PPh$_3$).

Preparation of Complex [Pt(C_6F_5)$_2$(PPh_3){S(H)AgPPh_3}] (10). To a solution of **8** (0.1 g, 0.094 mmol) in CH_2Cl_2 (20 mL) was added [Ag(O_3SCF_3)(PPh_3)] (48.66 mg, 0.094 mmol). The mixture was stirred at room temperature for 3 h and then filtered through a small column packed with florisil. The solvent was partially evaporated under reduced pressure. The addition of hexane caused the precipitation of a white solid, which was collected by filtration and air dried. Complex **10** was recrystallized from dry toluene/hexane.

Complex **10**: Yield: 67%. Anal. Calcd for $C_{48}H_{31}F_{10}AgP_2PtS$: C, 48.3; H, 2.6; S, 2.7. Found: C, 48.5; H, 2.8; S, 2.6. Mp: 161 °C. Dec IR (Nujol cm^{-1}) 798−784 (Pt−C_6F_5), 536, 524, 512, 492 (PPh_3). ^{1}H NMR ($CDCl_3$) δ 7.56−7.06 (m, 30H, Ph), −0.84 (d, 1H, SH, J_{PH} = 12.3, J_{PtH} = 42.4). ^{19}F NMR ($CDCl_3$) δ −114.9 (m, 2F$_o$, J_{PtFo} = 373), −118.9 (d, 2F$_o$, J_{om} = 27.6, J_{PtFo} = 424), −162.7 (t, 1F$_p$, J_{mp} = 19.2), −163.9 (m, 2F$_m$), −165.3 (t, 1F$_p$, J_{mp} = 19.2), −165.9 (m, 2F$_m$). ^{31}P NMR ($CDCl_3$) δ 16.5 (s, 1P, Pt−PPh$_3$, J_{PtP} = 2467), 12.0 (br, 2P, Ag−PPh$_3$).

Preparation of Complex [Pd(C_6F_5)$_2$(PPh_3){S(AuPPh_3)$_2$}] (11). To a solution of **7** (0.12 g, 0.123 mmol) in CH_2Cl_2 (20 mL) was added [Au(O_3SCF_3)(PPh_3)] (149.2 mg, 0.246 mmol). The mixture was stirred at room temperature for 30 min and then filtered through a small column packed with florisil. The solvent was partially evaporated under reduced pressure. The addition of hexane caused the precipitation of a white solid, which was collected by filtration and air dried.

Complex **11**: Yield: 59%. Anal. Calcd for $C_{66}H_{45}Au_2F_{10}P_3PdS$: C, 47.9; H, 2.7; S, 1.9. Found: C, 47.7; H, 2.7; S, 1.8. Mp: 245 °C. Dec IR (Nujol cm^{-1}) 780−770 (Pd−C_6F_5). ^{1}H NMR ($CDCl_3$) δ 7.68−7.09 (m, 45H, Ph). ^{19}F NMR ($CDCl_3$) δ −111.1 (d, 2F$_o$, J_{om} = 29.9), −115.6 (d, 2F$_o$, J_{om} = 35.3), −163.2 (t, 1F$_p$, J_{mp} = 19.7), −164.3 (m, 2F$_m$), −165.2 (m, 1F$_p$ + 2F$_m$). ^{31}P NMR ($CDCl_3$) δ 33.9 (s, 2P, Au−PPh$_3$), 13.8 (s, 1P, Pd−PPh$_3$).

Preparation of Complex [Pt(C_6F_5)$_2$(PPh_3){S(AuPPh_3)$_2$}] (12). To a solution of **8** (0.12 g, 0.112 mmol) in CH_2Cl_2 (20 mL) was added [Au(O_3SCF_3)(PPh_3)] (136.8 mg, 0.224 mmol). The mixture was stirred at room temperature for 3 h and then filtered through a small column packed with florisil. The solvent was partially evaporated under reduced pressure. The addition of hexane caused the precipitation of a white solid, which was collected by filtration and air dried. Complex **12** was recrystallized from dry toluene/CH_2Cl_2/hexane.

Complex **12**: Yield: 57%. Anal. Calcd for $C_{66}H_{45}Au_2F_{10}P_3PtS$: C, 45.5; H, 2.6; S, 1.8. Found: C, 45.3; H, 2.6; S, 1.6. Mp: 280 °C. Dec IR (Nujol cm^{-1}) 794−782 (Pt−C_6F_5). ^{1}H NMR ($CDCl_3$) δ 7.72−7.06 (m, 45H, Ph). ^{19}F NMR ($CDCl_3$) δ −114.6 (m, 2F$_o$, J_{PtFo} = 400), −118.6 (d, 2F$_o$, J_{om} = 31.0, J_{PtFo} = 427), −163.9 (t, 1F$_p$, J_{mp} = 19.7), −164.9 (m, 2F$_m$), −166.6 (t, 1F$_p$ + 2F$_m$). ^{31}P NMR ($CDCl_3$) δ 33.2 (s, 2P, Au−PPh$_3$), 12.0 (s, 1P, Pt−PPh$_3$, J_{PtP} = 2518).

X-ray Structure Determination of 3, 10, and 12. Crystals suitable for a diffraction study were grown from toluene/hexane (complexes **3** and **10**) or dichloromethane−toluene−hexane (complex **12**). Single crystals of dimensions 0.60 × 0.50 × 0.50 for **3**, 0.20 × 0.25 × 0.40 for **10**, and 0.05 × 0.25 × 0.35 for **12** were mounted on a glass fiber in a random orientation. Data collection for **10** and **12** was performed at 25 °C on a Bruker Smart CCD diffractometer using graphite monocromated Mo Kα radiation (λ = 0.71073 A), with a nominal crystal to detector distance of 4.5 cm. Diffraction data were colleted based on a $\phi-\omega$ scan run. A total of 1271 frames were collected at 0.3° intervals and 10 s per frame. The diffraction frames were integrated using the SAINT package[32] and corrected for absorption with SADABS.[33] Data collection for **3** was performed at −100 °C on a Siemens P4 diffractometer. The scan method was $\omega-2\theta$, and empirical ι-scan mode absorption correction was made.

The structures were solved by heavy-atom methods[34] and refined[35] by full-matrix least-squares techniques using anisotropic thermal

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(32) *SAINT*, Version 4.0, Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, 1996.

(33) Sheldrick, G. M. *SADABS*; University of Gottingen, 1996.

(34) Sheldrick, G. M. *SHELXS-97*; University of Gottingen, 1997.

(35) Sheldrick, G. M. *SHELXL-97*; University of Gottingen, 1997.

parameters for non-H atoms. Hydrogen atoms were introduced in calculated positions and refined during the last stages of the refinement. The final *R* factors were 0.041 for **10**, 0.0619 for **12**, and 0.0343 for **3** over 9479, 15334, and 4583 observed reflections, respectively.

In complex **12** there are two molecules with bond lengths and angles somewhat different in the asymmetric unit, which can justify the big unit cell. The structure contains CH_2Cl_2 as solvate, and the largest residual peaks appear near that molecule.

Further details are given in Table 4.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of compounds **3**, **10**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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