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Heterodi- [MAg, MAu (M = Pd, Pt)], Tri- [PdAg$_2$, PtAg$_2$, PtAu$_2$, Pt$_2$M (M = Ni, Pt, Cd, Hg)], and Tetranuclear (Pt$_2$Ag$_2$, Pt$_2$Au$_2$) 1,1-Ethylenedithiolato Complexes

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The reactions of $[M(PPh_3)_2\{S_2C{=}C\{C(O)Me\}_2\}]$ [M = Pd (**1a**), Pt (**1b**)] with $AgClO_4$ and PPh_3 or with $[Au(PPh_3)(OCMe_2)]ClO_4$ afford heterodinuclear $[\{M(PPh_3)_2\}\{M'(PPh_3)\}\{S_2C{=}C\{C(O)Me\}_2\}]ClO_4$ [M = Pd, M′ = Ag (**2a**), M = Pt, M′ = Ag (**2b**), Au (**4**)] or trinuclear $[\{M(PPh_3)_2\}\{M'(PPh_3)\}_2\{S_2C{=}C\{C(O)Me\}_2\}](ClO_4)_2$ [M = Pd, M′ = Ag (**3a**), M = Pt, M′ = Ag (**3b**), Au (**5**)] 1,1-ethylenedithiolato complexes, depending on the molar ratio of the reagents. We have recently reported that, in the absence of added PPh_3, the reactions of $[Pt\{S_2C{=}C\{C(O)Me\}_2\}L_2]$ [L = PPh_3 (**1b**), L_2 = 1,5-cyclooctadiene (cod) (**1c**)] with $AgClO_4$ produce the heterotetranuclear derivatives $[\{PtL_2\}_2Ag_2\{S_2C{=}C\{C(O)Me\}_2\}_2](ClO_4)_2$ [L = PPh_3 (**6a**), L_2 = cod (**6b**)], which have been used now as efficient transmetallating agents toward gold, platinum, mercury, nickel, copper, or cadmium metal centers to give new types of 1,1-ethylenedithiolato complexes: $[\{Pt(PPh_3)_2\}_2Au_2\{S_2C{=}C\{C(O)Me\}_2\}_2](ClO_4)_2$ (**7**), $[(PtL_2)_2M\{S_2C{=}C\{C(O)Me\}_2\}_2](ClO_4)_2$ [L_2 = cod, M = Pt (**8**), L = PPh_3, M = Hg (**9**)], $[\{Pt(PPh_3)_2\}_2\{S_2C{=}C\{C(Me){=}O\}_2\}_2Ni](ClO_4)_2$ (**10**), and $[\{Pt(PPh_3)_2\}_2\{S_2C{=}C\{C(Me){=}O\}_2\}_2\{M(OClO_3)_2\}]$ [M = Cu (**11**), Cd (**12**)]. The crystal structures of two different solvates of **7** and that of **11** have been determined. All of these display two $\{Pt(PPh_3)_2\}\{S_2C{=}C\{C(O)Me\}_2\}$ moieties but, whereas in **7** they bridge two gold(I) centers through the sulfur atoms, in **11** they chelate the copper(II) center through the oxygen atoms. The last one is the first example of such a coordination mode for the 2,2-diacetyl-1,1-ethylenedithiolato ligand.

Introduction

1,1-Ethylenedithiolato metal complexes are being extensively studied mainly because of their photophysical properties,[1−5] including solvatochromic behavior and room-temperature luminescence in solution,[6−8] which make them excellent candidates for applications as photocatalysts.[9]

Most 1,1-ethylenedithiolato metal complexes are mononuclear,[6−8,10−16] although some homopolynuclear complexes with bridging or chelating 1,1-ethylenedithiolato ligands,[17−19] including clusters,[20−24] are known. The only reported hetero-

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metallic complexes that are assumed to contain bridging 1,1-ethylenedithiolato ligands are a few of the general formula M[$Ag_2\{S_2C{=}C(CN)CO_2Et\}_2$] (M = Co, Ni, Cu, Cd, Hg, Pd)[25] and some trinuclear 1,1-dicyano-2,2-ethylenedithiolato (*i*-mnt) complexes [$\{Ni(mnt)_2\}\{ML_n\}_2$] [M = Ag, L_n = $(PR_3)_2$, R = Ph, C_7H_7; M = Cu, L_n = $(PPh_3)_2$, $(PPh_3)_3(C_3H_6O)$, $(PPh_3)(C_5H_5N)$)].[26,27] Their proposed structures are based on a variety of techniques, but only the crystal structure of [$\{Ni(mnt)_2\}\{Ag(PPh_3)_2\}_2$] has been reported.[26,27] Although a few dithiolene complexes of the type [$\{M(PPh_3)_2\}_n\{S_2C{=}CCHC(O)R\}$] [M = Pd, Pt; *n* = 1, R = $\{(\eta^5\text{-}C_5H_4)_2Fe(\eta^5\text{-}C_5H_5)\}$; *n* = 2, R = $\{(\eta^5\text{-}C_5H_4)_2Fe\}$][28] have been described, they are mononuclear or homodinuclear derivatives of ferrocenyl-substituted dithiolene ligands.

2,2-Diacetyl-1,1-ethylenedithiolato complexes are very scarce, and the great majority are mononuclear. Apart from some recently reported by Eisenberg[29] and by us,[30,31] only a few others with Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) have been described on the basis of only their elemental analyses.[32] We report here the use of 2,2-diacetyl-1,1-ethylenedithiolato complexes of palladium and platinum as ligands to prepare di-[MAg, MAu (M = Pd, Pt)], tri- [$PdAg_2$, $PtAg_2$, $PtAu_2$, Pt_2M (M = Ni, Pt, Cd, Hg)], and tetranuclear (Pt_2Ag_2, Pt_2Au_2) complexes. The Pt_2Cu complex is the first oxygen-coordinated 2,2-diacetyl-1,1-ethylenedithiolato complex to be structurally characterized.

Table 1. Crystallographic Data

	7a	**7b**	**11**
formula	$C_{90}H_{78}Au_2Cl_{20}$-$O_{12}P_4Pt_2S_4$	$C_{90}H_{84}Au_2Cl_2$-$O_{14}P_4Pt_2S_4$	$C_{84}H_{72}Cl_2Au$-$O_{12}P_4Pt_2S_4$
fw	3096.76	2496.71	2050.16
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	12.058(2)	12.1896(10)	12.2246(10)
b (Å)	19.540(3)	12.3262(10)	13.1026(10)
c (Å)	22.836(4)	15.5870(12)	13.6811(10)
α (deg)	90	78.878(3)	71.672(10)
β (deg)	92.964(10)	77.180(3)	88.366(10)
γ (deg)	90	74.962(3)	77.556(10)
V ($Å^3$)	5373.0	2182.5	2029.5
Z	2	1	1
ρ_{calcd} (g cm^{-3})	1.914	1.900	1.677
μ (mm^{-1})	6.01	6.84	4.01
T (°C)	−110	−130	−100
$R_w(F^2)^a$	0.066	0.061	0.138
$R(F)^b$	0.038	0.026	0.059
S^c	1.03	1.00	0.75
Δ*ρ* (e $Å^{-3}$)	1.22	1.49	3.8

[a] $wR2(F^2) = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{0.5}$ for all of the reflections; $w^{-1} = \sigma^2F_o^2 + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and *a* and *b* are constants adjusted by the program. [b] $R1(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for reflections with $F > 4\sigma F$. [c] $S = [\Sigma\{w(F_o^2 - F_c^2)^2\}/(n - p)]^{0.5}$, where *n* is the number of reflections and *p* is the number of refined parameters.

Experimental Section

Infrared spectra were recorded in the range of 4000−200 cm^{-1} on a Perkin-Elmer 16F PC FTIR spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured with a Philips PW9501 conductimeter. Melting points were determined on a Reichert apparatus and are uncorrected. C, H, N, and S analyses were carried out with a Carlo Erba 1106 microanalyzer. ^1H and $^{31}P\{^1H\}$ NMR spectra were measured in $CDCl_3$ or acetone-d_6 on a Varian Unity 300 spectrometer. Chemical shifts are given in ppm and referred to TMS (^1H) or to H_3PO_4 (^{31}P).

Magnetic measurements were performed on polycrystalline samples of complexes **10** and **11** in the temperature range of 2−300 K with an applied magnetic field of 1 T using a Quantum Design MPMS-XL-5 susceptometer equipped with a SQUID sensor. For both of the compounds, a sample holder correction (obtained by a previous measurement in the same conditions) and a diamagnetic correction (obtained from Pascal's tables) were applied.

X-ray Structure Determinations. The numerical data are presented in Table 1. Crystals were mounted on glass fibers and transferred to the cold gas stream of the diffractometer (Siemens or Bruker Smart CCD). Data were recorded with Mo Kα radiation (λ = 0.710 73 Å) in *ω*-scan mode (with the exception of **7**·$2Me_2CO$ in *ω* and *ϕ* scans). Absorption corrections were applied on the basis of multiple scans (SADABS). Structures were solved by direct methods and refined anisotropically on F^2 (program SHELXL-97, Sheldrick, G. M. University of Göttingen, Germany). Hydrogen atoms were included using a riding model or with rigid methyl groups. (Special features of refinement: in **7**·$2Me_2CO$, the acetone and the anion are disordered over two positions.)

[$PtCl_2(cod)$] (cod = 1,5-cyclooctadiene),[33] [AuCl(tht)] (tht = tetrahydrothiophene),[34] [$Tl_2\{S_2C{=}C\{C(O)Me\}_2\}$],[30] and CuCl[35] were prepared as previously reported. $NiCl_2{\cdot}6H_2O$ (Fluka), $AgClO_4$ (Aldrich), $CdCl_2$, and $HgCl_2$ (Probus) were obtained from commercial sources and used without further purification. [$M\{S_2C{=}C\{C(O)Me\}_2\}L_2$] [L = PPh_3, M = Pd (**1a**), Pt (**1b**); L_2 = cod, M = Pt (**1c**)] and [$(PtL_2)_2Ag_2\{S_2C{=}C\{C(O)Me\}_2\}_2$]$(ClO_4)_2$ [L = PPh_3 (**6a**), cod (**6b**)] have been reported recently by us.[31]

Warning: Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be prepared only in small amounts.

[$\{M(PPh_3)_2\}\{Ag(PPh_3)\}\{S_2C{=}C\{C(O)Me\}_2\}$]$ClO_4$ [M = Pd (2a), Pt (2b)]. To a solution of **1a** (149.6 mg, 0.19 mmol) or **1b** (96.8 mg, 0.11 mmol) in acetone (25 mL) were added equimolar amounts of $AgClO_4$ and PPh_3. The solution was stirred for 5 h and concentrated under vacuum (2 mL), and diethyl ether (40 mL) was added to precipitate **2a** or **2b** as a pale yellow solid, which was filtered, washed with diethyl ether (2 × 5 mL), and dried by suction. Data for **2a** follow. Yield: 201 mg, 83%. Anal. Calcd for $C_{60}H_{51}AgClO_6P_3PdS_2$: C, 56.53; H, 4.03; S, 5.03. Found: C, 56.39; H, 4.09; S, 4.80. Mp: 110 °C dec. Λ_M (Ω^{-1} cm^2 mol^{-1}): 125. IR (cm^{-1}): 1680 s, 1608 s, 1092 s, 621 s. ^1H NMR ($CDCl_3$): δ 2.11 (s, 6H, Me), 7.17−7.63 (m, 45H, PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 11.82 (s, br), 17.34 (s, br), 22.57 (d), 24.22 (s), 30.17 (s). $^{31}P\{^1H\}$ NMR (−60 °C): δ 8.53 [dd, $^2J(^{109}Ag^{31}P)$ = 717.6 Hz, $^2J(^{107}Ag^{31}P)$ = 626.4 Hz], 18.43 [dd, $^2J(^{109}Ag^{31}P)$ = 793.6 Hz, $^2J(^{107}Ag^{31}P)$ = 712.5 Hz], 30.69 (s). Data for **2b** follow. Yield: 130 mg, 88%. Anal. Calcd for $C_{60}H_{51}AgClO_6P_3PtS_2$: C, 52.85; H, 3.77; S, 4.70. Found: C, 52.61; H, 3.94; S, 4.71. Mp: 160 °C. Λ_M (Ω^{-1} cm^2 mol^{-1}): 106. IR (cm^{-1}): 1674 s, 1626 s, 1091 s, 621 s. ^1H NMR ($CDCl_3$): δ 2.14 (s, 6H, Me), 7.17−7.49 (m, 45H, PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 10−13 (s, br), 17.02 [s with ^{195}Pt satellites, $J(^{195}Pt^{31}P)$ = 3118 Hz]. $^{31}P\{^1H\}$ NMR (−60 °C): δ 8.62 [dd, $^2J(^{109}Ag^{31}P)$ = 710.7 Hz, $^2J(^{107}Ag^{31}P)$ = 638.3 Hz], 15.41

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[dd, $^2J(^{109}Ag^{31}P) = 720.8$ Hz, $^2J(^{107}Ag^{31}P) = 626.4$ Hz], 16.88 [s with ^{195}Pt satellites, $J(^{195}Pt^{31}P) = 3123$ Hz].

[{M(PPh$_3$)$_2$}{Ag(PPh$_3$)}$_2${S$_2$C═C{C(O)Me}$_2$}](ClO$_4$)$_2$ [M = Pd (3a), Pt (3b)]. To a solution of **1a** (162.4 mg, 0.20 mmol) or **1b** (110 mg, 0.12 mmol) in acetone (25 mL) was added 2 equiv of both AgClO$_4$ and PPh$_3$. The solution was stirred for 2 (**3a**) or 5 (**3b**) h in the dark and concentrated under vacuum (2 mL), and diethyl ether (40 mL) was added to precipitate **3a** or **3b** as a pale yellow solid, which was filtered, washed with diethyl ether (2 × 5 mL), and dried by suction. Data for **3a** follow. Yield: 296 mg, 85%. Anal. Calcd for $C_{78}H_{66}Ag_2Cl_2O_{10}P_4PdS_2$: C, 53.71; H, 3.81; S, 3.68. Found: C, 53.65; H, 3.83; S, 3.63. Mp: 105 °C dec. Λ_M (Ω^{-1} cm^2 mol^{-1}): 243. IR (cm^{-1}): 1675 s, 1633 s, 1091 s, 622 s. ^{1}H NMR (CDCl$_3$): δ 2.00 (s, 6H, Me), 7.18−7.45 (m, 60H, PPh$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$, 20 °C): δ 10.7 (s, br), 16.1 (s, br), 30.05 (s). ^{31}P{^{1}H} NMR (−60 °C): δ 12.50 [dd, $^2J(^{109}Ag^{31}P) = 737.8$ Hz, $^2J(^{107}Ag^{31}P) = 640.6$ Hz], 30.45 (s). Data for **3b** follow. Yield: 187 mg, 85%. Anal. Calcd for $C_{78}H_{66}Ag_2Cl_2O_{10}P_4PtS_2$: C, 51.11; H, 3.63; S, 3.50. Found: C, 50.66; H, 3.61; S, 4.00. Mp: 146 °C dec. Λ_M (Ω^{-1} cm^2 mol^{-1}): 247. IR (cm^{-1}): 1674 s, 1626 s, 1099 s, 622 s. ^{1}H NMR (CDCl$_3$, 20 °C): δ 2.11 (s, 6H, Me), 7.20−7.50 (m, 60H, PPh$_3$). ^{1}H NMR (−60 °C): δ 2.14 (s, 3H, Me), 2.27 (s, 3H, Me), 7.15−7.53 (m, 60H, PPh$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$, 20 °C): δ 10.65 (s, br), 15.70 [s with ^{195}Pt satellites, $J(^{195}Pt^{31}P) = 3163$ Hz]. ^{31}P{^{1}H} NMR (−60 °C): δ 12.21 [dd, $^2J(^{109}Ag^{31}P) = 738.6$ Hz, $^2J(^{107}Ag^{31}P) = 624.4$ Hz], 16.07 [s with ^{95}Pt satellites, $J(^{195}Pt^{31}P) = 3165$ Hz].

[{Pt(PPh$_3$)$_2$}{Au(PPh$_3$)}{S$_2$C═C{C(O)Me}$_2$}]ClO$_4$ (4). Under a nitrogen atmosphere, [AuCl(PPh$_3$)] (128.6 mg, 0.26 mmol) and AgClO$_4$ (53.6 mg, 0.26 mmol) were reacted in acetone (25 mL) for 0.5 h, the suspension was filtered to remove AgCl, and the solution was added dropwise to a suspension of **1b** (232 mg, 0.26 mmol) in acetone (40 mL). After being stirred for 2.5 h the reaction mixture was filtered through Celite, and the solution was concentrated (3 mL) under vacuum. Diethyl ether (40 mL) was added to precipitate **4** as a pale yellow solid, which was recrystallized from acetone and diethyl ether, dried by suction, and then dried in an oven at 60 °C for 1 h. Yield: 346.3 mg, 92%. Anal. Calcd for $C_{60}H_{51}AuClO_6P_3PtS_2$: C, 49.55; H, 3.54; S, 4.41. Found: C, 49.39; H, 3.63; S, 4.18. Mp: 209 °C dec. Λ_M (Ω^{-1} cm^2 mol^{-1}): 140. IR (cm^{-1}): 1687 s, 1634 s, 1087 s, 621 s. ^{1}H NMR (acetone-*d*$_6$): δ 2.19 (s, 6H, Me), 7.23−7.74 (m, 45H, PPh$_3$). ^{31}P{^{1}H} NMR (acetone-*d*$_6$): δ 16.76 [s with ^{95}Pt satellites, $J(^{195}Pt^{31}P) = 3170$ Hz], 34.61 (s, AuPPh$_3$).

[{Pt(PPh$_3$)$_2$}{Au(PPh$_3$)}$_2${S$_2$C═C{C(O)Me}$_2$}](ClO$_4$)$_2$ (5). [AuCl(PPh$_3$)] (383.2 mg, 0.77 mmol) and AgClO$_4$ (160.6 mg, 0.77 mmol) were reacted in acetone (35 mL) under a nitrogen atmosphere for 0.5 h. The suspension was filtered to remove AgCl, and the solution was added dropwise to a suspension of **1b** (344 mg, 0.39 mmol) in acetone (40 mL). After being stirred for 3 h, the reaction mixture was filtered through Celite, and the solution was concentrated (3 mL) under vacuum. Diethyl ether (40 mL) was added to precipitate a white solid, which was recrystallized from acetone and diethyl ether, dried by suction, and then dried in an oven at 60 °C for 2 h. Yield: 780 mg, 99%. Anal. Calcd for $C_{78}H_{66}Au_2Cl_2O_{10}P_4PtS_2$: C, 46.58; H, 3.31; S, 3.19. Found: C, 46.43; H, 3.37; S, 4.56. Mp: 176 °C. Λ_M (Ω^{-1} cm^2 mol^{-1}): 240. IR (cm^{-1}): 1674 s, 1650 s, 1087 s, 621 s. ^{1}H NMR (acetone-*d*$_6$): δ 2.23 (s, 6H, Me), 7.22−7.75 (m, 45H, PPh$_3$). ^{31}P{^{1}H} NMR (acetone-*d*$_6$): δ 15.97 [s with ^{195}Pt satellites, $J(^{195}Pt^{31}P) = 3195$ Hz], 34.24 (s, br, AuPPh$_3$), 45.20 [s, Au(PPh$_3$)$_2^+$].

[{Pt(PPh$_3$)$_2$}$_2$Au$_2${S$_2$C═C{C(O)Me}$_2$}$_2$](ClO$_4$)$_2$ (7). Solid [AuCl(tht)] (51.3 mg, 0.16 mmol) was added to a suspension of **6a** (179.0 mg, 0.08 mmol) in dichloromethane (15 mL), and the mixture was stirred for 17 h. The resulting suspension was filtered, the yellow solution was concentrated (2 mL), and diethyl ether (40 mL) was added to give a white solid, which was filtered, dried by suction, and recrystallized from acetone and diethyl ether. Yield: 147 mg, 76.2%. Anal. Calcd for $C_{84}H_{72}Au_2Cl_2O_{12}P_4Pt_2S_4$: C, 42.38; H, 3.05; S, 5.39. Found: C, 42.37; H, 3.28; S, 5.56. Mp: 225 °C dec. Λ_M (Ω^{-1} cm^2 mol^{-1}): 247. IR (cm^{-1}): 1685 s, 1673 s, 1533 s, 1093 s, 622 s, 565 s, 534 s, 515 s. ^{1}H NMR (CDCl$_3$): δ 2.67 (s, 12H, Me), 7.26−7.48 (m, 60H, PPh$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 9.78 (s with Pt satellites, $J_{PPt} = 3306$ Hz). Monoclinic crystals of **7**·6CDCl$_3$ grew by the slow evaporation of the solution used to study the NMR spectra of **7**. Triclinic crystals of **7**·2Me$_2$CO grew in an attempt to crystallize **5**. Both modifications were studied by X-ray diffraction methods.

[{Pt(cod)}$_2$Pt{S$_2$C═C{C(O)Me}$_2$}$_2$](ClO$_4$)$_2$ (8). To a suspension of **6b** (177.4 mg, 0.13 mmol) in acetone (40 mL) was added PtCl$_2$ (34.5 mg, 0.13 mmol). The resulting orange suspension was stirred for 22 h, the solvent was removed under vacuum, and the residue was extracted with dichloromethane (2 × 25 mL). The combined extracts were filtered through Celite, the solution was concentrated (3 mL) under vacuum, and diethyl ether (40 mL) was added to precipitate an orange solid, which was filtered, washed with diethyl ether (5 mL), and dried by suction. Yield: 143 mg, 82%. Anal. Calcd for $C_{28}H_{36}Cl_2O_{12}Pt_3S_4$: C, 24.95; H, 2.69; S, 9.49. Found: C, 24.24; H, 2.87; S, 9.03. Mp: 168 °C. Λ_M (Ω^{-1} cm^2 mol^{-1}): 171. IR (cm^{-1}): 1680−1638 s br, 1096 vs, 621 s. ^{1}H NMR (CDCl$_3$): δ 2.16−2.80 [m, 28H, Me + CH$_2$(cod)], 5.62 [s, 8H, CH (cod)].

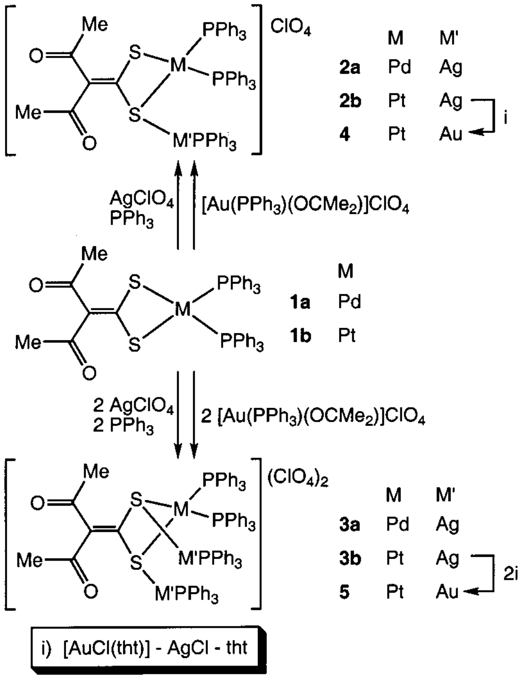
[{Pt(PPh$_3$)$_2$}$_2$Hg{S$_2$C═C{C(O)Me}$_2$}$_2$](ClO$_2$)$_2$ (9). Solid HgCl$_2$ (26.8 mg, 0.10 mmol) was added to a suspension of **6a** (217.5 mg, 0.10 mmol) in dichloromethane (30 mL). While being stirred, the suspension changed to pale yellow, intense yellow, and finally orange. After 18 h, the suspension was filtered, the orange solution was concentrated (3 mL), and diethyl ether (40 mL) was added to precipitate a yellow solid, which was filtered and suction dried. Yield: 175 mg, 80%. Anal. Calcd for $C_{84}H_{72}Cl_2HgO_{12}P_4Pt_2S_4$: C, 46.13; H, 3.32; S, 5.86. Found: C, 45.88; H, 3.23; S, 5.53. Mp: 145 °C dec. Λ_M (Ω^{-1} cm^2 mol^{-1}): 241. IR (cm^{-1}): 1687 m, 1637 m, 1580 m, 1092 s, 622 s. ^{1}H NMR (CDCl$_3$): δ 2.25 (s, 12H, Me), 7.27−7.47 (m, 60H, PPh$_3$). ^{31}P{^{1}H} NMR: δ 16.18 (s with Pt satellites, $J_{PPt} = 3183$ Hz).

[{Pt(PPh$_3$)$_2$}$_2${S$_2$C═C{C(Me)═O}$_2$}$_2$Ni](ClO$_4$)$_2$ (10). Solid NiCl$_2$·6H$_2$O (14.6 mg, 0.06 mmol) was added to a suspension of **6a** (134.9 mg, 0.06 mmol) in dichloromethane (30 mL). While being stirred, the suspension changed from pale yellow to bright yellow and then finally to greenish yellow. Nineteen hours later, the suspension was filtered through anhydrous MgSO$_4$, and the solution was concentrated to 3 mL. Diethyl ether (40 mL) was added to give a greenish-yellow solid, which was recrystallized from dichloromethane and diethyl ether and then suction dried. Yield: 99 mg, 80.7%. Anal. Calcd for $C_{84}H_{72}Cl_2NiO_{12}P_4Pt_2S_4$: C, 49.33; H, 3.55; S, 6.27. Found: C, 49.06; H, 3.87; S, 6.99. Mp: 90 °C dec. Λ_M (Ω^{-1} cm^2 mol^{-1}): 179. IR (cm^{-1}): 1608 w, 1092 s, 622 s. ^{1}H NMR (CDCl$_3$): δ 2.36 (s, br, 12H, Me), 7.00−7.60 (m, 60H, PPh$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 20.38 (s with Pt satellites, $J_{PPt} = 3131$ Hz).

[{Pt(PPh$_3$)$_2$}$_2${S$_2$C═C{C(Me)═O}$_2$}$_2${Cu(OClO$_3$)$_2$}] (11). Solid CuCl (13.3 mg, 0.13 mmol) was added to a suspension of **6a** (148.6 mg, 0.07 mmol) in dichloromethane (25 mL) under an N$_2$ atmosphere. While the resulting suspension was stirred for 24 h, it turned more pale and greenish. It was filtered through Celite, the solution was concentrated (3 mL), and diethyl ether (40 mL) was added to give a green solid, which was filtered, recrystallized from dichloromethane and diethyl ether, and then suction dried. It was then further dried in an oven at 60 °C overnight. Yield: 105 mg, 76%. Anal. Calcd for $C_{84}H_{72}Cl_2CuO_{12}P_4Pt_2S_4$: C, 49.21; H, 3.54; S, 6.25. Found: C, 48.92; H, 3.56; S, 6.29. Mp: 196 °C dec. Λ_M (Ω^{-1} cm^2 mol^{-1}): 388. IR (cm^{-1}): 1583 vs, 1093 vs, 622 s, 537 s, 518 s, 507 s, 494 s. ^{1}H NMR (CDCl$_3$): δ 2.17 (s, 12H, Me), 7.00−7.80 (m, 60H, PPh$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 18.73 [s (br) with Pt satellites, $J_{PPt} = 3049$ Hz]. Single crystals of **11** were grown from dichloromethane/diethyl ether.

[{Pt(PPh$_3$)$_2$}$_2${S$_2$C═C{C(Me)═O}$_2$}$_2${Cd(OClO$_3$)$_2$}] (12). Solid CdCl$_2$ (10.9 mg, 0.06 mmol) was added to a suspension of **6a** (130.6 mg, 0.06 mmol) in acetone (30 mL), and the reaction mixture was stirred for 18 h. The color of the suspension turned to pale yellow. The solvent was removed under vacuum, and the residue was extracted in dichloromethane (3 × 40 mL). The combined extracts were filtered through anhydrous MgSO$_4$. The solution was concentrated (1 mL), and diethyl ether (40 mL) was added to precipitate a yellow solid, which was filtered and dried first by suction and then in an oven at 80 °C for 15 min. Yield: 110 mg, 87%. Anal. Calcd for $C_{84}H_{72}CdCl_2O_{12}P_4Pt_2S_4$: C, 48.06; H, 3.46; S, 6.11. Found: C, 48.30; H, 3.79; S, 7.68. Mp: 97 °C dec. Λ_M (Ω^{-1} cm^2 mol^{-1}): 272. IR (cm^{-1}): 1626 s, 1092 vs, 622 s. ^{1}H NMR (CDCl$_3$): δ 2.18 (s, 12H, Me), 7.22−7.43 (m,

Scheme 1



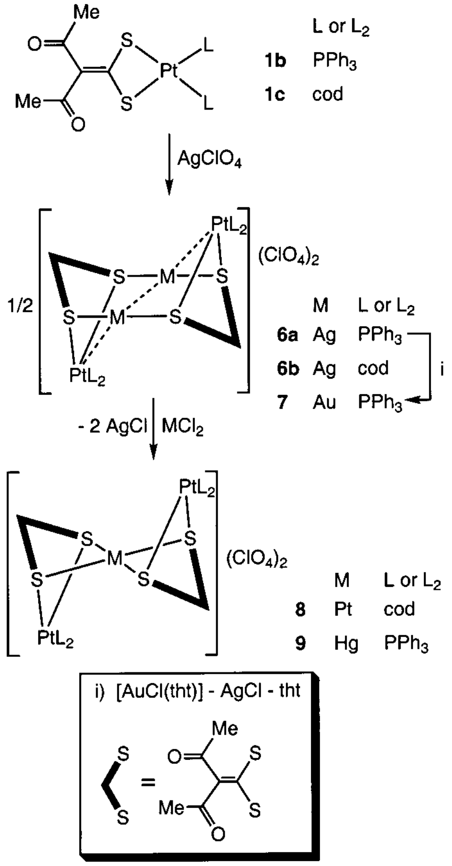
60H, PPh3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 17.98 (s with Pt satellites, J_{PPt} = 3076 Hz).

Results and Discussion

The syntheses of complexes $[M(PPh_3)_2\{S_2C{=}C\{C(O)Me\}_2\}L_2]$ [M = Pd (**1a**), Pt (**1b**)] from $[Tl_2\{S_2C{=}C\{C(O)Me\}_2\}]$,[30] $[MCl_2(NCPh_2)]$ (M = Pd, Pt), and PPh_3 have been recently reported by us.[31] These complexes can be used as sulfur-donor ligands toward Ag(I) and Au(I) centers. Thus, the reactions in acetone between **1a** or **1b** and $AgClO_4$ and PPh_3 produce heterodinuclear $[\{M(PPh_3)_2\}\{Ag(PPh_3)\}\{S_2C{=}C\{C(O)Me\}_2\}]ClO_4$ [M = Pd (**2a**), Pt (**2b**)] or trinuclear $[\{M(PPh_3)_2\}\{Ag(PPh_3)\}_2\{S_2C{=}C\{C(O)Me\}_2\}]ClO_4$ [M = Pd (**3a**), Pt (**3b**)] complexes depending on the molar ratio of the reagents, 1:1:1 or 1:2:2, respectively (Scheme 1). Similarly, the homologous PtAu or $PtAu_2$ complexes $[\{Pt(PPh_3)_2\}\{Au(PPh_3)\}\{S_2C{=}C\{C(O)Me\}_2\}]ClO_4$ (**4**) or $[\{Pt(PPh_3)_2\}\{Au(PPh_3)\}_2\ \{S_2C{=}C\{C(O)Me\}_2\}]ClO_4$ (**5**) can be obtained by the slow addition of an acetone solution of $[Au(PPh_3)(OCMe_2)]ClO_4$ [obtained by reacting in acetone under nitrogen equimolar amounts of $[AuCl(PPh_3)]$ and $AgClO_4$ and then filtering off the precipitated AgCl (see the Experimental Section)] to another containing 1 or 0.5 equiv, respectively, of **1b** in the same solvent. Complexes **4** and **5** can also be obtained by reacting **2b** or **3b**, respectively, with an equimolar amount of [AuCl(tht)]. In these reactions, the precipitation of AgCl and displacement of the labile tht ligand take place, resulting in the substitution of silver by gold (Scheme 1). Complexes **2**−**5** have been obtained in good to excellent yields (75−99%). They are stable in the solid state, and the photostability of the silver complexes is remarkable. In solution, they are also stable, with the exception of the gold derivatives **4** and **5** which decompose in dichloromethane to give mixtures containing $[Au(PPh_3)_2]ClO_4$ and $[AuCl(PPh_3)]$ (by ^{31}P NMR).

We have recently reported that, in the absence of added PPh_3, the reaction of **1b** or **1c** (Scheme 2) with $AgClO_4$ gives the tetranuclear Pt_2Ag_2 derivatives **6a** or **6b**, respectively.[31] Both complexes are efficient transmetallating reagents. Thus, **6a** reacts in dichloromethane with [AuCl(tht)] (1:2) to give AgCl and $[\{Pt(PPh_3)_2\}_2Au_2\{S_2C{=}C\{C(O)Me\}_2\}_2](ClO_4)_2$ (**7**). Similarly, heterotrinuclear complexes, namely, $[\{Pt(cot)\}_2Pt\{S_2C{=}C\{C(O)Me\}_2\}_2](ClO_4)_2$ (**8**) and $[\{Pt(PPh_3)_2\}_2Hg\{S_2C{=}C\{C(O)Me\}_2\}_2](ClO_4)_2$ (**9**), are obtained along with AgCl from the reaction of **6b** with $PtCl_2$ or of **6a** with $HgCl_2$, respectively (Scheme 2). A different family of heterotrinuclear complexes can be obtained by reacting **6a** with $NiCl_2{\cdot}6H_2O$, CuCl, or $CdCl_2$. Thus, in the first case, the complex $[\{Pt(PPh_3)_2\}_2\{S_2C{=}C\{C(Me){=}O\}_2\}_2Ni](ClO_4)_2$ (**10**) (Scheme 3) is obtained. The related reaction between **6a** and CuCl is rather different; the hexacoordinated copper(II) species $[\{Pt(PPh_3)_2\}_2\{S_2C{=}C\{C(Me){=}O\}_2\}_2\{Cu(OClO_3)_2\}]$ (**11**) results after a disproportionation process and the coordination of two perchlorato anions and both oxygen atoms of two 2,2-diacetyl-1,1-ethylenedithiolato ligands of complex **1b**. Copper(0) is removed along with AgCl by filtration through Celite. The reaction with $CdCl_2$ gives $[\{Pt(PPh_3)_2\}_2\{S_2C{=}C\{C(Me){=}O\}_2\}_2\{Cd(OClO_3)_2\}]$ (**12**). Although we could not get an appropriate sulfur analysis for complex **12** (Anal. Calcd: S, 6.11. Found: S, 7.50−7.64 in different samples), the satisfactory values for C and H as well as the spectroscopic data (see the following paragraphs) suggest that the compound is pure and that the problem is due to the analytical procedure.

Scheme 2



Crystal Structures of Complexes. The crystal structures (Table 1) of $\mathbf{7}{\cdot}6CDCl_3$ (monoclinic, Figure 1 and Table 2; henceforth **7a**), $\mathbf{7}{\cdot}2Me_2CO$ (triclinic, Table 2; henceforth **7b**), and **11** (Figure 2 and Table 3) have been measured, and all of these were found to exhibit crystallographic inversion symmetry. Those of complexes **1a**, **1b**, $\mathbf{6a}{\cdot}Me_2CO$, and $\mathbf{6a}{\cdot}2Et_2O$ were previously reported.[31]

Complex **7** results from the coordination to Au(I) of both sulfur atoms of the metalloligand complex **1b**, and its crystal structures show tetranuclear Pt_2Au_2 dications, perchlorate anions, and solvent molecules. Upon coordination of **1b** to gold, some

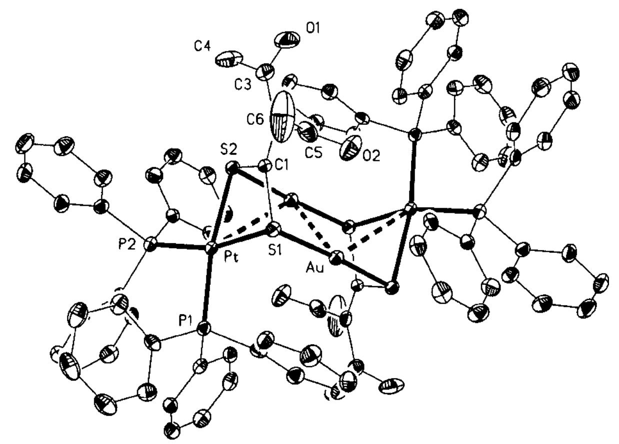


Figure 1. Structure of the cation of complex **7a** in the crystal. Ellipsoids represent 50% probability levels. Solvent and H atoms omitted for clarity. Only the shorter Au···Pt contacts are included as dashed lines.

Scheme 3

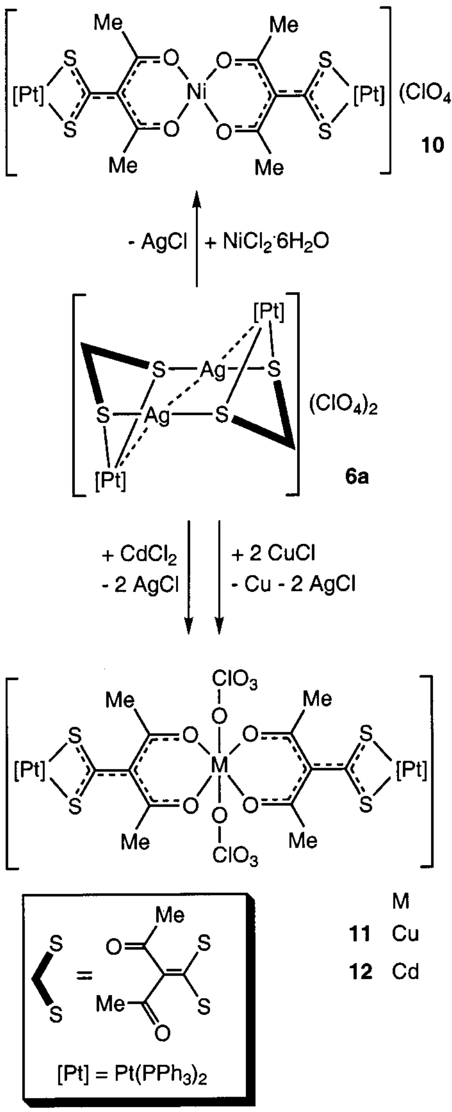


Table 2. Selected Bond and Interatomic Distances (Å) and Bond Angles (deg) for Complex **7**

	7a monoclinic	**7b** triclinic
Pt−P(1)	2.2773(12)	2.2876(9)
Pt−P(2)	2.2963(12)	2.2896(8)
Pt−S(2)	2.3717(12)	2.3704(7)
Pt−S(1)	2.3810(12)	2.3562(8)
Au−S(1)	2.3154(12)	2.3202(8)
Au−S(2)#1	2.3403(12)	2.3136(7)
Au···Au#1	2.9477(5)	3.0347(3)
Au···Pt#1	3.2235(5)	3.334(3)
Au···Pt	3.4861(5)	3.5014(3)
S(1)−C(1)	1.802(4)	1.792(3)
S(2)−C(1)	1.796(5)	1.805(3)
C(1)−C(2)	1.342(6)	1.325(4)
C(2)−C(3)	1.498(7)	1.519(4)
C(2)−C(5)	1.522(7)	1.503(4)
C(3)−O(1)	1.209(6)	1.196(4)
C(3)−C(4)	1.480(8)	1.485(5)
C(5)−O(2)	1.193(6)	1.214(4)
P(1)−Pt−P(2)	98.95(4)	100.17(3)
P(1)−Pt−S(2)	169.51(4)	170.73(3)
P(2)−Pt−S(2)	91.31(4)	89.08(3)
P(1)−Pt−S(1)	94.71(4)	95.52(3)
P(2)−Pt−S(1)	164.38(4)	159.39(3)
S(2)−Pt−S(1)	75.43(4)	75.63(3)
S(1)−Au−S(2)#1	176.44(4)	175.20(3)
C(2)−C(1)−S(2)	128.6(4)	126.5(2)
C(2)−C(1)−S(1)	122.8(4)	125.6(2)
S(2)−C(1)−S(1)	107.8(2)	107.35(16)
C(1)−C(2)−C(3)	127.9(5)	120.0(3)
C(1)−C(2)−C(5)	119.8(4)	118.8(3)
C(3)−C(2)−C(5)	112.2(4)	121.3(3)

of the main features of its crystal structure[31] are preserved in those of **7**, such as the *Z,E* conformation of the 2,2-diacetyl-1,1-ethylenedithiolato ligand, the nearly planar $C_2C{=}CS_2$ skeleton [mean deviations of the six atoms S(1), S(2), C(1), C(2), C(3), and C(5) are 0.05 (**7a**) and 0.03 (**7b**) Å], and the narrow S(1)−Pt-S(2) angle [74.43(4)° (**7a**) and 75.63(3)° (**7b**)] imposed by the chelating ligand. The environment of the platinum atom deviates from planarity appreciably more in **7** [mean deviations of the five atoms S(1), S(2), Pt, P(1), and P(2) are 0.095 (**7a**) and 0.141 (**7b**) Å] than in **1b** (0.061 Å). The Pt−S and C═C bond distances in **7** show only small variations with respect to the corresponding values in **1b**. The olefinic C(1) and C(2) atoms are in distorted but perfectly planar trigonal environments showing narrow S(1)−C(1)−S(2) angles [107.8(2)° (**7a**) and 107.35(16)° (**7b**)]. The gold atoms in **7** are in distorted linear environments [S−Au−S; 176.44(4)° (**7a**) and 175.20(3)° (**7b**)], display short aurophilic contacts [Au···Au; 2.9477(5) (**7a**) and 3.0347(3) (**7b**) Å],[36−54] and also weak

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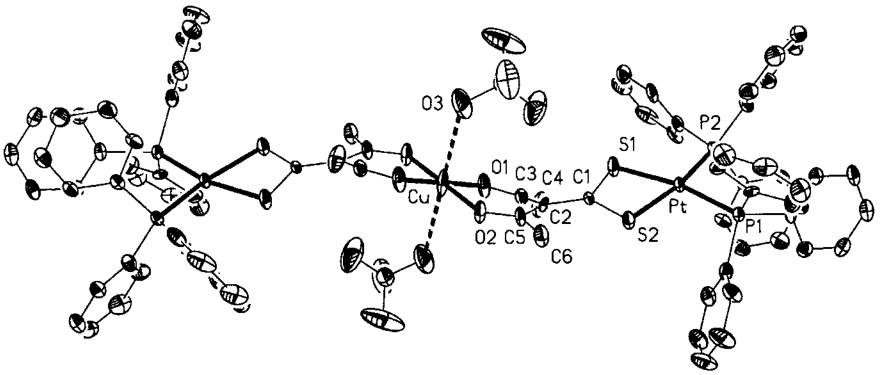

Figure 2. Structure of complex **11** in the crystal. Ellipsoids represent 50% probability levels. H atoms omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex **11**[a]

Pt−P(2)	2.280(2)	S(1)−C(1)	1.718(8)
Pt−P(1)	2.299(2)	S(2)−C(1)	1.738(9)
Pt−S(1)	2.328(2)	O(1)−C(3)	1.262(9)
Pt−S(2)	2.360(2)	O(2)−C(5)	1.270(9)
Cu−O(1)	1.892(6)	C(1)−C(2)	1.429(10)
Cu−O(2)	1.917(6)	C(2)−C(5)	1.437(12)
Cu−O(3)	2.715(9)	C(2)−C(3)	1.475(12)
P(2)−Pt−P(1)	98.41(8)	C(1)−S(1)−Pt	90.3(3)
P(2)−Pt−S(1)	94.10(8)	C(1)−S(2)−Pt	88.7(3)
P(1)−Pt−S(2)	94.23(8)	C(2)−C(1)−S(1)	123.0(7)
S(1)−Pt−S(2)	73.14(8)	C(2)−C(1)−S(2)	129.2(6)
O(1)−Cu−O(2)	90.0(3)	S(1)−C(1)−S(2)	107.8(4)
O(1)−Cu−O(3)	99.4(3)	C(1)−C(2)−C(5)	122.4(8)
O(2)−Cu−O(3)	92.4(3)	C(1)−C(2)−C(3)	117.8(7)
O(3)#1−Cu−O(3)	180	C(5)−C(2)−C(3)	119.7(7)

[a] Symmetry transformations used to generate equivalent atoms: (#1) $-x$, $-y+1$, $-z+1$.

Pt···Au [3.2235(5) (**7a**) and 3.334(3) (**7b**) Å] interactions. We regard the longer contacts of 3.4861(5) (**7a**) and 3.5014(3) Å (**7b**) from the gold to the second platinum atom as less important, and we have not included such a contact explicitly in Figure 1 or in Schemes 2 or 3. The S−Au bond distances in **7** [2.3154(12), 2.3403(12) Å (**7a**); 2.32136(7), 2.3202(8) Å (**7b**)] are shorter than the S−Ag distances found in the crystal structure of the homologous silver complex **6a**[31] [2.4265(11), 2.4591(11) Å (**6a**·Me$_2$CO); 2.4116(9), 2.4337(9) Å (**6a**·2Et$_2$O)], in agreement with the recent assignment of a smaller covalent radius for gold than for silver.[55] As in the case of **6a**, the coordination plane of platinum in **7** is perpendicular (within 7°) to the S$_4$Au$_2$ plane.

The crystal structure of **11** (Figure 2) shows the copper atom in a distorted octahedral environment of oxygen atoms from two mutually trans monocoordinated perchlorato ligands [Cu−O(3) 2.715(9) Å] and two molecules of complex **1b**. This requires that the 2,2-diacetyl-1,1-ethylenedithiolato ligands adopt the *E,E* conformation, in contrast with that in complexes **1b**, **6a**, and **7**. The coordination of the metalloligand **1b** to Cu(II) through the CO groups induces the lengthening of both the CO bonds [1.262(9), 1.270(9) Å (**11**); 1.223(7), 1.213(7) Å (**1b**)] and the C(1)═C(2) bonds [1.429(10) Å (**11**) and 1.349(7) Å (**1b**)] and the shortening of the S−C [1.718(8), 1.738(9) Å (**11**); 1.757(6), 1.783(6) Å (**1b**)] bonds. The C(2)−C(O) bond lengths in **11** and **1b** cannot be compared meaningfully because of their high standard deviations. However, the mean value for **11** [1.456 Å] is significantly shorter than that for complexes **1b**, **6a**, and **7**, [1.501 Å]. All of the above-mentioned changes suggest an electronic delocalization over the S$_2$−C−C−(CO)$_2$ bonds, as indicated in Scheme 3. In **11**, the weakening of the C═C bond allows the planar fragments C═CS$_2$ [mean deviation <0.001 Å] and C$_2$C═C [mean deviation 0.008 Å] to form an angle of 24.0°, while the P(1)−Pt−P(2) and C═CS$_2$ planes subtend to an angle of 7.0°. Both acetyl groups are rotated (by 29.1° and 15.8°) out of the C$_2$C═C plane.

Table 4. C−H···O Hydrogen Bonds[a]

	system C−H···O	H···O (Å)	C−H···O (deg)
7a	C(65)−H(65)···O(2)	2.47	122
	C(66)−H(66)···O(2)	2.46	122
	C(93)−H(93)···O(12)[b,c]	2.10	173
	C(92)−H(92)···O(13)[b,c]	2.41	127
7b	C(66)−H(66)···O(1)	2.56	126
	C(6)−H(6a)···O(2)[d]	2.51	169
11	C(34)−H(34)···O(5)[c]	2.49	141

[a] C−H are from phenyl groups and O from ligands unless otherwise stated. [b] Solvent C−H. [c] Perchlorate oxygen. [d] Ligand C−H.

All three of the structures display C−H···O contacts that might reasonably be interpreted as hydrogen bonds; the corresponding dimensions (excluding those involving disordered groups) are presented in Table 4. The shortest involve the well-ordered deuteriochloroform solvent molecules of **7a**.

NMR Spectra. In the ^{1}H NMR spectra of complexes **6b** and **8**, the resonances of the methylene protons of the cod ligand overlap with those of the methyl protons of the dithiolene ligand, which cannot be inequivocally assigned. For all of the other complexes these protons give a unique resonance (broad in the case of **10**) in the range of 2.00−2.80 ppm. The equivalence of the methyl groups could be related to an *E,E* conformation of the 1,1-ethylenedithiolato ligands in solution (as confirmed for **11** by its crystal structure) or, if the ligands adopt the *E,Z* conformation (see the crystal structures of **1b**, **6a**, and **7**),[31] to the free rotation of the acetyl groups around the C−C bond in solution. This was confirmed for **1b**[31] by its ^{13}C{^{1}H} NMR spectrum, which shows one resonance for each of the Me, C(O), and C═C nuclei.

Coordination of **1a** to silver in complexes **2a** and **3a** does not produce any significant shifting of the ^{31}P{^{1}H} NMR singlet

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resonance of the $Pd(PPh_3)_2$ moiety [29.71 (**1a**), 30.17 (**2a**), and 30.45 (**3a**) ppm]. In complex **1b** and those that contain it as a ligand, the $Pt(^{31}PPh_3)_2$ resonance is observed at room temperature as a singlet with ^{195}Pt satellites. In most cases, the δ and $J(^{195}Pt-^{31}P)$ values (in the ranges of 15.70−20.38 ppm and 3049−3195 Hz) are similar to those of **1b** [δ 19.15 ppm; $J(^{195}Pt-^{31}P) = 3041$ Hz]. When the chemical shift of the resonance due to the $M(^{31}PPh_3)_2$ moiety is compared for the pairs of complexes **(2a** and **2b**; **3a** and **3b)**, which differ only in the metal [**a** (Pd), **b** (Pt)], an appreciable low-field shift is observed for the palladium complexes, as we had previously observed in the pair of complexes **1a** and **1b**[31] and had related to the greater strength of the P−Pt with respect to the P−Pd bonds. While for complex **6a** this resonance (δ 18.78 ppm) and the $J(^{195}Pt-^{31}P)$ coupling constant (3068 Hz) are included in the above-mentioned ranges, its homologous gold complex **7** gives lower δ (9.78 ppm) and higher $J(^{195}Pt-^{31}P)$ (3306 Hz) values. This is especially surprising, taking into account that no appreciable modification of these parameters occurs when silver in **2b** [δ 17.02 ppm; $J(^{195}Pt-^{31}P) = 3118$ Hz] or **3b** [δ 15.70 ppm; $J(^{195}Pt-^{31}P) = 3163$ Hz] is replaced by gold to give **4** [δ 16.76 ppm; $J(^{195}Pt-^{31}P) = 3170$ Hz] or **5** [δ 15.97 ppm; $J(^{195}Pt-^{31}P) = 3195$ Hz], respectively. Because all of the phosphorus nuclei of **7** are isochronous, the different Au···Pt contacts in the solid state are not preserved in solution.

In the room-temperature spectra of complexes **2** and **3**, broad resonances are observed for the $Ag^{31}PPh_3$ units, suggesting that, in solution, intermolecular interchange processes occur, as we have previously observed in other $AgPPh_3$ complexes.[36] In the low-temperature spectra of **2a** and **2b**, these resonances split into three pairs of doublets. Because each pair of doublets arises from $^{31}P-^{107}Ag$ and $^{31}P-^{109}Ag$ spin−spin coupling, we assume that three complexes are present in the $CDCl_3$ solutions of complexes **2a** and **2b** at low temperatures.[36] When the influence of the coordination number on the J_{AgP} values for $[Ag(PAr_3)_nX]$ complexes are taken into account,[56,57] the most abundant species in the low-temperature solution of **2a** or **2b** [(**2a**) δ 15.66 ppm, $J_{AgP} = 626, 717$ Hz; (**2b**) δ 15.41 ppm, $J_{AgP} = 626, 721$ Hz] could be a dicoordinated complex. The second most abundant complex, with similar J_{AgP} values, could also be a dicoordinated complex [(**2a**) δ 12.66 ppm, $J_{AgP} = 608, 694$ Hz; (**2b**) δ 12.13 ppm, $J_{AgP} = 638, 711$ Hz] while the scarcest one seems to be a tricoordinated complex [(**2a**) δ 8.53 ppm, $J_{AgP} = 409, 468$ Hz; (**2b**) δ 8.62 ppm, $J_{AgP} = 413, 471$ Hz]. Because PPh_3 is coordinated in the three species, the second ligand in the dicoordinated complexes could be an S-donor atom or ClO_4. In the tricoordinated complex, the other two ligands could be both S-donor atoms, one S-donor atom and ClO_4, or ClO_4 acting as a chelate.

The low-temperature ^{31}P NMR spectra of **2a** or **2b** shows the resonance corresponding to the moiety $M(PPh_3)_2$ (M = Pd, Pt) as a singlet, indicating that, even at −60 °C, a fast interchange occurs.

At −60 °C, the ^{1}H NMR spectrum of **3b** shows inequivalent dithiolene methyl protons, indicating an *E,Z* configuration for the ligand and a restricted rotation of the acetyl groups around the C−C bond. At this temperature, one pair of doublets [(**3a**) δ 12.50 ppm, $J_{AgP} = 641, 738$ Hz; (**3b**) δ 12.21 ppm, $J_{AgP} = 642, 739$ Hz] in the $^{31}P\{^1H\}$ NMR spectrum of **3a** or **3b** is indicative of only one species in solution with equivalent $AgPPh_3$ groups, which must be interpreted, assuming that a rapid interchange of the $AgPPh_3$ units takes place or that an accidental coincidence occurs. The J_{AgP} values suggest that the complexes of **3** be dicoordinated at silver. In the gold complexes **4** and **5**, the Me protons are isochronous as are the ^{31}P nuclei.

IR Spectra. The IR spectra, measured in the solid state, show several bands (see the Experimental Section) in the 1690−1450 cm^{-1} region that cannot be unequivocally assigned to $\nu(C{=}O)$ or $\nu(C{=}C)$ stretching modes because these have proved to be coupled in other carbonyl-containing push−pull ethylenes.[58] The bands at higher frequencies (over 1600 cm^{-1}) largely reflect the strength of the C═O bond,[58] and their lowering in energy could be attributed to conjugation within the $S_2C{=}C\{C(O)Me\}_2$ ligand or to coordination of the carbonyl oxygen atoms to a metal center. In the 1800−1600 cm^{-1} region, the spectra of complexes **10**−**12** have the same appearance, showing only one strong absorption band close to 1600 cm^{-1}, while in those of **1b**, **1c**, **6a**, and **7**−**9**, several other intense bands are also observed at higher frequencies. On the basis of the analogy of their IR spectra and on the crystal structure of **11**, we assume that, also in complexes **10** and **12**, the 1,1-ethylenedithiolato ligands coordinate to Ni or Cd, respectively, through the carbonyl oxygen atom, which accounts for the shift to a lower energy in the carbonyl frequency. Similarly, on the basis of the crystal structures of complexes **1b**, **6a**, and **7** and the analogy of their IR spectra with those of **8** and **9**, we assume that, in all of them, the 1,1-ethylenedithiolato ligands act as sulfur donors. It is reasonable to assume that, in **8**, the geometry around the central platinum atom is square planar. However, the geometry around the mercury atom in complex **9** could be tetrahedral or square planar because both geometries are found in some related diorganodithiocarbamate complexes.[59−63]

The bands at ca. 1500 cm^{-1}, which in the spectra of **7**−**9** could be tentatively assigned to $\nu(C{=}C)$, are absent in those of **10**−**12**. The spectra of complexes **2**−**12** show intense perchlorate bands at around 1100 and 620 cm^{-1}. The broadening or splitting of the higher-energy band in the spectra of **3a**, **3b**, or **12** is indicative of the symmetry descent caused on the perchlorato group upon its interaction ($Ag\cdots OClO_3$) or coordination ($Cd-OClO_3$) in the solid state. On the basis of this, complexes **3** and **12** are probably tricoordinated and octahedral, respectively, in the solid state. In fact, 6−8 are the usual coordination numbers found in cadmium perchlorato complexes.[64−69] Surprisingly, no splitting is observed in the spectrum of **11**, despite its crystal structure showing weakly coordinating $OClO_3$ ligands.

Magnetic Measurements. The copper complex **11** presents a constant value of 0.37 emu K mol^{-1} for the Curie constant in the temperature range of 2−300 K. This value is in good agreement with that expected for a Cu(II), $S = {}^1/_2$ isolated ion

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(0.375 emu K mol^{-1}), indicating the presence of the Cu(II) ion in the complex and its magnetic isolation because its nearest neighbors are two diamagnetic Pt(II) ions. The Ni complex **10** is diamagnetic in the same temperature range, indicating a square planar environment of the Ni(II) ion ($S = 0$).

Complexes **1a** and **1b** are nonconducting in an acetone solution, and in general, the values found for the molar conductivities correspond to those accepted for 1:1 (**2a**, **2b**, **4**) or 2:1 (**3a**, **3b**, **5**−**10**, and **12**) electrolytes.[70] The value found for complex **11** (388 Ω^{-1} cm^2 mol^{-1}) is abnormally high for a 2:1 electrolyte and proves that the coordination of the two perchlorato groups observed in its crystal structure is not maintained in an acetone solution, which suggests displacement of perchlorato by acetone.

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Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for complexes **7** and **11** have been deposited as a CIF. This material is available free of charge via the Internet at http://pubs.acs.org.

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