

Mononuclear (Pd, Pt), Heterodinuclear (PdAg, PtAg), and Tetranuclear (Pd₂Ag₂, Pt₂Ag₂) 1,1-Ethylenedithiolato Complexes[‡]

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The reactions of $[\text{Ti}_2\{\text{S}_2\text{C}=\text{C}\{\text{C}(\text{O})\text{Me}\}_2\}_n]$ with $[\text{MCl}_2\text{L}_2]$ (1:1) or with $[\text{MCl}_2(\text{NCPH})_2]$ and PPh_3 (1:1:2) give complexes $[\text{M}\{\eta^2\text{-S}_2\text{C}=\text{C}\{\text{C}(\text{O})\text{Me}\}_2\}\text{L}_2]$ [$\text{M} = \text{Pt}$, $\text{L}_2 = 1,5\text{-cyclooctadiene (cod)}$ (**1**); $\text{L}_2 = \text{bpy}$, $\text{M} = \text{Pd}$ (**2a**), Pt (**2b**), $\text{L} = \text{PPh}_3$, $\text{M} = \text{Pd}$ (**3a**), Pt (**3b**)] whereas with MCl_2 and QCl (2:1:2) anionic derivatives $\text{Q}_2[\text{M}\{\eta^2\text{-S}_2\text{C}=\text{C}\{\text{C}(\text{O})\text{Me}\}_2\}_2]$ [$\text{M} = \text{Pd}$, $\text{Q} = \text{NMe}_4$ (**4a**), $\text{Ph}_3\text{P}=\text{N}=\text{PPh}_3$ (PPN) (**4a'**), $\text{M} = \text{Pt}$, $\text{Q} = \text{NMe}_4$ (**4b**)] are produced. Complexes **1** and **3** react with AgClO_4 (1:1) to give tetranuclear complexes $[\{\text{ML}_2\}_2\text{Ag}_2\{\mu^2,\eta^2\text{-(S,S')-}\{\text{S}_2\text{C}=\text{C}\{\text{C}(\text{O})\text{Me}\}_2\}_2\}(\text{ClO}_4)_2]$ [$\text{L} = \text{PPh}_3$, $\text{M} = \text{Pd}$ (**5a**), Pt (**5b**), $\text{L}_2 = \text{cod}$, $\text{M} = \text{Pt}$ (**5b'**)], while the reactions of **3** with AgClO_4 and PPh_3 (1:1:2) give dinuclear $[\{\text{M}(\text{PPh}_3)_2\}\{\text{Ag}(\text{PPh}_3)_2\}\{\mu^2,\eta^2\text{-(S,S')-}\{\text{S}_2\text{C}=\text{C}\{\text{C}(\text{O})\text{Me}\}_2\}_2\}]\text{ClO}_4$ [$\text{M} = \text{Pd}$ (**6a**), Pt (**6b**)]. The crystal structures of **3a**, **3b**, **4a**, and two crystal forms of **5b** have been determined. The two crystal forms of **5b** display two $\{\text{Pt}(\text{PPh}_3)_2\}\{\mu^2,\eta^2\text{-(S,S')-}\{\text{S}_2\text{C}=\text{C}\{\text{C}(\text{O})\text{Me}\}_2\}_2\}$ moieties bridging two $\text{Ag}(\text{I})$ centers.

Introduction

Certain ketene dithioacetals with electron-withdrawing substituents and certain 1,1-ethylenedithiolato metal complexes display interesting photophysical properties.^{1–5} Indeed, the increasing attention paid nowadays to these species arises from their solvatochromic behavior and room-temperature luminescence in solution^{6–8} and their status as excellent candidates for applications as photocatalysts in light-to-chemical-energy con-

version processes.⁹ Much of the effort currently being expended is devoted to finding how the excited-state properties can be altered in a predictable manner through systematic ligand modification.⁹ In addition, the use of 1,1-ethylenedithiolate ligands may facilitate the syntheses of clusters^{10–14} or stabilize unusually high oxidation states.^{15–17}

Most 1,1-ethylenedithiolato metal complexes are mononuclear,^{6–8,15–21} although some homopolynuclear complexes with bridging or chelating 1,1-ethylenedithiolato ligands,^{22–24}

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Table 1. Crystallographic Data for Complexes **3a**, **3b**, **4a**, **5b**·C₃H₆O, and **5b**·2C₄H₁₀O

	3a	3b	4a	5b ·C ₃ H ₆ O	5b ·2C ₄ H ₁₀ O
chemical formula	C ₄₆ H ₃₆ O ₂ P ₂ PdS	C ₄₆ H ₃₆ O ₂ P ₂ PdS	C ₂₀ H ₃₆ N ₂ O ₄ PdS ₄	C ₈₇ H ₇₈ Ag ₂ Cl ₂ O ₁₃ P ₄ Pt ₂ S ₄	C ₉₂ H ₉₂ Ag ₂ Cl ₂ O ₁₄ P ₄ Pt ₂ S ₄
fw	805.17	893.96	603.15	2260.43	2350.60
space group	<i>Pbca</i> (No. 61)	<i>Pbca</i> (No. 61)	<i>Pbca</i> (No. 61)	<i>P1</i> (No. 2)	<i>P2₁/n</i> (No. 11)
<i>a</i> (Å)	19.2590(5)	19.290(3)	11.9402(11)	10.6869(10)	11.0089(2)
<i>b</i> (Å)	16.9889(5)	16.927(3)	18.9221(12)	12.574(2)	29.4225(5)
<i>c</i> (Å)	22.5659(6)	22.475(3)	25.580(2)	16.482(2)	14.0317(3)
α (deg)	90	90	90	80.422(10)	90
β (deg)	90	90	90	73.741(10)	100.846(10)
γ (deg)	90	90	90	87.582(10)	90
<i>V</i> (Å ³)	7383	7338	5779.4	2096.6	4463.8
<i>Z</i>	8	8	8	1	2
ρ_{calcd} (g cm ⁻³)	1.449	1.618	1.386	1.790	1.749
μ (mm ⁻¹)	0.74	4.06	0.956	4.09	3.85
<i>T</i> (°C)	-100	-100	25	-100	-110
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
<i>R_w</i> (<i>F</i> ² , all reflns) ^a	0.066	0.059	0.1731	0.084	0.057
<i>R</i> (<i>F</i> > 4 σ (<i>F</i>)) ^a	0.031	0.031	0.0515	0.034	0.032
<i>S</i> ^a	1.07	0.79	0.97	1.00	1.03

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

including clusters,^{10,13,25–27} are known. In a few 1,1-ethylenedithiolato “MFe” or “M₂Fe” complexes of the type $\{[M(\text{Ph}_3)_2]_n \{S_2C=CCHC(O)R\}\}$ [*M* = Pd, Pt; *n* = 1, *R* = $\{(\eta^5\text{-C}_5\text{H}_4)_2\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}$; *n* = 2, *R* = $\{(\eta^5\text{-C}_5\text{H}_4)_2\text{Fe}\}$]²⁸—obtained from ferrocenyl-substituted 3-hydroxydithioacrylic acid—the Fe atom forms part of the R group. The only heterometallic complexes in which 1,1-ethylenedithiolato ligands are assumed to bridge two different metal centers are a few of general formula $M[\text{Ag}_2(\text{S}_2\text{C}=\text{C}(\text{CN})\text{CO}_2\text{Et})_2]$ (*M* = Co, Ni, Cu, Cd, Hg, Pd).²⁹ Their proposed nature is based on a variety of techniques, but unfortunately, none of them has been structurally characterized. We report here the syntheses and structural characterization of heterodinuclear (PdAg, PtAg) and -tetranuclear (Pd₂Ag₂, Pt₂Ag₂) 1,1-ethylenedithiolato derivatives. Complexes with the ligand 2,2-diacetyl-1,1-ethylenedithiolato are extremely scarce. Apart from some complexes of Tl(I), Au(I), and Au(III) recently reported by us,³⁰ only a few with Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) have been reported, but their nature was only established by elemental analysis.³¹ We report here 2,2-diacetyl-1,1-ethylenedithiolato complexes of palladium and platinum.

Experimental Section

Infrared spectra were recorded in the range 4000–200 cm⁻¹ on a Perkin-Elmer 16F PC FT-IR spectrophotometer using Nujol mulls between polyethylene sheets. We give only the values of $\nu(\text{C}=\text{O})$ or $\nu(\text{C}=\text{C})$ stretching modes. 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 ¹³C NMR spectra were measured in CDCl₃ or d⁶-dmso (**2a**, **2b**) on a Varian Unity 300 spectrometer. Chemical shifts are given in ppm and referenced to TMS (¹H and ¹³C) or to H₃PO₄ (³¹P).

X-ray Structure Determinations of 3a, 3b, 5b·Me₂CO, 5b·2Et₂O, and 4a. Numerical data are presented in Table 1. Crystals were mounted on glass fibers (**4a** with glue) and transferred to the cold gas stream of the diffractometer. Data were recorded with Mo K α radiation ($\lambda = 0.710 73$ Å) in ω -scan mode. Structures of **3a**, **3b**, **5b·Me₂CO** and **5b·2Et₂O** were solved by direct methods and refined anisotropically on *F*² [program SHELXL-97 (**4a** SHELXL-93), G. M. Sheldrick, University of Göttingen, Germany]. Hydrogen atoms were included using a riding model or with rigid methyl groups. A special feature of refinement is that in **5b·Me₂CO** the acetone is disordered over two positions.

[PtCl₂(cod)] (cod = 1,5-cyclooctadiene),³² [AuCl(tht)] (tht = tetrahydrothiophene),³³ [Tl₂{S₂C=C{C(O)Me}₂}],³⁰ and CuCl³⁴ were prepared as previously reported. PPh₃, NiCl₂·6H₂O (Fluka), AgClO₄ (Aldrich), CdCl₂, and HgCl₂ (Probus) were obtained from commercial sources and used without further purification.

[Pt{ η^2 -S₂C=C{C(O)Me}₂}(cod)] (**1**). Solid [PtCl₂(cod)] (cod = 1,5-cyclooctadiene, 114.7 mg, 0.31 mmol) was added to a suspension of [Tl₂{ η^2 -S₂C=C{C(O)Me}₂}] (180.7 mg, 0.31 mmol) in acetone (20 mL). A white precipitate in a yellow solution readily formed, and the suspension was stirred for 30 min. The solvent was removed under vacuum, the residue extracted with dichloromethane, and the extract filtered through Celite. The solution was concentrated (3 mL) and diethyl ether (40 mL) added to precipitate **1** as a yellow solid, which was filtered and suction-dried. Yield: 129.5 mg, 87%. Anal. Calcd for C₁₄H₁₈O₂PtS₂: C, 35.22; H, 3.80; S, 13.43. Found: C, 35.16; H, 3.71; S, 13.30. Mp: 191 °C (dec). Λ_M (Ω^{-1} cm² mol⁻¹): 2. IR (cm⁻¹): 1674 s, 1615 s, 1509 s, 1499 s, 1489 s. ¹H NMR: δ 2.26–2.36 (m, 10 H, Me + cod), 2.62 (m, 4 H, cod), 5.29 (s with Pt satellites, 4 H, cod), ²*J*_{PH} = 57.9 Hz). ¹³C{¹H} NMR: δ 30.71 (CH₂, cod), 31.90 (Me), 100.84 (s with Pt satellites, CH, cod), *J*_{CPt} = 75.4 Hz), 136.89 (C=CS₂), 175.20 (C=CS₂), 196.95 (CO).

[M{ η^2 -S₂C=C{C(O)Me}₂}(bpy)]·*n*H₂O [*M* = Pd, *n* = 1 (**2a**); M = Pt, *n* = 0 (**2b**)]. Solid [MCl₂(bpy)] (bpy = 2,2'-bipyridine, 214 mg, 0.64 mmol for **2a**; 114.3 mg, 0.27 mmol for **2b**) was added to a

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suspension containing an equimolar amount of $[\text{Ti}_2\{\eta^2\text{-S}_2\text{C}=\text{C}\{\text{C}(\text{O})\text{Me}\}_2\}]$ in chloroform (40 mL). The mixture was refluxed for 6 (**2a**) or 6.5 (**2b**) h and filtered. The brown residue was extracted with chloroform (**2a**, 3×40 mL) or dichloromethane (**2b**, 4×40 mL), and the combined extracts were filtered through Celite and added to the initial filtrate. The solution was concentrated (5 mL) and diethyl ether (40 mL) added to precipitate a cream (**2a**) or orange (**2b**) solid that was filtered, washed with diethyl ether (2×5 mL), and suction-dried.

2a. Yield: 198 mg, 69%. Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2\text{PdS}_2$: C, 42.25; H, 3.55; N, 6.16; S, 14.10. Found: C, 42.78; H, 3.00; N, 6.26; S, 14.35. Mp: 97 °C (dec). IR (cm^{-1}): 1636 m, 1596 s, br. ^1H NMR: δ 2.28 (s, 6 H, Me), 3.32 (s, H_2O), 7.76 (t, 2 H, bpy), 8.30–8.35 (m, 4 H, bpy), 8.66 (d, 2 H, bpy). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 30.89 (Me), 123.81, 127.74 (bpy), 139.74 ($\text{C}=\text{CS}_2$), 140.61, 148.66, 154.28 (bpy), 190.10 ($\text{C}=\text{CS}_2$), 197.15 (CO).

2b. Yield: 91 mg, 64%. Anal. Calcd for $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_2\text{PtS}_2$: C, 36.57; H, 2.69; N, 5.33; S, 12.20. Found: C, 36.03; H, 2.41; N, 5.36; S, 12.30. Mp: 280 °C (dec). IR (cm^{-1}): 1680 m, 1614 s, br. ^1H NMR: δ 2.29 (s, 6 H, Me), 7.76 (t, 2 H, bpy), 8.41 (t, 2 H, bpy), 8.53 (d, 2 H, bpy), 8.68 (d, 2 H, bpy).

$[\text{M}\{\eta^2\text{-S}_2\text{C}=\text{C}\{\text{C}(\text{O})\text{Me}\}_2\}(\text{PPh}_3)_2]$ [**M** = Pd (**3a**), Pt (**3b**)]. To a suspension of $[\text{Ti}_2\{\eta^2\text{-S}_2\text{C}=\text{C}\{\text{C}(\text{O})\text{Me}\}_2\}]$ (256.5 mg, 0.44 mmol for **3a**; 239.0 mg, 0.41 mmol for **3b**) in dichloromethane (40 mL) were added an equimolar amount of $[\text{MCl}_2(\text{NCPH}_2)]$ and 2 equiv of PPh_3 . After 10 min (**3a**) or 24 h (**3b**) of stirring, the suspension was filtered through Celite, the solution concentrated (3 mL) under vacuum, and diethyl ether (40 mL) added to precipitate **3a** and **3b** as yellow solids that were filtered, washed with diethyl ether (2×5 mL), and suction dried.

3a. Yield: 312 mg, 88%. Anal. Calcd for $\text{C}_{42}\text{H}_{36}\text{O}_2\text{P}_2\text{PdS}_2$: C, 62.65; H, 4.51; S, 7.96. Found: C, 62.90; H, 4.52; S, 7.59. Mp: 91 °C (dec). IR (cm^{-1}): 1658 s, 1630 s, 1091 s. ^1H NMR: δ 2.25 (s, 6 H, Me), 7.18–7.38 (m, 30 H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 31.69 (Me), 128.33 (m, *o*-C, PPh_3), 129.05 (m, *ipso*-C, PPh_3), 130.72 (m, *p*-C, PPh_3), 134.33 (m, *m*-C, PPh_3), 137.00 ($\text{C}=\text{CS}_2$), 187.04 ($\text{C}=\text{CS}_2$), 198.03 (CO). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 29.71 (s). Crystals of **3a** were grown from dichloromethane/diethyl ether.

3b. Yield: 315 mg, 86%. Anal. Calcd for $\text{C}_{42}\text{H}_{36}\text{O}_2\text{P}_2\text{PtS}_2$: C, 56.43; H, 4.06; S, 7.17. Found: C, 56.06; H, 4.07; S, 7.30. Mp: 133 °C (dec). IR (cm^{-1}): 1659 s, 1636 s, 1092 m, 571 s, 537 s, 505 s, 455 s. ^1H NMR: δ 2.24 (s, 6 H, Me), 7.18–7.44 (m, 30 H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 32.07 (Me), 128.14 (m, *o*-C, PPh_3), 129.11 (m, *ipso*-C), 130.87 (m, *p*-C, PPh_3), 134.47 (m, *m*-C, PPh_3), 138.20 ($\text{C}=\text{CS}_2$), 183.00 ($\text{C}=\text{CS}_2$), 197.67 (CO). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 19.15 (s with Pt satellites, $J_{\text{PPT}} = 3041$ Hz). Single crystals of **3b** were grown from acetone/diethyl ether.

$\text{Q}_2[\text{M}\{\eta^2\text{-S}_2\text{C}=\text{C}\{\text{C}(\text{O})\text{Me}\}_2\}_2]$ [**M** = Pd, **Q** = NMe_4 (**4a**), $\text{Ph}_3\text{P}=\text{N}=\text{PPh}_3$ (PPN) (**4a'**); **M** = Pt, **Q** = NMe_4 (**4b**)]. To a suspension of $[\text{Ti}_2\{\eta^2\text{-S}_2\text{C}=\text{C}\{\text{C}(\text{O})\text{Me}\}_2\}]$ (658.8 mg, 1.13 mmol for **4a**; 697.8 mg, 1.20 mmol for **4a'**; 618 mg, 1.06 mmol for **4b**) in acetone (50 mL) were added an equimolar amount of the corresponding MCl_2 and 2 equiv of Me_4NCl (**4a**, **4b**) or PPNCl (**4a'**), and the mixture was refluxed for 8 h. The solvent was removed under vacuum, and the residue was extracted with dichloromethane (4×25 mL). The extracts were filtered through Celite, the solution concentrated (3 mL), and diethyl ether (40 mL) added to precipitate orange (**4a**, **4a'**) or brown-orange solids (**4b**) that were filtered and dried under a N_2 atmosphere.

4a. Yield: 236 mg, 70%. Anal. Calcd for $\text{C}_{20}\text{H}_{36}\text{N}_2\text{O}_4\text{PdS}_4$: C, 39.83; H, 6.02; N, 4.64; S, 21.26. Found: C, 38.83; H, 5.18; N, 5.01; S, 19.96. Mp: 227 °C (dec). Λ_{M} ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$): 164. IR (cm^{-1}): 1678 s, 1567 m, 946 s. ^1H NMR: δ 2.22 (s, 12 H, Me), 3.48 (s, 24 H, NMe_4). Crystals of **4a** were grown from acetone/diethyl ether.

4a'. Yield: 850 mg, 92%. Anal. Calcd for $\text{C}_{64}\text{H}_{72}\text{N}_2\text{O}_4\text{PdS}_4$: C, 65.87; H, 4.74; N, 1.83; S, 8.36. Found: C, 62.08; H, 4.95; N, 1.70; S, 6.82. Mp: 208 °C (dec). Λ_{M} ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$): 158. IR (cm^{-1}): 1681 s, 1562 m, 1298 s, br. ^1H NMR: δ 2.33 (s, 12 H, Me), 7.43–7.70 (m, 60 H, PPN).

4b. Yield: 339 mg, 92%. Anal. Calcd for $\text{C}_{20}\text{H}_{36}\text{N}_2\text{O}_4\text{PtS}_4$: C, 34.72; H, 5.24; N, 4.05; S, 18.53. Found: C, 37.12; H, 4.89; N, 4.13; S, 15.91. Mp: 207 °C (dec). Λ_{M} ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$): 161. IR (cm^{-1}): 1672 s, 1562 m, 945 s. ^1H NMR: δ 2.20 (s, 12 H, Me), 3.50 (s, 24 H, NMe_4).

$[\{\text{ML}_2\}_2\text{Ag}_2\{\mu^2\eta^2\text{-}(\text{S,S}')\text{-}\{\text{S}_2\text{C}=\text{C}\{\text{C}(\text{O})\text{Me}\}_2\}_2\}](\text{ClO}_4)_2$ [**L** = PPh_3 , **M** = Pd (**5a**), Pt (**5b**), **L}_2 = \text{cod}, **M** = Pt (**5b'**)]. To a solution of $[\text{M}\{\eta^2\text{-S}_2\text{C}=\text{C}\{\text{C}(\text{O})\text{Me}\}_2\}_2\text{L}_2]$ [**M** = Pd, **3a** (154.3 mg, 0.19 mmol); **M** = Pt, **3b** (101.8 mg, 0.11 mmol), or **1** (170.2 mg, 0.36 mmol)] in acetone (20 mL) an equimolar amount of AgClO_4 was added. The resulting yellow solution was stirred for 1 (**5a**, **5b'**) or 3 h (**5b**) in the dark and filtered through Celite. The filtrate was concentrated (3 mL), and diethyl ether (35 mL) was added to precipitate an off-white solid, which was filtered, washed with diethyl ether (5 mL), and suction-dried.**

5a. Yield: 167 mg, 87%. Anal. Calcd for $\text{C}_{84}\text{H}_{72}\text{Ag}_2\text{Cl}_2\text{O}_{12}\text{P}_4\text{Pd}_2\text{S}_4$: C, 49.82; H, 3.58; S, 6.33. Found: C, 49.62; H, 3.55; S, 6.69. Mp: 71 °C (dec). Λ_{M} ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$): 313. IR (cm^{-1}): 1667 s, 1091 s, 622 s, 514 s. ^1H NMR: δ 2.13 (s, 12 H, Me), 7.07–7.47 (m, 60 H, PPh_3). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 26.0 (s).

5b. Yield: 102 mg, 84%. Anal. Calcd for $\text{C}_{84}\text{H}_{72}\text{Ag}_2\text{Cl}_2\text{O}_{12}\text{P}_4\text{Pt}_2\text{S}_4$: C, 45.81; H, 3.29; S, 5.82. Found: C, 45.34; H, 3.45; S, 5.45. Mp: 85 °C (dec). Λ_{M} ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$): 345. IR (cm^{-1}): 1686 s, 1667 s, 1521 m, 1090 s, 622 s, 568 s, 536 s, 518 s, 507 s, 491 s. ^1H NMR: δ 2.04 (s, 12 H, Me), 7.16–7.34 (m, 60 H, PPh_3). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 18.78 (s with Pt satellites, $J_{\text{PPT}} = 3068$ Hz). In various attempts to crystallize complexes resulting from the reactions of **5b** with $[\text{Ag}(\text{PPh}_3)(\text{ClO}_4)]$, 1:1 and 1:2, crystals of **5b**· Me_2CO (triclinic) and **5b**· $2\text{Et}_2\text{O}$ (monoclinic), respectively, were obtained; both modifications were studied crystallographically.

5b'. Yield: 226 mg, 92%. Anal. Calcd for $\text{C}_{28}\text{H}_{36}\text{Ag}_2\text{Cl}_2\text{O}_{12}\text{Pt}_2\text{S}_4$: C, 24.55; H, 2.67; S, 9.36. Found: C, 24.88; H, 2.50; S, 9.23. Mp: 173 °C (dec). Λ_{M} ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$): 298. IR (cm^{-1}): 1668 s, 1615 s, 1075 s, 620 s. ^1H NMR: δ 2.22–2.33 [m, 28 H, Me + CH_2 (cod)], 5.28 (s, br, with Pt satellites, 8 H, CH (cod), $J_{\text{HPt}} = 55$ Hz).

$[\{\text{M}(\text{PPh}_3)_2\}\{\text{Ag}(\text{PPh}_3)_2\}\{\mu^2\eta^2\text{-}(\text{S,S}')\text{-}\{\text{S}_2\text{C}=\text{C}\{\text{C}(\text{O})\text{Me}\}_2\}_2\}]\text{-ClO}_4$ [**M** = Pd (**6a**), Pt (**6b**)]. To a solution of the complex $[\text{M}\{\eta^2\text{-S}_2\text{C}=\text{C}\{\text{C}(\text{O})\text{Me}\}_2\}(\text{PPh}_3)_2]$ (**3a**, 157.2 mg, 0.20 mmol; **3b**, 82.1 mg, 0.09 mmol) in acetone (40 mL) were added an equimolar amount of AgClO_4 and 2 equiv of PPh_3 . The resulting solution was stirred in the dark for 2 (**6a**) or 4 h (**6b**). It was then concentrated (3 mL), and diethyl ether (40 mL) was added to precipitate a pale-yellow solid that was filtered, washed with diethyl ether (5 mL), and suction-dried.

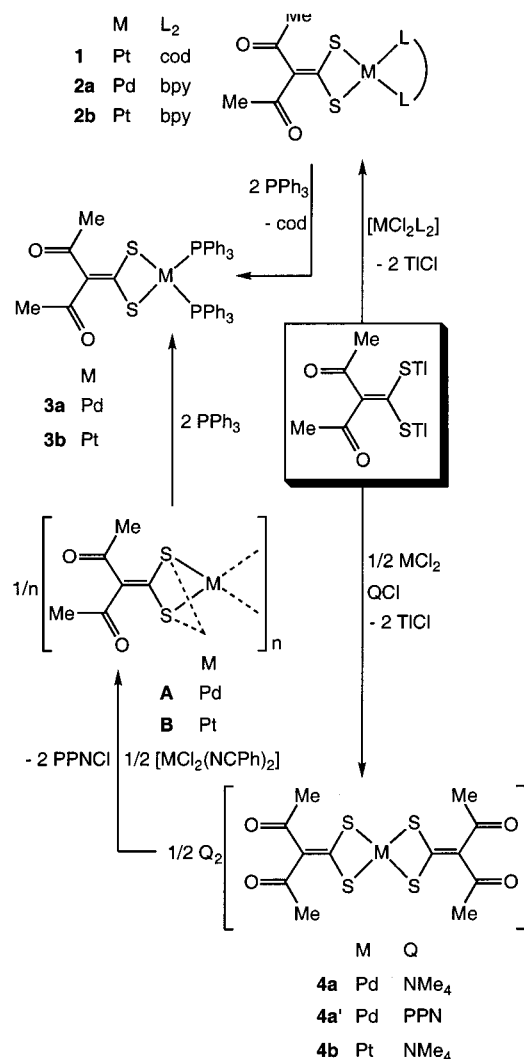
6a. Yield: 230 mg, 75%. Anal. Calcd for $\text{C}_{78}\text{H}_{66}\text{AgClO}_6\text{P}_4\text{PdS}_2$: C, 60.95; H, 4.33; S, 4.17. Found: C, 60.80; H, 4.51; S, 3.92. Mp: 135 °C (dec). Λ_{M} ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$): 116. IR (cm^{-1}): 1680 s, 1658 m, 1089 s, 621 s, 512 s. ^1H NMR: δ 1.92 (s, 6 H, Me), 7.15–7.64 (m, 60 H, PPh_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (20 °C): δ 5–13 (v br, AgPPh_3), 30.37 (s, PdPPh_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (−60 °C): δ 8.52 [dd, $J(^{31}\text{P}^{109}\text{Ag}) = 470$ Hz, $J(^{31}\text{P}^{107}\text{Ag}) = 409$ Hz], 25–36 (br).

6b. Yield: 138 mg, 92%. Anal. Calcd for $\text{C}_{78}\text{H}_{66}\text{AgClO}_6\text{P}_4\text{PtS}_2$: C, 57.62; H, 4.09; S, 3.94. Found: C, 57.59; H, 4.15; S, 4.07. Mp: 146 °C (dec). Λ_{M} ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$): 146. IR (cm^{-1}): 1680 s, 1608 vs, 1091 s, 620 s, 518 s. ^1H NMR: δ 1.92 (s, 6 H, Me), 7.13–7.43 (m, 60 H, PPh_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (20 °C): δ 6–13 (v br), 18.15 [s with ^{195}Pt satellites, $J(^{31}\text{P}^{195}\text{Pt}) = 3093$ Hz]. $^{31}\text{P}\{^1\text{H}\}$ NMR (−60 °C): δ 8.52 [dd, $J(^{31}\text{P}^{109}\text{Ag}) = 472$ Hz, $J(^{31}\text{P}^{107}\text{Ag}) = 410$ Hz], 18.20 (br).

Results and Discussion

Synthesis. Complexes $[\text{M}\{\eta^2\text{-S}_2\text{C}=\text{C}\{\text{C}(\text{O})\text{Me}\}_2\}_2\text{L}_2]$ [**M** = Pt, **L}_2 = 1,5\text{-cyclooctadiene} (cod) (**1**); **L}_2 = \text{bpy}, **M** = Pd (**2a**), Pt (**2b**), **L} = \text{PPh}_3, **M** = Pd (**3a**), Pt (**3b**)] were obtained along with TiCl_4 by reacting equimolar amounts of $[\text{Ti}_2\{\text{S}_2\text{C}=\text{C}\{\text{C}(\text{O})\text{Me}\}_2\}_2]$ ³⁰ and the corresponding $[\text{MCl}_2\text{L}_2]$ complexes in acetone (**1**) or chloroform (**2**) or dichloromethane (**3**) (see Scheme 1). Replacement of the labile cod ligand in **1** with 2 equiv of PPh_3 also leads to complex **3b**, but both **3a** and **3b** were best obtained through a third method: by reacting the thallium derivative with the corresponding $[\text{MCl}_2(\text{NCPH}_2)]$ complex and PPh_3 in a 1:1:2 molar ratio. The reaction in dichloromethane between equimolar amounts of $[\text{Ti}_2\{\text{S}_2\text{C}=\text{C}\{\text{C}(\text{O})\text{Me}\}_2\}]$ and $[\text{MCl}_2(\text{NCPH}_2)]$ (**M** = Pd, Pt) produced a brownish suspension from which, after extraction with CH_2Cl_2 and filtration of the insoluble TiCl_4 , a brown (Pd) or an orange******

Scheme 1

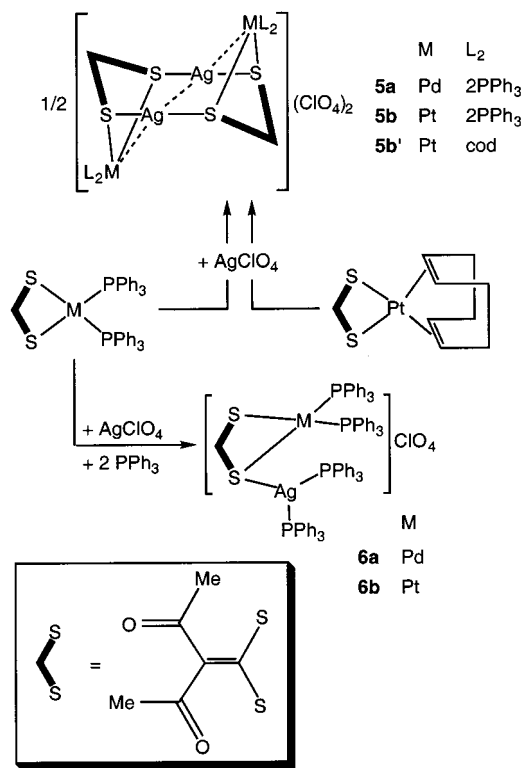


(Pt) solid was precipitated by the addition of diethyl ether. We assume these to be oligomeric species (**A** and **B** in Scheme 1) of stoichiometry $M\{S_2C=C\{C(O)Me\}_2\}$ based on their reactions with 2 equiv of PPh_3 to give complexes **3a** and **3b**. We have not been able to obtain good elemental analyses of these species even after many recrystallizations (Anal. Calcd for $C_{12}H_{12}O_4Pd_2S_4$: C, 25.68; H, 2.16; S, 22.85. Found: C, 24.26; H, 2.02; S, 22.01. Anal. Calcd for $C_{12}H_{12}O_4Pt_2S_4$: C, 19.50; H, 1.64; S, 17.36. Found: C, 19.02; H, 1.60; S, 14.51). Because the 1H NMR of spectra of **A** and **B** show many singlets in the 2.3–2.7 ppm region, suggesting mixtures of oligomers, we do not know if the wrong analysis results are due to combustion problems or to the presence of some impurities. Resonances due to the PhCN ligand are absent in these spectra. However, from a synthetic point of view, these oligomeric species behave as pure compounds because the yields of those reactions are comparable to those obtained with other methods.

The reaction of $[Ti_2\{S_2C=C\{C(O)Me\}_2\}]$ with $[MCl_2(cod)]$ ($M = Pd, Pt$) reveals the greater lability of the cod ligand in the palladium complex. In fact, whereas the reaction with the platinum complex produces only substitution of the chloro ligands to give **1**, in the case of palladium the diolefin is also displaced, yielding complex **A**. The same result is obtained when starting from $[PdCl_2(norbornadiene)]$.

The reaction in acetone of MCl_2 ($M = Pd, Pt$), $[Ti_2\{S_2C=C\{C(O)Me\}_2\}]$, and QCl ($Q = NMe_4, PPN$) in a 1:2:2 molar

Scheme 2



ratio produces $TiCl$ together with the anionic complexes $Q_2-[M\{\eta^2-S_2C=C\{C(O)Me\}_2\}_2]$ [$M = Pd, Q = NMe_4$ (**4a**), $Ph_3P=N=PPh_3$ (PPN) (**4a'**), $M = Pt, Q = NMe_4$ (**4b**)], which can be isolated in good yield. Although their NMR spectra prove the purity of all the three compounds and the crystal structure of **4a** confirms the proposed structure, the elemental analysis results found for carbon and sulfur of samples obtained after many recrystallizations differ from the calculated values (see Experimental Section), which could be due to combustion problems. We have shown that **4a'** reacts with $[PdCl_2(NCPh)_2]$ and PPh_3 (1:1:2) to give **3a** (80% yield) and $PPNCl$ and also that **A** is an intermediate species in this reaction (See Scheme 1). This proves that the sulfur atoms of the 1,1-ethylenedithiolato ligand coordinated to Pd in **4a'** retain enough coordinating ability to replace not only the labile PhCN ligands in $[PdCl_2(NCPh)_2]$ but also the chloro ligands.

Similarly, complexes **1**, **3a**, and **3b** can act as ligands toward other metal centers. Thus, from their reactions with $AgClO_4$ (1:1 in acetone), very high yields are obtained of the tetranuclear complexes $[\{ML_2\}_2Ag_2\{\mu^2, \eta^2-(S, S')-\{S_2C=C\{C(O)Me\}_2\}_2\}](ClO_4)_2$ [$L = PPh_3, M = Pd$ (**5a**), Pt (**5b**), $L_2 = cod, M = Pt$ (**5b'**)] (see Scheme 2). Similarly, when **3a** and **3b** were reacted with $AgClO_4$ in the presence of PPh_3 (1:1:2), the dinuclear complexes $[\{M(PPh_3)_2\}\{Ag(PPh_3)_2\}\{\mu^2, \eta^2-(S, S')-\{S_2C=C\{C(O)Me\}_2\}_2\}]ClO_4$ [$M = Pd$ (**6a**), Pt (**6b**)] result (see Scheme 2) likely because the coordination of silver to two PPh_3 ligands avoids the dimerization process that leads to **5** in the absence of PPh_3 .

Crystal Structures of Complexes. The crystal structures of complexes **3a** (Figure 1), **3b** (Figure 2), **4a** (Figure 3), **5b**·Me₂CO (Figure 4), and **5b**·2Et₂O (Figure 4) have been determined (see Tables 2–5). Complexes **3a** and **3b** are isostructural; both show two phosphine ligands and the two sulfur atoms of a *Z,E*-2,2-diacetyl-1,1-ethylenedithiolato ligand coordinated to palladium (**3a**) or platinum (**3b**), which are in slightly distorted square planar environments [S(1), S(2), M, P(1), P(2) mean

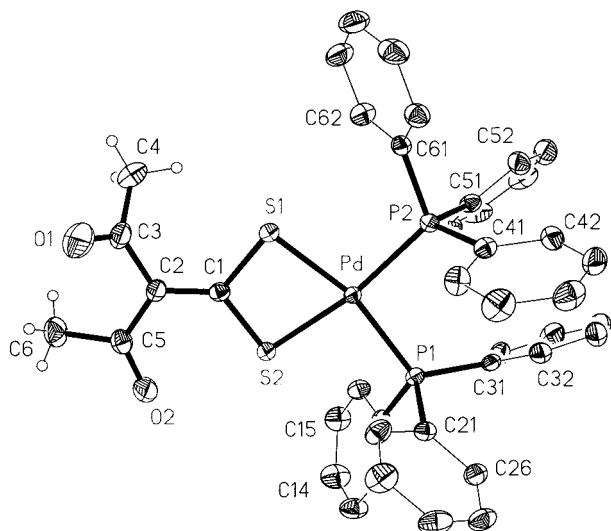


Figure 1. Structure of complex **3a** in the crystal. Ellipsoids represent 50% probability levels. Phenyl H atoms omitted for clarity.

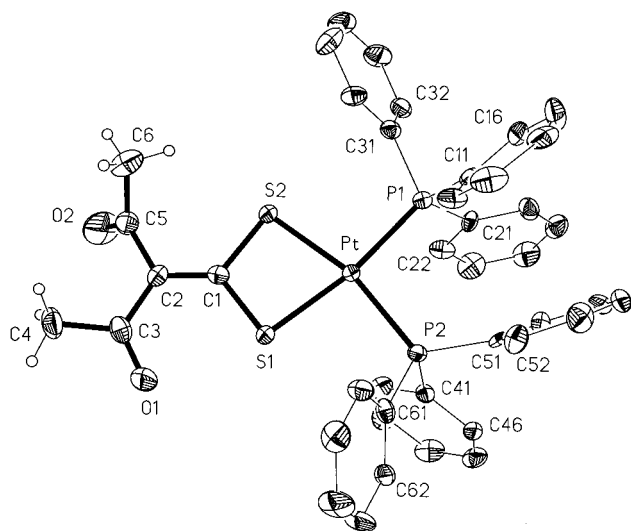


Figure 2. Structure of complex **3b** in the crystal. Ellipsoids represent 50% probability levels. Phenyl H atoms are omitted for clarity.

deviation: 0.07 (**3a**), 0.06 (**3b**) Å]. The $C_2C=CS_2$ skeleton of the sulfur donor ligand is also planar [mean deviation: 0.01 (**3a**), 0.02 (**3b**) Å] with both acetyl groups rotated out of the plane, one of them considerably [interplanar angle: 58° (**3a**), 59° (**3b**)], the other one only slightly [torsion angle: 12° (**3a**), 13° (**3b**)]. The S_2MP_2 and $C_2C=CS_2$ planes subtend an angle of only 4.8° (**3a**) or 4.7° (**3b**). Both complexes display narrow $S(1)MS(2)$ [74.595(18) (**3a**), 74.46(5) (**3b**) Å] and $S(1)C(1)S(2)$ [107.19(11)° (**3a**), 105.9(3)° (**3b**)] angles associated with the small chelate bite. The Pd–P bond distances in **3a** [2.3282(5), 2.3306(5) Å] are significantly longer than the Pt–P distances in **3b** [2.2909(14), 2.2920(16) Å], despite the marginally smaller covalent radius of palladium compared to that of platinum. This difference is reflected in the ^{31}P NMR spectra of these complexes (see below). A search of the Cambridge Structural Database reveals longer Pd–P with respect to Pt–P bond distances to be a common feature in pairs of complexes cis -[MP_2L_2] (P = any phosphorus donor ligand, L = Cl^{35–42} or

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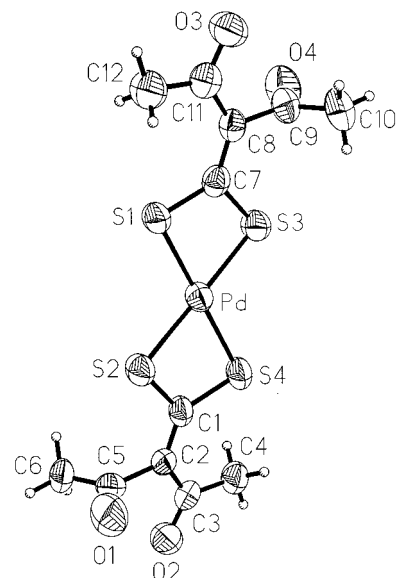


Figure 3. Structure of the anion of complex **4a** in the crystal. Ellipsoids represent 50% probability levels.

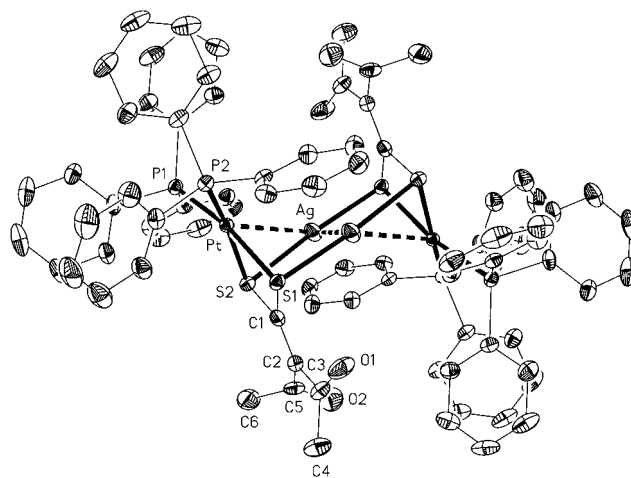


Figure 4. Structure of the cation of complex **5b**·2Et₂O in the crystal. Ellipsoids represent 50% probability levels. Solvent and H atoms are omitted for clarity.

any sulfur donor ligand^{43–46}) that differ only in the metal (M = Pd, Pt).

The bond distances and angles in **3b** are similar to those found in [Pt{ η^2 -S₂C=CH{C(O)Ph}(PPh₃)₂]²⁰ but compared to [Pt{ η^2 -S₂C=C(CN)CO₂Et}(cod)],⁷ **3b** displays longer Pt–S bond distances [2.3363(15), 2.3326(15) vs 2.299(2), 2.298(2) Å], in agreement with the greater trans influence of phosphine compared with olefin ligands⁴⁷ and a shorter C=C bond distance

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Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex **3a**

Pd–P(1)	2.3306(5)	O(1)–C(3)	1.210(3)
Pd–P(2)	2.3282(5)	O(2)–C(5)	1.223(3)
Pd–S(2)	2.3286(5)	C(1)–C(2)	1.374(3)
Pd–S(1)	2.3294(5)	C(2)–C(3)	1.495(3)
S(1)–C(1)	1.761(2)	C(2)–C(5)	1.472(3)
S(2)–C(1)	1.746(2)		
P(1)–Pd–P(2)	98.792(18)	C(3)–C(2)–C(5)	118.05(19)
P(1)–PdS(2)	91.170(18)	O(1)–C(3)–C(2)	120.0(2)
P(2)–Pd–S(1)	95.623(18)	O(1)–C(3)–C(4)	120.4(2)
S(2)–PdS(1)	74.595(18)	C(2)–C(3)–C(4)	119.5(2)
C(2)–C(1)–S(1)	126.01(16)	O(2)–C(5)–C(2)	122.3(2)
C(2)–C(1)–S(2)	126.79(16)	O(2)–C(5)–C(6)	119.2(2)
S(1)–C(1)–S(2)	107.19(11)	C(2)–C(5)–C(6)	118.4(2)
C(1)–C(2)–C(3)	120.7(2)		
C(1)–C(2)–C(5)	121.26(19)		

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

Pt–P(1)	2.2909(14)	O(1)–C(3)	1.223(7)
Pt–P(2)	2.2920(16)	O(2)–C(5)	1.213(7)
Pt–S(2)	2.3326(15)	C(1)–C(2)	1.349(7)
Pt–S(1)	2.3363(15)	C(2)–C(3)	1.467(8)
S(1)–C(1)	1.757(6)	C(2)–C(5)	1.491(8)
S(2)–C(1)	1.783(6)		
P(1)–Pt–P(2)	98.33(6)	C(3)–C(2)–C(5)	118.2(6)
P(1)–Pt–S(2)	95.97(6)	O(1)–C(3)–C(2)	122.0(6)
P(2)–Pt–S(1)	91.36(5)	O(1)–C(3)–C(4)	120.3(6)
S(2)–Pt–S(1)	74.46(5)	C(2)–C(3)–C(4)	117.7(6)
C(2)–C(1)–S(1)	127.5(5)	O(2)–C(5)–C(2)	119.9(6)
C(2)–C(1)–S(2)	126.6(5)	O(2)–C(5)–C(6)	119.6(6)
S(1)–C(1)–S(2)	105.9(3)	C(2)–C(5)–C(6)	120.4(6)
C(1)–C(2)–C(3)	121.0(6)		
C(1)–C(2)–C(5)	120.7(6)		

Table 4. Selected Bond Distances (Å) and Angles (deg) for Complex **4a**

Pd–S(1)	2.315(2)	C(7)–C(8)	1.378(9)
Pd–S(2)	2.312(2)	C(2)–C(3)	1.427(10)
Pd–S(3)	2.323(2)	C(2)–C(5)	1.510(10)
Pd–S(4)	2.321(2)	C(8)–C(9)	1.522(9)
S(1)–C(7)	1.736(7)	C(8)–C(11)	1.429(10)
S(3)–C(7)	1.741(7)	O(1)–C(5)	1.215(9)
S(2)–C(1)	1.745(7)	O(2)–C(3)	1.230(8)
S(4)–C(1)	1.738(7)	O(3)–C(11)	1.256(9)
C(1)–C(2)	1.382(9)	O(4)–C(9)	1.204(8)
S(1)–Pd–S(2)	104.67(7)	C(7)–C(8)–C(9)	117.4(7)
S(3)–Pd–S(4)	105.81(7)	C(11)–C(8)–C(9)	113.8(6)
S(1)–Pd–S(3)	74.69(6)	O(1)–C(5)–C(6)	122.0(8)
S(2)–Pd–S(4)	74.84(6)	O(1)–C(5)–C(2)	120.5(8)
C(2)–C(1)–S(2)	122.3(6)	C(6)–C(5)–C(2)	117.5(7)
S(4)–C(1)–S(2)	107.8(4)	O(2)–C(3)–C(2)	118.7(7)
S(4)–C(1)–S(3)	107.8(4)	O(2)–C(3)–C(4)	119.2(8)
C(8)–C(7)–S(1)	129.9(6)	C(2)–C(3)–C(4)	122.1(8)
C(8)–C(7)–S(3)	122.0(6)	O(4)–C(9)–C(10)	122.1(7)
S(1)–C(7)–S(3)	108.0(4)	O(4)–C(9)–C(8)	120.9(7)
C(1)–C(2)–C(3)	129.9(8)	C(10)–C(9)–C(8)	116.9(7)
C(1)–C(2)–C(5)	117.0(7)	O(3)–C(11)–C(8)	118.4(7)
C(3)–C(2)–C(5)	113.1(6)	O(3)–C(11)–C(12)	118.1(7)
C(7)–C(8)–C(11)	128.8(7)	C(8)–C(11)–C(12)	123.5(7)

[1.349(7) vs 1.381(1) Å], suggesting stronger delocalization over the π -electron system of the $S_2C=C(CN)CO_2Et$ ligand.

The crystal structure of **4a** shows NMe_4 cations (disordered) and $[Pd\{\eta^2-S_2C=C\{C(O)Me\}_2\}_2]^{2-}$ anions in which two *E,E*-2,2-diacetyl-1,1-ethylenedithiolato ligands coordinate the palladium atom in a distorted square planar environment [S(1), S(2), Pd, S(3), S(4) mean deviation: 0.002 Å] with narrow SPDS

Table 5. Selected Bond Distances (Å) and Angles (deg) for Complex **5b**

	5b ·2Et ₂ O, monoclinic	5b ·Me ₂ CO, triclinic
Pt–P(2)	2.2912(10)	2.2989(9)
Pt–P(1)	2.2999(11)	2.3065(8)
Pt–S(2)	2.3625(10)	2.3588(8)
Pt–S(1)	2.3700(10)	2.3589(8)
Pt–Ag	3.1204(5)	3.2387(3)
Ag–S(1)#1	2.4265(11)	2.4116(9)
Ag–S(2)	2.4591(11)	2.4337(9)
Ag–Ag#1	3.1363(8)	3.0588(6)
S(1)–C(1)	1.791(4)	1.782(4)
S(2)–C(1)	1.785(4)	1.787(3)
O(1)–C(3)	1.214(6)	1.211(5)
O(2)–C(5)	1.232(6)	1.222(4)
C(1)–C(2)	1.348(5)	1.355(4)
C(2)–C(5)	1.499(6)	1.510(5)
C(2)–C(3)	1.514(6)	1.499(5)
P(1)–Pt–Ag	97.51(3)	94.87(2)
P(1)–Pt–S(2)	88.79(4)	93.81(3)
P(2)–Pt–Ag	121.72(3)	139.17(2)
P(2)–Pt–P(1)	100.92(4)	99.79(3)
P(2)–Pt–S(1)	96.33(4)	90.30(3)
S(1)–Pt–Ag	80.70(3)	82.19(2)
S(2)–Pt–Ag	51.04(3)	48.47(2)
S(2)–Pt–S(1)	74.98(4)	74.97(3)
S(2)–Ag–Pt	48.33(2)	46.51(2)
Pt–Ag–Ag#1	71.321(15)	65.823(10)

angles [S(1)PdS(3), 74.69(6)°; S(2)PdS(4), 74.84(6)°] similar to those found in **3**. The different conformation of the ligands in **4a** with respect to the *Z,E* found in **3** affects neither their planarity [S(2)S(4)C(1)C(2)C(4)C(5) and S(1)S(3)C(7)C(8)C(9)C(11) mean deviations: 0.04 and 0.03 Å, respectively] nor the fact that in each ligand only one of the acetyl groups [C(2)C(5)O(1) and C(8)C(9)O(4)] deviates markedly from that plane (torsion angles of 6.7° and 8.1°, respectively) while the other [C(2)C(3)O(2) and C(8)C(11)O(3)] is nearly coplanar (torsion angles of 4.4° and 2.7°, respectively).

Complex **5b** has been obtained in monoclinic (**5b**·2Et₂O) and triclinic (**5b**·Me₂CO) crystal forms. Both exhibit crystallographic inversion symmetry. The complex results from the coordination to Ag(I) of both sulfur atoms of the metalloligand complex **3b**, and its crystal structures show tetranuclear Pt₂M₂ cations, perchlorate anions, and solvent molecules. Upon coordination to silver, only some of the main features of **3b** are preserved, such as the *Z,E* conformation of the 2,2-diacetyl-1,1-ethylenedithiolato ligand and the planarity of its C₂C=CS₂ skeleton [mean deviations: 0.01 (**5b**·2Et₂O), 0.02 (**5b**·Me₂CO) Å]. However, compared to that of **3b**, the structures of **5b** show some differences. Thus, in complex **5b** the platinum environment deviates significantly from planarity; mean deviation for the five atoms S(1), S(2), Pt, P(1), P(2) is 0.05 Å for the monoclinic modifications and 0.13 Å for the triclinic one. Although a smaller mean deviation is found in the monoclinic modification of **5b**, the Pt atom lies 0.13 Å out of the P₂S₂ plane (displaced toward the silver atom) and the P(1)–Pt–P(2) plane is rotated by 20° (in the triclinic form 24°) with respect to the plane of the C₂C=CS₂ skeleton of the ligand, thus avoiding steric congestion. Coordination of **3b** to silver causes significant lengthening in the Pt–S bond distances, while in general, only small variations are observed for S–C and C=C. The bond angles in the platinum moiety are similar in complexes **3b** and **5b**, which in all cases display a narrow S(1)–Pt–S(2) angle [74.46(5)–75.63(3)°] imposed by the chelating ligand. The olefinic C(1) and C(2) atoms in **5b** are in planar, distorted trigonal environments, showing narrow S(1)–C(1)–S(2) angles [105.9(3)–107.8(2)°]. The silver atoms in these complexes are

Table 6. Dimensions of Possible Intermolecular C–H···O Hydrogen Bonds^a

compound	system	H···O (Å)	C–H···O (deg)
3a	C(13)–H(13)···O(1)	2.47	148
	C(55)–H(55)···O(2)	2.48	168
3b	C(13)–H(13)···O(1)	2.51	166
	C(63)–H(63)···O(2)	2.48	150
5b ·Me ₂ CO	C(66)–H(66)···O(1)	2.55	137
	C(33)–H(33)···O(2)	2.51	130
	C(13)–H(13)···O(6)	2.49	158
5b ·2Et ₂ O	C(63)–H(63)···O(12)	2.54	120

^a The cutoff criterion is H···O < 2.6 Å. Key to atom numbering: the oxygen atoms O1 and O2 are those of the ethylenedithiolate ligand; others are perchlorate oxygens.

in distorted linear environments [S–Ag–S, 168.32(4)°, 174.10(3)°] and display short numismophilic⁴⁸ [Ag···Ag, 3.1361(8), 3.0588(6) Å] and weak Pt···Ag [3.1205(5), 3.2387(3) Å] contacts. In both structures of **5b** the coordination plane of platinum is perpendicular (within 7°) to the S₄M₂ plane.

The structures of **3a**, **3b**, and **5b** display C–H···O contacts that might reasonably be interpreted as hydrogen bonds; corresponding dimensions (excluding those involving disordered groups) are presented in Table 6.

NMR Spectra. The ¹H NMR spectra of complexes **1**–**6** show a unique resonance in the range 1.92–2.36 ppm. The equivalence of the methyl groups could be associated with an *E,E* conformation of the 1,1-ethylenedithiolato ligands in solution, as confirmed in the solid state for **4a**, or, if the ligands adopt the *E,Z* conformation (see crystal structures of **3a**, **3b**, and **5b**), with free rotation of the acetyl groups around the C–C bond in solution. This is confirmed for **1**, **2a**, and **3a**, and **3b** by their ¹³C{¹H} NMR spectra, which show unique resonances for each of the nuclei CH₃ (30.8–32.1 ppm), C=CS₂ (136.8–139.8 ppm), C=CS₂ (175.2–190.1 ppm), and C(O) (196.9–198.1 ppm). The ³¹P{¹H} NMR spectra of complexes **3a** and **5a** show one singlet resonance at 29.71 and 26.0 ppm, respectively, indicating the equivalence of both phosphine ligands. In the spectra of their platinum analogues **3b** and **5b**, this resonance shows ¹⁹⁵Pt satellites [*J*(³¹P¹⁹⁵Pt) of 3041 and 3068 Hz, respectively] and is appreciably highfield-shifted (**3b**, 19.15 ppm; **5b**, 18.78 ppm). It is widely accepted that for ¹³C and heavier nuclei (³¹P) the chemical shifts depend on the paramagnetic contribution (σ_p) to the total screening constant (σ).⁴⁹ σ_p is negative, and its absolute value $|\sigma_p|$ varies inversely with the energy difference (ΔE) between the occupied and unoccupied molecular orbitals in which the atom is involved. For stronger bonds one expects larger ΔE , smaller $|\sigma_p|$, larger σ , and thus lower δ values. Accordingly, the lower ³¹P chemical shifts observed in the P–Pt complexes suggest that P–Pt bonds

are stronger than P–Pd in the homologous complexes. This is also supported by the shorter Pt–P bond distances found in the crystal structure of **3b** compared with Pd–P in the homologous complex **3a**.

The spectra of complexes **6a** and **6b** show one broad resonance (**6a**, 5–13; **6b**, 6–13 ppm) due to the Ag(PPh₃)₂ fragment, suggesting that in solution an intermolecular interchange process of PPh₃ occurs at room temperature; we have previously observed this in other AgPPh₃ complexes.⁴⁸ When the spectra are measured at low temperature (–60 °C), both resonances are affected. The wide P–Ag resonance splits into two doublets [**6a**, δ 8.52, *J*(³¹P¹⁰⁹Ag) = 470 Hz, *J*(³¹P¹⁰⁷Ag) = 409 Hz; **6b**, δ 8.52, *J*(³¹P¹⁰⁹Ag) = 472 Hz, *J*(³¹P¹⁰⁷Ag) = 410 Hz] as expected for the coupling of ³¹P with ¹⁰⁷Ag and ¹⁰⁹Ag.⁴⁸ The measured coupling constants are in the range reported in the literature for sp²-hybridized silver(I) complexes of the type AgL₂X (L = monodentate arylphosphine).⁵⁰ The resonance due to the M(PPh₃)₂ moiety is a sharp singlet downfield-shifted for the palladium complex (**6a**, 30.37 ppm) with respect to the platinum analogue (**6b**, 18.15 ppm, ¹⁹⁵Pt satellites, *J* = 3093 Hz) as in the case of the **3a**, **3b** couple. However, at –60 °C this resonance broadens significantly. This suggests that rapid interchange of the Ag(PPh₃)₂ unit between both sulfur donor atoms lead to the singlet resonance observed at room temperature for the P nuclei of the M(PPh₃)₂ group and that the coalescence temperature for this fluxional process is close to –60 °C.

IR Spectra. The IR spectra, measured in the solid state, show several bands (see Experimental Section) in the 1690–1450 cm^{–1} region that cannot be unequivocally assigned to ν (C=O) or ν (C=C) stretching modes because these have proved to be coupled to other carbonyl-containing *push–pull* ethylenes.⁵¹ The bands at higher frequencies (over 1600 cm^{–1}) largely reflect the strength of the C=O bond,⁵¹ and their lowering in energy could be attributed to conjugation within the S₂C=C{C(O)Me}₂ ligand or to coordination of the carbonyl oxygen atoms to a metal center. The spectra of complexes **4** show bands due to the corresponding cations at around 950 (**4a**, **4b**: NMe₄) or 1300 and 525 (**4a'**: PPN) cm^{–1}, while those of **5** and **6** show intense perchlorate bands at around 1100 and 620 cm^{–1}.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of complexes **3a**, **3b**, **4a**, **5b**·Me₂CO and **5b**·2Et₂O. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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