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2-(Aminomethyl)phenyl Complexes of Au(III), Mixed Au(III)/Ag(I), and Pd(II) with the 2,2-Diacetyl-1,1-Ethylenedithiolato Ligand: Dancing of Palladacycles around a Juggler Ligand[†]

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The reaction of [Tl$_2${μ-*S*,*S*-S$_2$C=C{C(O)Me}$_2$}] with [Au(*C*,*N*-C$_6$H$_4$CH$_2$NMe$_2$-2)Cl$_2$] (1:1) gives [{Au(*C*,*N*-C$_6$H$_4$CH$_2$NMe$_2$-2)}{*S*,*S*-S$_2$C=C{C(O)Me}$_2$}] (**1**) which, in turn, reacts with AgClO$_4$ (1:1) to give [{Au(*C*,*N*-C$_6$H$_4$CH$_2$NMe$_2$-2)}{Ag(OClO$_3$)}{S$_2$C=C{C(O)Me}$_2$}] (**2**). Complexes [{Au(*C*,*N*-C$_6$H$_4$CH$_2$NMe$_2$-2)}{Ag(X)(PPh$_3$)}{S$_2$C=C{C(O)Me}$_2$}] [X = OClO$_3$ (**3**), ONO$_2$ (**4**)] have been obtained by reaction of **1** with PPh$_3$ and AgClO$_4$ or AgNO$_3$, respectively (1:1:1). Complex **3** can also be obtained by reacting **2** with PPh$_3$ (1:1). Complexes [Pd(*C*,*N*-C$_6$H$_4$CH$_2$NR$_2$-2)(μ-Cl)]$_2$ (R = Me, H) react (i) with [Tl$_2${S$_2$C=C{C(O)Me}$_2$}] and [PPN]Cl (0.5:1:1, PPN = Ph$_3$P=N=PPh$_3$) to form PPN[Pd(*C*,*N*-C$_6$H$_4$CH$_2$NR$_2$-2){*S*,*S*-S$_2$C=C{C(O)Me}$_2$}] [R = H (**5a**), Me (**5b**)], or (ii) with [Tl$_2${S$_2$C=C{C(O)Me}$_2$}] (1:1) to form [{Pd(*C*,*N*-C$_6$H$_4$CH$_2$NR$_2$-2)}$_2${μ-*S*,*S*,*O*-S$_2$C=C{C(O)Me}$_2$}] [R = H (**6a**), Me (**6b**)]. The trinuclear complexes [{Pd(*C*,*N*-C$_6$H$_4$CH$_2$NR$_2$-2)}$_3${μ_3-*O*,*S*,*S*,*O*-S$_2$C=C{C(O)Me}$_2$}]ClO$_4$ [R = H (**7a**), Me (**7b**)] can be prepared by reacting the corresponding dinuclear complex **6a** or **6b** with [Pd(*C*,*N*-C$_6$H$_4$CH$_2$NR$_2$-2)(NCMe)$_2$]ClO$_4$ (1:1). The crystal structures of **1**, **6b·CH$_2$Cl$_2$**, and **7b**·CH$_2$Cl$_2$ have been determined. NMR studies have been carried out to explain the solution behavior of these complexes. VT-NMR and line shape analysis for the species where R = Me (**5b**, **6b**, **7b**) have allowed the estimation of the activation parameters for these exchange processes.

Introduction

Transition metal complexes containing unsaturated dithiolato ligands attract considerable attention because of their electronic, magnetic, and redox properties.[1] 1,1-Ethylenedithiolato complexes have been less studied[2] than their 1,2 structural isomers (**I** and **II**, Chart 1), probably because the former are less prone to undergo facile redox transformations. Some 1,1-ethylenedithiolato complexes show interesting photophysical properties,[3−5] including solvatochromic behavior and luminescence,[6−9] and are thus potential photocatalysts in light-to-chemical energy conversion.[10] Additionally,

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[†] Dedicated to Prof. Dr. Aurelia Arcas on the occasion of her 60th birthday

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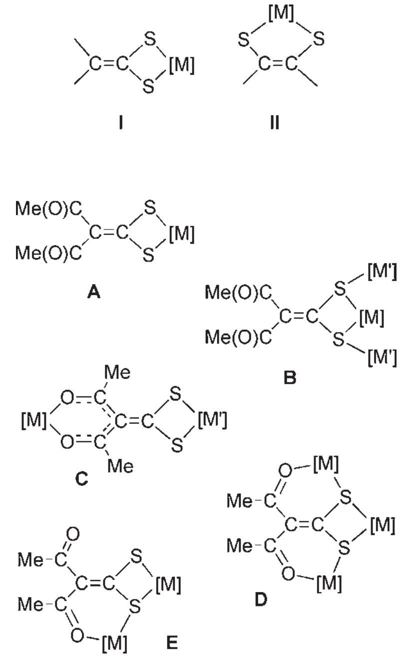
1,1-ethylenedithiolato ligands have attracted interest in their ability to stabilize high oxidation states,[11,12] to form homo-[13−15] or heteropolynuclear complexes,[9,14,16−18] clusters,[15,19] or condensed thiolato ligands,[9,12,20] and because of the variety of coordination modes they display. In particular, for the $S_2C{=}C\{C(O)Me\}_2$ ligand coordination modes **A**−**D** (Chart 1), have been reported.[5,8,14,17,18,21,22] However, there are still very few examples of organometallic 1,1-ethylenedithiolato complexes, and in all of them the organic ligand is a neutral species (cod,[7,14,23] isocyanide,[18,24] carbene,[18] vinylidene[25] or carbonyl[24,26,27]) or a η^5-Cp group.[28] The only exceptions are the 1,1-ethylenedithiolato Pd(II) complexes **6b** and **7b** (Scheme 2) that we have preliminarily reported,[22] which were the first containing an anionic σ C-donor ligand, namely, $C_6H_4CH_2NMe_2$-2. In this paper we report (1) the synthesis of the mononuclear Pd(II) complex that completes this series and its homologous Au(III) complex, (2) the use of the latter as a metallaligand toward Ag(I), (3) the synthesis of the three Pd(II) homologues with the ligand $C_6H_4CH_2NH_2$-2, and (4) an extensive investigation of the dynamic behavior of all these complexes in solution. The synthesis of these Au and Pd complexes was devised with the aim of finding novel structural and/or chemical features, associated with the significant *trans* effect of the aryl group. Indeed, we had previously found that such influence produces interesting fluxional behaviors in $[Au(C,N\text{-}C_6H_4CH_2NMe_2\text{-}2)_2Cl]$[29] and in the trinuclear Pd(II) complex **7b** (Scheme 2),[22] where the dithiolato acts as a "juggler" ligand that moves the three "$[Pd(C,N\text{-}C_6H_4CH_2NMe_2\text{-}2)]$" fragments around all the coordination positions. We have already reported the activation parameters for this process and suggested a possible mechanism.[22] In this paper we put these results into context with the complete DNMR investigation of the behavior in solution of the mono-, di-, and trinuclear Pd(II) complexes.

Chart 1



Experimental Section

IR spectroscopy, elemental analyses, conductance measurements in acetone solution, melting point determinations,

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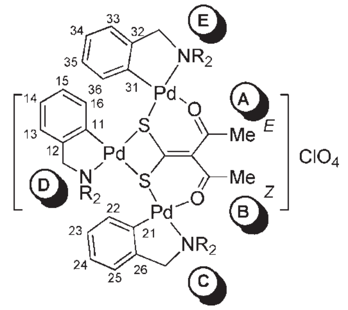
Chart 2



and NMR spectroscopy were carried out as described elsewhere.[30] $AgClO_4$ (Aldrich), acetylacetone (Scharlau), PPh_3 (Fluka), $C_6H_5CH_2NR_2$ (R = H, Me, Merck), Li^nBu (Aldrich), and CS_2 (Fluka) were obtained from commercial sources and used without further purification. Complexes $[Tl_2\{S_2C{=}C\{C(O)Me\}_2]$,[5] $[Au(C,N\text{-}C_6H_4CH_2NMe_2\text{-}2)Cl_2]$,[31] $[Pd(C,N\text{-}C_6H_4CH_2NR_2\text{-}2)(\mu\text{-}Cl)]_2$ (R = H,[32] Me[33]), $[Pd(C,N\text{-}C_6H_4CH_2NR_2\text{-}2)(NCMe)_2]ClO_4$,[34] **6b** and **7b**[22] were prepared following the methods reported in the literature. Chemical shifts are referenced to TMS (^{1}H, ^{13}C{^{1}H}) or H_3PO_4 (^{31}P{^{1}H}). Chart 2 shows the atom numbering used for the assignment of NMR resonances. The notation pd means pair of doublets. The assignment of the ^{1}H and ^{13}C NMR resonances was carried out with the help of APT, ^{1}H-DQF-COSY, ^{1}H-NOESY, HMBC, and HMQC experiments. Some of these spectra are reproduced in the Supporting Information. The phase-sensitive ^{1}H-NOESY measurements were carried out with mixing times D8 = 600 ms−1 s. The VT NMR studies of **7b** have been reported.[22] The details of the calculation of the activation parameters can be found in the Supporting Information.

Synthesis of [{Au(*C*,*N*-$C_6H_4CH_2NMe_2$-2)}{*S*,*S*-$S_2C{=}C\{C(O)Me\}_2$}] (1). $[Tl_2\{S_2C{=}C\{C(O)Me\}_2\}]$ (495.8 mg, 0.85 mmol) was added to a solution of $[Au(C,N\text{-}C_6H_4CH_2NMe_2\text{-}2)Cl_2]$ (342.0 mg, 0.85 mmol) in acetone (25 mL). The resulting suspension was stirred for 4 h. The solvent was removed under vacuum, the residue extracted with CH_2Cl_2 (20 mL), and the suspension filtered through Celite. The yellow solution was concentrated to 3 mL under vacuum, and Et_2O (20 mL) was added to precipitate a yellow solid that was filtered, washed with Et_2O (5 mL), and suction-dried to give **1**. Yield (%): 74. Mp (°C): 148. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 2.25 (s, 3 H, C(O)Me), 2.55 (s, 3 H, C(O)Me), 3.06 (s, 6 H, NMe_2), 4.25 (s, 2 H, CH_2), 7.12−7.15 (m, 1 H, H15), 7.18−7.24 (m, 3 H, H13, H14, H16). ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$, 25 °C): δ 30.2 (*Z*-C(O)*Me*), 32.8 (*E*-C(O)*Me*), 51.5 (NMe_2), 73.0 (CH_2), 124.0 (CH13), 127.8 (CH15), 128.1 (CH14), 129.0 (CH16), 136.1 (= *C*(C(O)Me)$_2$), 146.5 (C12), 151.8 (C11), 180.7 (CS_2), 194.2 (*Z*-CO), 199.7 (*E*-CO). IR (cm^{-1}): 1636 s, 1623 s, 1350 s, 1282 s, 1198 m, 862 m, 843 m, 811 w, 615 m, 599 w, 574 w, 421 w, 354 w. Anal. Calcd for $C_{15}H_{18}AuNO_2S_2$: C, 36.65; H, 3.59; N, 2.77; S, 12.69. Found: C, 36.55; H, 3.84; N, 3.15; S, 12.30. Crystals suitable for an X-ray diffraction study were obtained by slow diffusion of *n*-hexane into a solution of **1** in $CDCl_3$.

Synthesis of [{Au(*C*,*N*-$C_6H_4CH_2NMe_2$-2)}{Ag($OClO_3$)}{*μ*-*S*,*S*,*O*-$S_2C{=}C\{C(O)Me\}_2$}] (2). A solution of $AgClO_4$ (19.7 mg; 0.10 mmol) in acetone (8 mL) was added dropwise to a solution of **1** (48.1 mg; 0.10 mmol) in the same solvent (4 mL). The resulting suspension was stirred in the dark for 5 h and then filtered. The pale yellow solid obtained was washed with Et_2O (2 × 5 mL) and suction-dried to give **2**. Yield (%): 77. Dec. point (°C): 194. IR (cm^{-1}): 1642 m, 1607 vs, 1545 w, 1254 s, 1205 m, 1112 s, br, 1045 s, 974 m, 926 m, 852 s, 779 s, 622 s, 605 s, 468 w, 429 w, 358 w. Anal. Calcd for $C_{15}H_{18}AgAuClNO_6S_2$: C, 25.28; H, 2.55; N, 1.97; S, 9.00. Found: C, 25.56; H, 2.47; N, 2.00; S, 8.93.

Synthesis of [{Au(*C*,*N*-$C_6H_4CH_2NMe_2$-2)}{Ag($OClO_3$)(PPh_3)}{*μ*-*S*,*S*,*O*-$S_2C{=}C\{C(O)Me\}_2$}] (3). A solution of $AgClO_4$ (35.5 mg, 0.16 mmol) in acetone was added dropwise to a solution of **1** (80 mg, 0.16 mmol) in acetone (15 mL). The reaction mixture was stirred for 5 h, and then a solution of PPh_3 (41.4 mg, 0.16 mmol) in acetone (15 mL) was added. After stirring for 5 h the reaction mixture was filtered through Celite. The solution was concentrated under vacuum (3 mL), and Et_2O (20 mL) was added to precipitate a pale yellow solid that was filtered, washed with Et_2O (5 mL), and suction-dried to give **3**. Yield (%): 84. Mp (°C): 164. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 2.18 (s, 3 H, *Z*-C(O)Me), 2.48 (s, 3 H, *E*-C(O)Me), 3.09 (s, 6 H, NMe_2), 4.29 (s, 2 H, CH_2), 7.06−7.09 (m, 2 H, H15, H16), 7.20−7.23 (m, 1 H, H13), 7.23−7.26 (m, 1 H, H14), 7.35−7.40 (m, 6 H, *m*-H, PPh_3), 7.41−7.47 (m, 9 H, *o*-H, *p*-H, PPh_3). ^{31}P{^{1}H} NMR (242,9 MHz, $CDCl_3$, 25 °C): δ 12.9 (br s), 15.6 (br s); (−60 °C): δ 12.0 [pd, $J_{\mathrm{P}^{109}\mathrm{Ag}}$ = 554 Hz, $J_{\mathrm{P}^{107}\mathrm{Ag}}$ = 482 Hz]; (CD_2Cl_2, −90 °C): δ 11.4 [pd, $J_{\mathrm{P}^{109}\mathrm{Ag}}$ = 710 Hz, $J_{\mathrm{P}^{107}\mathrm{Ag}}$ = 615 Hz], 15.2 [pd, $J_{\mathrm{P}^{109}\mathrm{Ag}}$ = 623 Hz, $J_{\mathrm{P}^{107}\mathrm{Ag}}$ = 540 Hz]. ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$, 25 °C): δ 30.5 (*Z*-C(O)*Me*), 32.7 (*E*-C(O)*Me*), 51.9 (NMe_2), 73.2 (CH_2), 124.4 (CH13), 128.0 (CH15), 128.4 (CH16), 128.6 (CH14), 129.5 (*m*-CH, PPh_3), 130.1 (v br, *i*-C, PPh_3), 131.3 (*p*-CH, PPh_3), 134.2 (br, *o*-CH, PPh_3), 137.9 (= *C*(C(O)Me)$_2$), 146.7 (C12), 150.4 (C11), 194.0 (*Z*-CO), 200.5 (*E*-CO). IR (cm^{-1}): 1660 w, 1625 m, 1250 m, 1202 m, 1093 s, br, 1056 s, 840 m, 620 m, 602 m, 509 m, 422 w, 349 w. Anal. Calcd for $C_{33}H_{33}AgAuClNO_6PS_2$: C, 40.65; H, 3.41; N, 1.44; S, 6.58. Found: C, 40.95; H, 3.36; N, 1.47; S, 6.31.

Synthesis of [{Au(*C*,*N*-$C_6H_4CH_2NMe_2$-2)}{Ag(ONO_2)(PPh_3)}{*μ*-*S*,*S*,*O*-$S_2C{=}C\{C(O)Me\}_2$}] (4). $AgNO_3$ (20.8 mg, 0.12 mmol) and PPh_3 (32.0 mg, 0.122 mol) were successively added to a solution of **1** (62.0 mg, 0.12 mmol) in acetone (25 mL). The resulting solution was stirred in the dark for 1 h and then filtered through Celite. The filtrate was concentrated (2 mL) and *n*-hexane (15 mL) was added to precipitate a white solid that was recrystallized from acetone/*n*-hexane to give **4**. Yield (%): 71. Mp (°C): 112. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 2.18 (s, 3 H, *Z*-C(O)Me), 2.53 (s, 3 H, *E*-C(O)Me), 3.09 (s, 6 H, NMe_2), 4.28 (s, 2 H, CH_2), 7.09−7.13 (m, 1 H, H15), 7.14−7.16 (m, 1 H, H16), 7.20−7.22 (m, 1 H, H13), 7.22−7.26 (m, 1 H, H14), 7.39−7.45 (m, 12 H, *m*-H, *o*-H, PPh_3), 7.45−7.50 (m, 3 H, *p*-H, PPh_3). ^{31}P{^{1}H} NMR (242.9 MHz, $CDCl_3$, 25 °C): δ 14.7 (v br s), 17.5 (v br s); (−60 °C): δ 10.7 [pd, $J_{\mathrm{P}^{109}\mathrm{Ag}}$ = 536 Hz, $J_{\mathrm{P}^{107}\mathrm{Ag}}$ = 465 Hz], 14.1 [pd, $J_{\mathrm{P}^{109}\mathrm{Ag}}$ = 751 Hz, $J_{\mathrm{P}^{107}\mathrm{Ag}}$ = 651 Hz]. ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$, 25 °C): δ 30.3 (*Z*-C(O)*Me*), 32.8 (*E*-C(O)*Me*), 51.6 (NMe_2), 73.1 (CH_2), 124.1 (CH13), 127.9 (CH15), 128.3 (CH14), 128.8 (CH16), 129.5 (d, *m*-CH, PPh_3, $^3J_{PC}$ = 11 Hz), 130.3 (v br, *i*-C, PPh_3), 131.3 (*p*-CH, PPh_3), 134.1 (d, *o*-CH, PPh_3, $^3J_{PC}$ = 17 Hz), 137.1 (= *C*(C(O)Me)$_2$), 146.5 (C12), 151.0 (C11), 175.8 (CS_2), 193.9 (*Z*-CO), 200.0 (*E*-CO). IR (cm^{-1}): 1644 s, 1626 m, 1354 s, 1288 s, 1202 m, 1052 s, 846 m, 694 s, 602 m, 516 s, 422 w, 349 w. Anal. Calcd for $C_{33}H_{33}AgAuN_2O_5PS_2$: C, 42.28; H, 3.55; N, 2.99; S, 6.84. Found: C, 42.61; H, 3.35; N, 2.64; S, 7.31.

Synthesis of PPN[Pd(*C*,*N*-$C_6H_4CH_2NR_2$-2){*μ*-*S*,*S*-$S_2C{=}C\{C(O)Me\}_2$}] [R = H (5a), Me (5b)]. $[Tl_2\{S_2C{=}C\{C(O)Me\}_2\}]$ (**5a:** 269.6 mg, 0.46 mmol; **5b:** 236.7 mg, 0.41 mmol) and [PPN]Cl (**5a**: 254.3 mg, 0.46 mmol; **5b**: 233.1 mg, 0.41 mmol) were successively added to a solution of $[Pd(C,N\text{-}C_6H_4CH_2NR_2\text{-}2)(\mu\text{-}Cl)]_2$ (**5a:** 114.6 mg, 0.23 mmol; **5b**: 112.1 mg, 0.20 mmol) in CH_2Cl_2 (20 mL, for **5a** freshly distilled under N_2). A yellow

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suspension formed immediately, which was stirred for 3 h (**5a**) or 1.5 h (**5b**) and then filtered through Celite. The resulting yellow (**5a**) or orange (**5b**) solution was concentrated under vacuum (3 mL), and Et_2O (20 mL) was added. For **5a** an oily material formed, which was converted into a solid upon stirring with Et_2O in an ice/water bath for 15 min. This solid was filtered and dried, first under a N_2 stream and then in an oven at 60 °C for 4 h to give **5a**·$0.5CH_2Cl_2$. **5b** precipitated as a yellow solid, which was filtered, washed with Et_2O (5 mL) and suction-dried.

5a·$0.5CH_2Cl_2$: Yield (%): 83. Mp (°C): 98. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 2.33 (s, 2 H, NH_2), 2.45 (s, 6 H, Me), 4.12 (br s, 2 H, CH_2), 5.30 (s, 1 H, CH_2Cl_2), 6.79 (br t, 1 H, C_6H_4, $^3J_{HH}$ = 7.2 Hz), 6.85 (td, 1 H, C_6H_4, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.3 Hz), 6.92 (br d, 1 H, C_6H_4, $^3J_{HH}$ = 7.7 Hz), 7.05 (br d, 1 H, C_6H_4, $^3J_{HH}$ = 6.5 Hz), 7.40−7.51 (m, 24 H, PPN), 7.64−7.69 (m, 6 H, PPN). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, 25 °C): δ 21.6 (s). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 31.9 (Me), 53.2 (CH_2Cl_2), 77.2 (CH_2), 120.5 (CH13), 123.0 (CH14), 124.5 (CH15), 126.8 (m, *i*-C, PPN), 129.5 (m, *m*-CH, PPN), 131.9 (m, *o*-CH, PPN), 133.4 (CH16), 133.8 (*p*-C, PPN), 138.1 (=*C*(C(O)Me)$_2$), 150.9 (C12), 155.2 (C11), 198.4 (CS_2), 199.0 (v br s, CO). IR (cm^{-1}): 1688 m, 1575 m, br, 1300 m, 1266 m, 1114 s, 998 m, 850 w, 820 w, 798 w, 624 m, 548 s, 534 s, 500 s, 394 w, 322 w. Λ_M (Ω^{-1} cm^2 mol^{-1}): 108. Anal. Calcd for $C_{49.5}H_{45}ClNO_2P_2PdS_2$: C, 61.42; H, 4.69; N, 2.89; S, 6.62. Found: C, 61.31; H, 4.95; N, 2.81; S, 6.97.

5b: Yield (%): 68. Mp (°C): 110. ^1H NMR (600 MHz, CD_2Cl_2, 25 °C): δ 2.36 (s, 6 H, C(O)Me), 2.75 (s, 6 H, NMe_2), 3.85 (s, 2 H, CH_2), 6.80 (t, 1 H, H15, $^3J_{HH}$ = 7.3 Hz), 6.86 (t, 1 H, H14, $^3J_{HH}$ = 7.3 Hz), 6.91 (d, 1 H, H16, $^3J_{HH}$ = 7.0 Hz,), 6.95 (d, 1 H, H13, $^3J_{HH}$ = 7.3 Hz), 7.47−7.50 (m, 24 H, *o*-H, *m*-H, PPN), 7.65−7.68 (m, 6 H, *p*-H, PPN). (−90 °C): δ 2.35 (s, 3 H, C(O)Me), 2.42 (s, 3 H, C(O)Me), 2.78 (s, 6 H, NMe_2), 3.91 (s, 2 H, CH_2), 6.83 (br s, 2 H, H15, H16), 6.96 (br t, 1 H, H14, $^3J_{HH}$ = 6.5 Hz), 7.06 (d, 1 H, H13, $^3J_{HH}$ = 6.5 Hz), 7.52 (m, 12 H, *o*- or *m*-H, PPN), 7.59−7.65 (m, 12 H, *m*- or *o*-H, PPN), 7.70 (br t, 6 H, *p*-H, PPN, $^3J_{HH}$ = 7.2 Hz). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, 25 °C): δ 21.5 (s). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, 25 °C): δ 31.8 (C(O)Me), 51.8 (NMe_2), 73.1 (CH_2), 121.6 (CH13), 123.0 (CH14), 124.9 (CH15), 127.4 (d, *i*-C, PPN, $^1J_{CP}$ = 109.6 Hz), 129,8 (m, *m*-CH, PPN), 132.5 (m, *o*-CH, PPN), 133.5 (CH16), 134.1 (*p*-CH, PPN), 139.2 (=*C*(C(O)Me)$_2$), 149.4 (C12), 156.8 (C11), 197.5 (CS_2), 198.9 (br s, CO). IR (cm^{-1}): 1680 m, 1580 m, br, 1261 m, 1100 m, 995 m, 846 m, 817 w, 795 vw, 623 m, 542 m, 525 m, 492 m, 392 w, 321 w. Λ_M (Ω^{-1} cm^2 mol^{-1}): 109. Anal. Calcd for $C_{51}H_{48}N_2O_2P_2PdS_2$: C, 64.25; H, 5.07; N, 2.94; S, 6.73. Found: C, 64.22; H, 5.09; N, 2.88; S, 6.67.

Synthesis of [{Pd(*C*,*N*-$C_6H_4CH_2NR_2$-2)}$_2${*μ*-*S*,*S*,*O*-S_2C=C{C(O)Me}$_2$}] [R = H (6a), Me (6b)]. Solid [Tl_2{S_2C=C{C(O)Me}$_2$}] (**6a**: 252.4 mg, 0.43 mmol; **6b**: 345.8 mg; 0.59 mmol) was added to a solution of the appropriate [Pd(*C*,*N*-$C_6H_4CH_2NR_2$-2)(*μ*-Cl)]$_2$ (**6a**: 215.0 mg, 0.43 mmol; **6b**: 327.5 mg, 0.59 mmol) in CH_2Cl_2 (20 mL; for **6a** freshly distilled under N_2). A yellow suspension formed immediately, which was stirred for 1.5 h. For **6a** the suspension was concentrated to dryness, and the residue was extracted in a Soxhlet with acetone until the extract was colorless. The yellow solution was concentrated (2 mL), and Et_2O (20 mL) was added to precipitate a dark yellow solid, which was filtered and dried in an oven at 80 °C for 4 h to give **6a**·$0.5H_2O$. For **6b** the suspension was filtered through Celite, the resulting solution was concentrated under vacuum (3 mL), and *n*-hexane (20 mL) was added to precipitate a lemon yellow solid that was filtered, washed with *n*-hexane (5 mL), and air-dried.

6a·$0.5H_2O$. Yield (%): 57. Dec. point (°C): 185. ^1H RMN (400 MHz, d^6-dmso, 25 °C): δ 1.54 (s, 1 H, H_2O), 1.93 (s br, 3 H, C(O)Me), 2.53 (br s, 3 H, C(O)Me), 3.94 (br s, 2 H, CH_2), 3.99 (br s, 2 H, CH_2), 5.17 (br s, 2 H, NH_2), 5.46 (br s, 2 H, NH_2), 6.63−6.88 (several m, 8 H, C_6H_4). (60 °C): δ 2.23 (v br s, 6 H, Me), 3.99 (t, 4 H, CH_2, $^2J_{NH}$ = 5.7 Hz), 5.16 (br s, 4 H, NH_2), 6.67−6.89 (several m, 8 H, C_6H_4). (90 °C): δ 2.23 (br s, 6 H, Me), 4.01 (t, 4 H, CH_2, $^2J_{NH}$ = 5.6 Hz), 5.04 (br s, 4 H, NH_2), 6.71−6.88 (several m, 7 H, C_6H_4), 7.3 (m, 1 H, C_6H_4). $^{13}C\{^1H\}$ RMN (75.4 MHz, d^6-dmso, 25 °C): 28.1 (C(O)*Me*), 32.2 (C(O)*Me*), 50.9 (CH_2), 52.1 (CH_2), 121.1 (br, CH13,23), 123.9 (br, CH14,24), 124.7 (br, CH15,25), 133.0 (br, CH16,26), 135.2 (=*C*(C(O)Me)$_2$), 143−144 (several br, C11,21,12,22), 183.7 (br s, CO), 195.6 (s, CS_2), 203.2 (br s, CO). IR (cm^{-1}): 3324 m, 3266 w, 1702 s, 1686 s, 1552 s, 1224 m, 1208 m, 1042 m, 1024 m, 866 w, 636 w, 592 w, 532 w, 470 w. Anal. Calcd for $C_{20}H_{23}N_2O_{2.5}Pd_2S_2$: C, 39.50; H, 3.81; N, 4.60; S, 10.54. Found: C, 39.75; H, 3.72; N, 4.43; S, 10.10.

6b. Yield (%): 67. Dec. point (°C): 212. ^1H NMR (600 MHz, CD_2Cl_2, 25 °C): δ 2.04 (s, 3 H, C(O)Me^B), 2.58 (s, 3 H, C(O)Me^A), 2.64 (s, 6 H, $NMe_2{}^C$), 2.78 (s, 6 H, $NMe_2{}^C$), 3.85 (s, 2 H, $CH_2{}^D$), 3.98 (s, 2 H, $CH_2{}^C$), 6.85−6.90 (m, 3 H, H15,25,16), 6.94−7.00 (m, 4 H, H13, H23, H14, H24), 7.08 (d, 1 H, H26, $^3J_{HH}$ = 7.0 Hz). $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$, 25 °C): δ 29.0 (C(O)Me^B), 32.1 (C(O)Me^A), 50.2 ($NMe_2{}^C$), 51.9 ($NMe_2{}^D$), 72.2 ($CH_2{}^C$), 72.7 ($CH_2{}^D$), 122.2 (CH13), 122.7 (CH23), 124.6 (CH14,24), 125.1 (CH25), 125.8 (CH15), 134.3 (CH16), 134.5 (CH26), 135.4 (C2), 144.0 (C21), 147.0 (C11), 147.4 (C12), 148.2 (C22), 184.5 (CO^B), 194.5 (C1), 203.8 (CO^A). IR (cm^{-1}): 1677 s, 1531 s, 1198 m, 875 m, 844 s, 813 w, 637 m, 560 w, 514 w, 379 w. Λ_M (Ω^{-1} cm^2 mol^{-1}): 3. Anal. Calcd for $C_{24}H_{30}N_2O_2Pd_2S_2$: C, 43.98; H, 4.61; N, 4.27; S, 9.78. Found: C, 44.20; H, 4.86; N, 4.31; S, 9.56.

Synthesis of [{Pd(*C*,*N*-$C_6H_4CH_2NR_2$-2)}$_3${*μ*-*O*,*S*,*S*,*O*-S_2C=C{C(O)Me}$_2$}]ClO_4 [R = H (7a), Me (7b)]. The appropriate [Pd(*C*,*N*-$C_6H_4CH_2NR_2$-2)(NCMe)$_2$]ClO_4 (**7a**: 52.6 mg, 0.13 mmol; **7b**: 145.1 mg, 0.34 mmol) was added to a solution of **6** (**a:** 80.0 mg, 0.13 mmol; **b**: 225.3 mg, 0.34 mmol) in CH_2Cl_2 (20 mL, for **7a** freshly distilled under N_2), and the resulting solution was stirred for 40 min. For **7a** an abundant deep yellow suspension formed; the solid was filtered off, washed with Et_2O, and dried in an oven at 80 °C for 4 h to give **7a**·CH_2Cl_2. For **7b**, the solution was concentrated under vacuum (3 mL), and Et_2O (20 mL) was added to precipitate a yellow solid that was recrystallized from CH_2Cl_2 and Et_2O, filtered, washed with Et_2O (2 × 10 mL), and suction-dried.

7a·CH_2Cl_2. Yield (%): 68. Dec. point (°C): 197. ^1H RMN (400 MHz, d^6-dmso, 25 °C): δ 1.93−2.07 (several br s, 6 H, Me), 3.80−4.05 (br m, 6 H, CH_2), 5.16 (br s, 2 H, NH_2), 5.31 (s, 2 H, CH_2Cl_2), 5.43 (br s, 2 H, NH_2), 5.75 (br s, 2 H, NH_2), 6.56−7.05 (several m, 11 H, C_6H_4), 7.40 (d, 1 H, H36, $^3J_{HH}$ = 7.2 Hz). (60 °C): δ 2.00−2.37 (v br m, 6 H, Me), 4.00 (br s, 6 H, CH_2), 5.16 (br s, 4 H, NH_2), 5.62 (br s, 2 H, NH_2), 6.63−6.74 (m, 2 H, C_6H_4), 6.74−7.04 (m, 9 H, C_6H_4), 7.34 (d, 1 H, H36, $^3J_{HH}$ = 7.4 Hz). (90 °C): δ 2.24 (br s, 6 H, Me), 4.01 (br t, 6 H, CH_2, $^3J_{HH}$ = 5.1 Hz), 5.04 (br s, 4 H, NH_2), 5.50 (br s, 2 H, NH_2), 6.71 (s, 2 H, C_6H_4), 6.78−7.00 (m, 9 H, C_6H_4), 7.28 (br s, 1 H, H36). $^{13}C\{^1H\}$ RMN (75.4 MHz, d^6-dmso, 25 °C): δ 28.2 (br, C(O)*Me*), 32.2 (br, C(O)*Me*), 51.2 (CH_2), 53.2 (CH_2Cl_2), 121.2 (br), 121.6 (CH13, CH23, CH33), 124.0 (br), 124.5 (br), 124.8 (v br), 125.2, and 125.4 (CH14, CH24, CH34 and CH15, CH25, CH35), 132.5 and 133.1 (br) CH16, CH26, CH36), 135.4 (C2), 143.0−154.1 (several br, C11, C21, C31, C12, C22, C32), 183.9 (br, CO), 195.1 (C1), 203.3 (br, CO). IR (cm^{-1}): 3306 s, 3250 m, 1585 s, br, 1266 s, 1084 s, 995 m, 1044 m, 1024 m, 850 w, 624 m, 470 w, 430 w. Λ_M (Ω^{-1} cm^2 mol^{-1}) 143. Anal. Calcd for $C_{28}H_{32}Cl_3N_3O_6Pd_3S_2$: C, 33.76; H, 3.23; N, 4.13; S, 6.44. Found: C, 33.38; H, 2.94; N, 4.29; S, 6.76.

7b. Yield (%): 91. Dec. point (°C): 170 °C. ^1H RMN (600 MHz, CD_2Cl_2, 25 °C): δ 2.54 (br s, 6 H, C(O)Me); 2.84 (br s, 18 H, NMe_2); 4.04 (br s, 6 H, CH_2); 6.72 (br s, 3 H, C_6H_4); 6.94−7.00 (m, 6 H, C_6H_4); 7.20 (br s, 3 H, C_6H_4). (400 MHz, CD_2Cl_2, −80 °C): δ 2.47 (s, 3 H, C(O)Me^B), 2.66 (br s, 3 H, Me^E), 2.71 (s, 3 H, C(O)Me^A), 2.79 (br s, 3 H, Me^{C28}), 2.85 and 2.87 (br s, 3 H, Me^D), 3,02 (br s, 3 H, Me^{C29}), 3.04 (br s, 3 H,

Table 1. Crystallographic Data for **1**, **6b**·CH_2Cl_2, and **7b**·CH_2Cl_2

	1	**6b**·CH_2Cl_2	**7b**·CH_2Cl_2
formula	$C_{15}H_{18}AuNO_2S_2$	$C_{25}H_{32}Cl_2N_2O_2Pd_2S_2$	$C_{34}H_{44}Cl_3N_3O_6Pd_3S_2$
Fw	505.39	740.35	1080.39
temperature (K)	173(2)	143(2)	133(2)
crystal system	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	11.561(3)	11.3598(12)	12.0425(11)
b (Å)	15.624(3)	11.6148(12)	13.1177(11)
c (Å)	9.317(2)	11.6365(12)	13.2231(11)
α (deg)	90	101.931(3)	92.137(4)
β (deg)	105.97(2)	92.169(3)	95.079(4)
γ (deg)	90	108.554(3)	105.373(4)
volume (Å^3)	1618.0(6)	1415.2(3)	2002.2(3)
Z	4	2	2
ρ_{calcd} (Mg m^{-3})	2.075	1.737	1.792
μ (Mo K_α)(mm^{-1})	9.353	1.633	1.683
F(000)	968	740	1076
crystal size (mm)	0.40 × 0.35 × 0.10	0.37 × 0.19 × 0.19	0.30 × 0.09 × 0.07
θ range (deg)	3.19 to 25.00	1.80 to 30.03	1.55 to 30.51
no. of rflns coll	5935	16952	43418
no. of indep rflns/R_{int}	2843/0.0439	8208/0.0294	12150/0.0406
transmissn	0.999 and 0.305	0.970 and 0.684	0.8913 and 0.7309
restraints/parameters	32/194	31/350	0/468
goodness-of-fit on F^2	0.994	1.046	1.033
$R1$ ($I > 2\sigma(I)$)	0.0250	0.0220	0.0347
$wR2$ (all reflns)	0.0551	0.0543	0.0815
largest diff. peak/hole (e Å^{-3})	1.283/−0.860	0.569/−0.797	1.297/−1.345

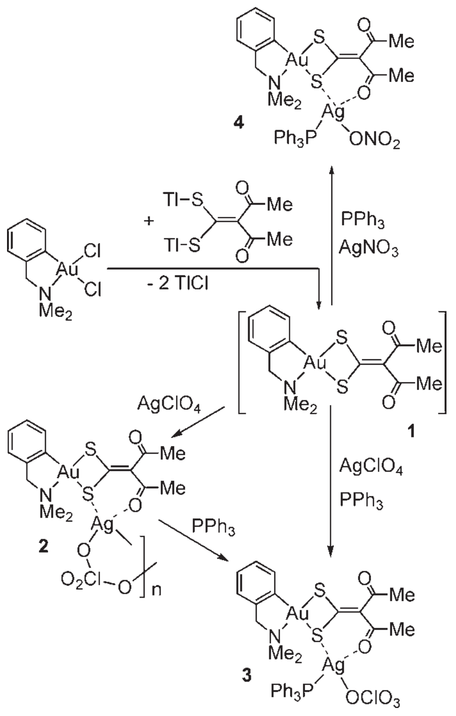
Me^D), 3.60 (d, 1 H, CH$_2{}^E$), 3.83 (br t, 2 H, CH$_2{}^{C,D}$), 4.44−4.54 (m, 3 H, CH$_2{}^{C,D,E}$), 6.47 (t, 1 H, H35, $^3J_{HH}$ = 6.9 Hz), 6.56 (d, 1 H, H16, $^3J_{HH}$ = 7.5 Hz), 6.70 (t, 1 H, H15, $^3J_{HH}$ = 7.1 Hz), 6.85 (t, 1 H, H34, $^3J_{HH}$ = 7.0 Hz), 6.93 (d, 1 H, H33, $^3J_{HH}$ = 7.0 Hz), 6.99 (t, 1 H, H14, $^3J_{HH}$ = 7.1 Hz), 7.02 (br t, 1 H, H25, $^3J_{HH}$ = 7.0 Hz), 7.07 (d, 1 H, H13, $^3J_{HH}$ = 7.0 Hz), 7.10−7.16 (m, 2 H, H23,24), 7.18 (d, 1 H, H26, $^3J_{HH}$ = 7.3 Hz), 8.10 (d, 1 H, H36, $^3J_{HH}$ = 7.7 Hz). $^{13}C\{^1H\}$ RMN (150.9 MHz, CD_2Cl_2, 25 °C): 32.3 (br s, C(O)Me), 52.0 (br s, NMe$_2$), 72.7 (br s, CH$_2$), 123.3 (br s, CH13, CH23, CH33), 125.8 and 126.0 (br s, CH14, CH24, CH34 and CH15, CH25, CH35), 134.3 (br s, CH16, CH26, CH36), 148.3 (br s, C12, C22, C32). IR (cm^{-1}): 1614 s, 1522 s, 1278 m, 1100 s, br, 990 m, 846 m, 622 m, 516 w, 424 w, 384 w. Λ_M (Ω^{-1} cm^2 mol^{-1}) 124. Anal. Calcd for $C_{33}H_{42}ClN_3O_6Pd_3S_2$: C, 39.82; H, 4.25; N, 4.22; S, 6.44. Found: C, 39.68; H, 4.24; N, 4.07; S, 5.91.

X-ray Crystallographic Analysis of 1, 6b·CH_2Cl_2, and 7b·CH_2Cl_2. Crystals suitable for X-ray analyses were obtained by slow diffusion of *n*-hexane into a solution of **1** in $CDCl_3$ or by slow diffusion of Et_2O into CH_2Cl_2 solutions of **6b**. The crystal structure of **7b**·CH_2Cl_2 has been reported in a preliminary communication.[22] Crystal data and refinement details are shown in Table 1. Intensity measurements were recorded using monochromated Mo *K*α radiation on a Siemens P4 (**1**) or SMART 1000 diffractometer. Absorption corrections were performed on the basis of ψ-scans (**1**) or multiscans. Structures were refined anisotropically on F^2 using the program SHELXL-97;[35] hydrogen atoms were included using a riding model or rigid idealized methyl groups. For **6b**, the dichloromethane molecule is disordered over two positions.

Results and Discussion

Synthesis. The reaction of [Au(C,N-$C_6H_4CH_2NMe_2$-2)-Cl_2][31] with [$Tl_2\{S_2C{=}C\{C(O)Me\}_2\}$][5] (Scheme 1) caused the immediate precipitation of TlCl and the formation of [Au(C,N-$C_6H_4CH_2NMe_2$-2){S,S-$S_2C{=}C\{C(O)Me\}_2$}] (**1**), which was isolated in good yield (74%). We have previously described[21] the synthesis of the non-organometallic Au(I) 1,1-dithiolato complex $(PPN)_2[Au_2\{\mu\text{-}S,S\text{-}S_2C{=}C\{C(O)Me\}_2\}]$ by reacting PPN[Au(acac)$_2$] (acac = acetylacetonate) and CS_2. However, after refluxing a mixture of [Au(acac)(C,N-$C_6H_4CH_2NMe_2$-2)Cl][36] and NEt_3 (1:5) in CS_2 (5 mL) for 3 h, the starting materials were recovered and neither **1** nor the intermediate complex [Au(C,N-$C_6H_4CH_2NMe_2$-2)Cl{SC(=S)CH{C(O)Me}$_2$}] were even detected by NMR spectroscopy. The reaction of

Scheme 1



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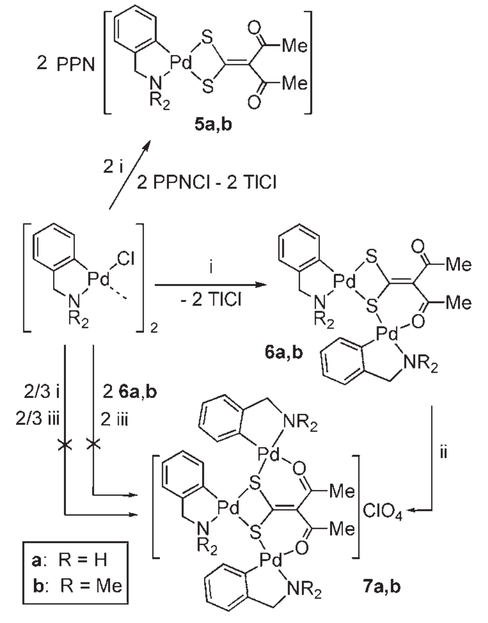
Scheme 2



i = $[Tl_2\{S_2C{=}C\{C(O)Me\}_2\}]$
ii = $[Pd(C,N\text{-}C_6H_4CH_2NR_2\text{-}2)(NCMe)_2]ClO_4$
iii = $AgClO_4$

1 with $AgClO_4$ (1:1, in acetone) afforded in good yield (77%) the heterodinuclear complex, $[\{Au(C,N\text{-}C_6H_4\text{-}CH_2NMe_2\text{-}2)\}\{Ag(OClO_3)\}\{S,S,O\text{-}S_2C{=}C\{C(O)Me\}_2\}]_n$ (**2**), the insolubility of which in all common organic solvents prevented its characterization by NMR or X-ray diffraction studies. In Scheme 1 we show a reasonable representation of its structure as a polymeric complex. The reaction of **2** with PPh_3 (1:1, in acetone) gave the soluble complex $[\{Au(C,N\text{-}C_6H_4CH_2NMe_2\text{-}2)\}\{Ag(OClO_3)(PPh_3)\}\text{-}\{S,S,O\text{-}S_2C{=}C\{C(O)Me\}_2\}]$ (**3**) in 68% yield, along with an insoluble material that could not be identified. Complex **3** can also be obtained by reacting **1** with $AgNO_3$ and PPh_3 (1:1:1, in acetone, 84% yield). Similarly, the analogous complex $[\{Au(C,N\text{-}C_6H_4CH_2NMe_2\text{-}2)\}\{Ag\text{-}(ONO_2)(PPh_3)\}\{S,S,O\text{-}S_2C{=}C\{C(O)Me\}_2\}]$ (**4**) was isolated in 60% yield from the reaction of **1** with $AgNO_3$ and PPh_3 (1:1:1, in acetone). The behavior in solution of **3** and **4** shows equilibria between various complexes (see below). Scheme 1 shows the structure of one of them.

We have tried to obtain mixed valence Au(III)/Au(I) derivatives by reaction of the labile Au(I) complexes [AuCl-(tht)] (tht = tetrahydrothiophene)[37] or $[Au(NH_3)_2]ClO_4$[38] with **1** under various reaction conditions. However, all these reactions led to mixtures of products that could not be separated or even identified. The attempt to replace Ag(I) by Au(I) in complex **2** by reaction with [AuCl(tht)] led to massive decomposition.

The reaction of $[Pd(C,N\text{-}C_6H_4CH_2NR_2\text{-}2)(\mu\text{-}Cl)]_2$ with $[Tl_2\{S_2C{=}C\{C(O)Me\}_2\}]$ and [PPN]Cl (1:2:2) afforded $PPN[Pd(C,N\text{-}C_6H_4CH_2NR_2\text{-}2)\{S,S\text{-}S_2C{=}C\{C(O)Me\}_2\}]$ [R = H (**5a**), Me (**5b**)] (Scheme 2). When complexes $[Pd(C,N\text{-}C_6H_4CH_2NR_2\text{-}2)(\mu\text{-}Cl)]_2$ were reacted with 1 equiv of $[Tl_2\{S_2C{=}C\{C(O)Me\}_2\}]$ the dinuclear complexes $[\{Pd(C,N\text{-}C_6H_4CH_2NR_2\text{-}2)\}_2\{\mu\text{-}S,S,O\text{-}S_2C{=}C\{C(O)Me\}_2\}]$ [R = H (**6a**), Me (**6b**)] were obtained. Whereas **6b** was easily separated from TlCl, **6a** precipitated as a hemihydrate insoluble in CH_2Cl_2 and only slightly soluble in acetone. This required repeated extraction with acetone in a Soxhlet, which restricted the yield (57%). **6a**$\cdot 0.5H_2O$ could not be dehydrated even by heating it in an oven at 80 °C for 4 h.

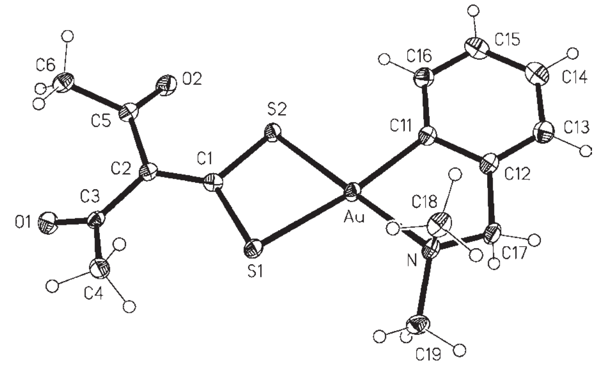


Figure 1. Thermal ellipsoid representation plot (50% probability) of complex **1**. Selected bond lengths (Å) and angles (deg): Au−C(11) 2.029(5), Au−N 2.140(5), Au−S(1) 2.3646(15), Au−S(2) 2.2846(16), S(1)−C(1) 1.754(6), S(2)−C(1) 1.761(5), C(1)−C(2) 1.361(8), C(2)−C(3) 1.474(7), C(2)−C(5) 1.488(7), O(1)−C(3) 1.232(7), O(2)−C(5) 1.223(6); C(11)−Au−N 82.3(2), N−Au−S(1) 104.20(13), S(2)−Au−S(1) 74.86(5), C(11)−Au−S(2) 98.46(17).

The reaction of $[Pd(C,N\text{-}C_6H_4CH_2NMe_2\text{-}2)(\mu\text{-}Cl)]_2$ with $[Tl_2\{S_2C_2\{C(O)Me\}_2\}]$ and $AgClO_4$ (1.5:1:1), or with **6b** and $AgClO_4$ (0.5:1:1) was expected to afford the tripalladated complex **7b** (Scheme 2) but, instead, complex mixtures of products formed, among which **7b** could not be identified.[22] Nevertheless, the tripalladated complexes $[\{Pd(C,N\text{-}C_6H_4CH_2NR_2\text{-}2)\}_3\{\mu\text{-}O,S,S,O\text{-}S_2C_2\text{-}\{C(O)Me\}_2\}]ClO_4$ [R = H (**7a**), Me (**7b**)] could be obtained in good yield by displacement of the labile nitrile ligands in $[Pd(C,N\text{-}C_6H_4CH_2NR_2\text{-}2)(NCMe)_2]ClO_4$ by the corresponding dinuclear complex **6**, acting as an S,O chelating ligand. Complex **7a** precipitated in situ as **7a**$\cdot CH_2Cl_2$, which was isolated in 70% yield by filtration. The CH_2Cl_2 solvent molecule could not be removed even by heating at 80 °C for 4 h. The low solubility of complexes **6a**$\cdot 0.5H_2O$ and **7a**$\cdot CH_2Cl_2$, together with their tendency to crystallize with solvent molecules, differentiates them from their NMe_2 homologues (soluble and unsolvated), which suggests the presence of significant hydrogen bonds involving the NH_2 fragments in the **a** derivatives.

Crystal Structures. The crystal structures of complexes **1** (Figure 1) and **6b**$\cdot CH_2Cl_2$ (Figure 2) have been determined. That of **7b**$\cdot CH_2Cl_2$ (Figure 3) was reported in a preliminary communication.[22]

The dithiolato ligand in **1** is S,S-chelating and adopts an *E,Z* conformation while in **6b** and **7b** is *Z,Z* and S,S-chelating toward Pd(1) and, simultaneously, S,O-chelating toward Pd(2) (**6b**) or, in addition, toward Pd(3) (**7b**). A Re[26] complex is the only example of a dithiolato ligand adopting the same coordination mode as that of $S_2C{=}C\{C(O)Me\}_2$ in **6b**, while the coordination mode found in **7b** is unprecedented.

The metal atoms are in all these complexes in essentially planar environments. While the best coordination planes

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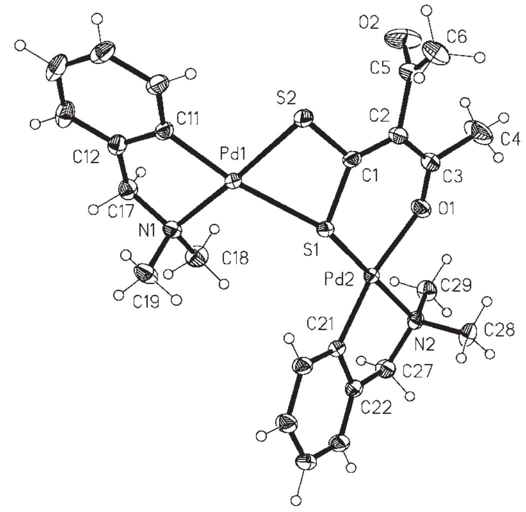


Figure 2. Thermal ellipsoid representation plot (50% probability) of complex **6b** omitting the solvent. Selected bond lengths (Å) and angles (deg): Pd(1)−C(11) 1.9887(15), Pd(2)−C(21) 1.9875(15), Pd(1)−N(1) 2.1037(13), Pd(2)−N(2) 2.1061(13), Pd(1)−S(1) 2.4422(4), Pd(1)−S(2) 2.2908(4), Pd(2)−S(1) 2.2459(4), Pd(2)−O(1) 2.0886(11), S(1)−C(1) 1.7462(15), S(2)−C(1) 1.7479(16), C(1)−C(2) 1.382(2), C(2)−C(3) 1.432(2), C(2)−C(5) 1.514(2),C(5)−C(6) 1.497(3), O(1)−C(3) 1.258(2), O(2)−C(5) 1.217(2); C(11)−Pd(1)−N(1) 82.35(6), C(11)−Pd(1)−S(2) 96.83(5), N(1)−Pd(1)−S(1) 108.16(4), S(2)−Pd(1)−S(1), 72.940(14), C(21)−Pd(2)−N(2) 83.06(6), O(1)−Pd(2)−N(2) 89.11(5), C(21)−Pd(2)−S(1) 94.79(4), O(1)−Pd(2)−S(1) 92.33(3).

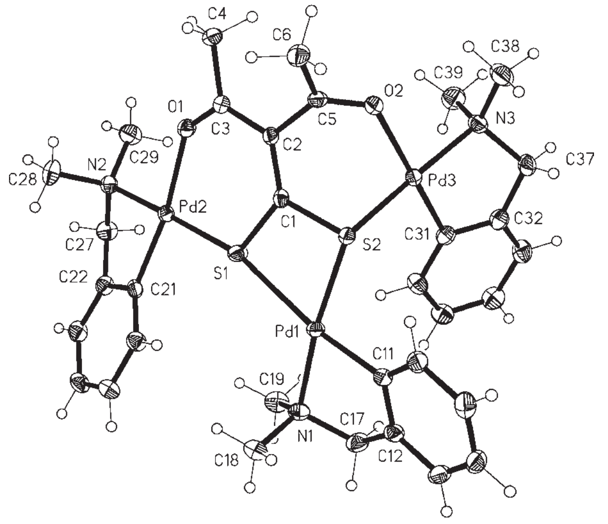
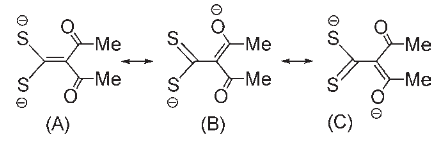


Figure 3. Thermal ellipsoid representation plot (50% probability) of complex **7b** omitting the solvent and the anion. Selected bond lengths (Å) and angles (deg): Pd(1)−C(11) 1.981(3), Pd(2)−C(21) 1.971(3), Pd(3)−C(31) 1.971(3), Pd(1)−N(1) 2.112(3), Pd(2)−N(2) 2.110(3), Pd(3)−N(3) 2.097(3), Pd(1)−S(1) 2.4798(8), Pd(1)−S(2) 2.2873(8), Pd(2)−O(1) 2.101(2), Pd(2)−S(1) 2.2342(8), Pd(3)−O(2) 2.181(2), Pd(3)−S(2) 2.3068(8), S(1)−C(1) 1.711(3), S(2)−C(1) 1.776(3), C(1)−C(2) 1.391(4), C(2)−C(3) 1.445(4), C(2)−C(5) 1.493(4), O(1)−C(3) 1.250(4), O(2)−C(5) 1.234(4); C(11)−Pd(1)−N(1) 82.06(11), C(11)−Pd(1)−S(2) 94.39(9), S(2)−Pd(1)−S(1) 71.56(3), N(1)−Pd(1)−S(1) 113.00(8), C(21)−Pd(2)−N(2) 82.47(11), O(1)−Pd(2)−N(2) 93.01(9), O(1)−Pd(2)−S(1) 91.83(6), C(21)−Pd(2)−S(1) 93.72(9), C(31)−Pd(3)−N(3) 81.92(12), N(3)−Pd(3)−O(2) 96.79(9), O(2)−Pd(3)−S(2) 79.40(6), C(31)−Pd(3)−S(2) 102.26(10). Pd(1)···H(36) 2.55.

of Pd(1) and Pd(2) in **7b** are almost coplanar (11°), that of Pd(3) is nearly perpendicular to them, because of the steric hindrance between arenes C(11)···C(16) and C(31)···C(36), which adopt this disposition instead of a less crowded one because the C/S *transphobia*[39] is larger than the C/O one. In most of the structurally characterized Pd(II) complexes bearing simultaneously C-, O-, and S-donor ligands, C is *trans* to O,[40] and the few cases with C *trans* to S are forced by the geometry of the ligands, or by the C/C-[41] or C/P[42] *transphobia* being higher than the C/S one, with only two exceptions.[43,44]

Chart 3



The M−S bond distances *trans* to C are significantly longer than those *trans* to N, as expected for the larger *trans* influence of C- than of N-donor ligands, which is partly responsible for the differences in the activation energy of the dynamic processes capable of interconverting in solution the $\{M(C,N\text{-}C_6H_4CH_2NMe_2\text{-}2)\}$ groups in complexes **6** and **7** and making equivalent the two acetyl groups in all complexes.

The bond distances within the dithiolato fragments are within the intervals found for other 2,2-diacetyl-1,1-ethylenedithiolato complexes[5,8,14,17,18,21] and reflect somehow the different contribution of the resonance forms **A**−**C** (see Chart 3), depending on the coordination mode of the ligand, the electronegativity of the metal, and the neutral (**1**, **6b**) or charged (**7b**) nature of the complex. Thus, the C(1)−C(2) bond distances are intermediate between the $C(sp^3)-C(sp^3)$ and $C(sp^2)=C(sp^2)$ typical values,[45] and increase with the number of metal centers. The coordination of one acetyl group to Pd(2) in **6b** or **7b** causes the lenghthening the C(3)−O(1) and the shortening of C(2)−C(3) [**6b**: 1.258(2) and1.432(2); **7b**: 1.250(4), and, 1.445(4) Å, respectively] although, surprisingly, the acetyl group coordinated to Pd(3) in **7b** shows parameters [C(5)−O(2) 1.234(4), C(2)−C(5) 1.493(4) Å] more similar

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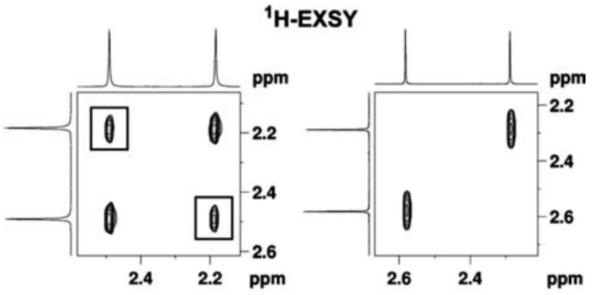


(a) (3) **Exchange**

(b) (1) **No exchange**

Figure 4. Sections of the phase-sensitive ^{1}H-EXSY spectra (600 MHz, $CDCl_3$, room temperature) of complexes **3** (a) and **1** (b), showing, respectively, the presence or absence of exchange cross-peaks between the two acetyl groups.

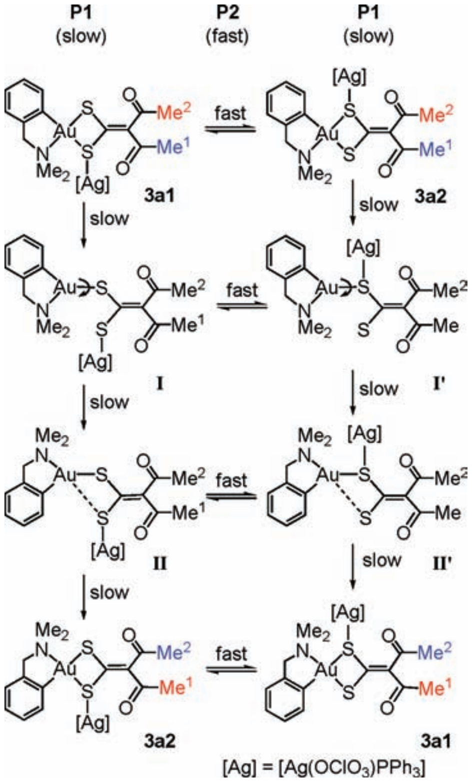
to those found for the *uncoordinated* groups in **6b** (see above) and in **1** [C(3)−O(1) 1.232(7), C(5)−O(2) 1.223(6), C(2)−C(3) 1.474(7), C(2)−C(5) 1.514(2) Å]. This anomaly must be accounted for in terms of the additional influence of steric effects caused, in part, by transphobic reasons (see above).

In the absence of X−ray diffraction data we tentatively assign a polymeric structure to **2** in the solid state, although a dimeric chair structure as that found in some silver−palladium or silver−platinum 2,2-diacetyl-1,1-ethylenedithiolato complexes cannot be ruled out.[14]

NMR Spectra of Gold Complexes. Complexes 1 and 2. The ^{1}H NMR spectrum of **1** in $CDCl_3$ at room temperature shows the two expected resonances for the acetyl protons. In contrast, a single ^{1}H resonance is observed for both the methyl and the methylene protons of the CH_2NMe_2 fragment, suggesting that in solution there is free rotation of the acetyl groups around the C−C(O)Me bonds, as well as sulfur inversion, a common process in organosulfur transition metal complexes.[22,46] Similarly, the $^{13}C\{^1H\}$ NMR spectrum of **1** in $CDCl_3$ shows two resonances for the acetyl groups and a single resonance for the NMe_2 group.

Complex **2** is insoluble in most common solvents. The ^{1}H NMR spectrum in d^6-dmso is identical to the spectrum of complex **1** in the same solvent, suggesting that dmso coordinates to Ag, displacing the dithiolene ligand to give **1** and some Ag-dmso complex. Interestingly, in these ^{1}H NMR spectra of complexes **1** and **2** in dmso there is only a single ^{1}H resonance for the two C(O)Me groups, suggesting that the dmso cleaves the Au−N and/or Au−S bonds, allowing the exchange of coordination positions around the Au atom.

Scheme 3



Complex 3. Room Temperature Spectra. The ^{1}H and ^{13}C NMR spectra of the mixed (Au,Ag) dinuclear complex **3** in $CDCl_3$ are similar to those of complex **1**: two acetyl and one NMe_2 and CH_2 resonances. However, a ^{1}H-EXSY spectrum of **3** in $CDCl_3$ reveals the presence of a slow exchange process between the two C(O)Me groups (Figure 4a).[47] This dynamic behavior is not observed in the ^{1}H-EXSY spectrum of **1**, under the same conditions (Figure 4b). It is reasonable to assume that the exchange between the two acetyl groups in complex **3** takes place by process **P1** (Scheme 3), involving the cleavage of the weakest Au−S bond, namely, that trans to aryl, to give intermediates **I**/**I′**, followed by 180° rotation around the other Au−S bond to give **II**/**II′** and recoordination of S to Au.[48] Simultaneously, a fast exchange of the $[Ag(PPh_3)(OClO_3)]$ moiety between the two S atoms (process **P2**) explains (1) the observation of only two acetyl resonances, instead of the four expected for the two isomers **3a1** and **3a2**, and (2) the different behavior in solution of **1** and **3**, caused by the additional weakening of both Au−S bonds arising from the coordination of Ag to S. This kind of fluxionality is typical in the coordination chemistry of Ag, and there are precedents for such rapid site exchange of Ag between S-donors of the same ligand even at 213 K.[49] More details of this process will be discussed below. The ^{31}P NMR resonances of **3** at room temperature appear as two very broad signals (Figure 5).

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(46) Abel, E. W.; Bhargava, S. K.; Orrell, K. G. *Prog. Inorg. Chem.* **1984**, *32*, 1. Abel, E. W.; Cooley, N. A.; Kite, K.; Orrell, K. G.; Sik, V.; Hursthouse, H. B.; Dawes, H. M. *Polyhedron* **1987**, *6*, 1261. Abel, E. W.; Orrell, K. G.; Poole, M. C.; Sik, V. *Polyhedron* **1999**, *18*, 1345.

(47) Exchange cross-peaks are distinguished from possible NOE peaks because they have the same phase as diagonal peaks. No NOE peaks are observed between the two acetyl groups, neither for **1** nor for **3**. For more information on EXSY/NOESY spectra see: Claridge, T. O. W. *High Resolution NMR Techniques in Organic Chemistry*, 2nd ed.; Elsevier: Boston, 2009.

(48) Another possible mechanism for the slow exchange of the two C(O)Me groups would be rotation around the C-C bond of the dithiolene, thanks to the contribution of resonance forms B and C shown in Chart 3. However, the coordination of Ag to S in complex **3** would favor the resonance form A making the exchange process less favored in **3** than in **1**, which is not the case. Consequently, we think that process P1 in Scheme 3 is the most likely mechanism for the exchange.

(49) Bailey, P. J.; Dawson, A.; McCormack, C.; Moggach, S. A.; Oswald, I. D. H.; Parsons, S.; Rankin, D. W. H.; Turner, A. *Inorg. Chem.* **2005**, *44*, 8884.

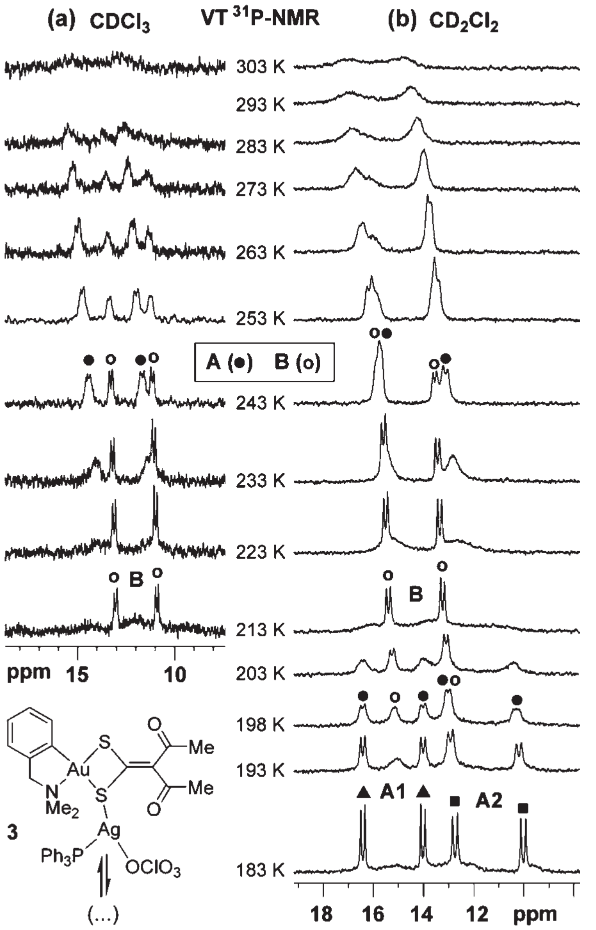
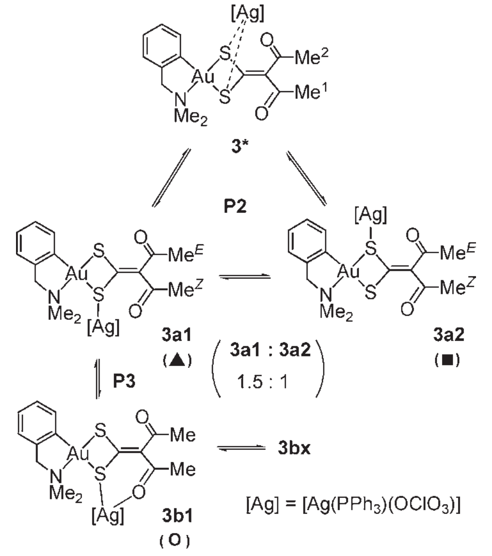


Figure 5. VT ^{31}P NMR spectra (242.9 MHz) of complex **3** in $CDCl_3$ (a) and CD_2Cl_2 (b).

Low Temperature ^{31}P NMR Spectra. When the temperature is decreased, the two broad ^{31}P resonances transform into four resonances that at 243 K resolve into two pairs of doublets (pd),[50] **A**(●) and **B**(○) (Figure 5). The $J_{\mathrm{P^{109}Ag}}$ value in **A** (713 Hz) is similar to others reported in the literature for tricoordinated Ag complexes[51,52] with one P-donor ligand.[53] Thus, the pd **A** seems to correspond to the species **3a1** and **3a2**, which

Scheme 4



at 243 K are still exchanging rapidly the $[Ag(PPh_3)(OClO_3)]$ moiety between the two S atoms (P2 in Schemes 3 and 4). The $J_{\mathrm{P^{109}Ag}}$ value in **B** (554 Hz) is indicative of a tetracoordinated complex[52,54] such as **3b1** (Scheme 4). The tri- (**3a1**/**3a2**) and tetracoordinated (**3b1**) isomers of complex **3** would be in fast exchange at room temperature (process P3, Scheme 4).

Below 243 K the pd **A** starts broadening and virtually disappears at 213 K (while the pd **B** remains[55]) reappearing at lower temperatures (CD_2Cl_2, Figure 5b) as two new sharp pd, **A1**(▲) and **A2**(■), which we assign to **3a1** and **3a2**, respectively. This assignment is based on the J_{PAg} values: both correspond to tricoordinated species ($J_{\mathrm{P^{109}Ag}}$ = 623 and 710 Hz, respectively, at 183 K) and J_{PAg}(**A1**) < J_{PAg}(**A2**). This relationship suggests that the pd **A1** corresponds to the isomer with S trans to C (**3a1**) in which a weaker S−Au bond induces a stronger S−Ag interaction and therefore a weaker Ag−P bond and a lower J_{PAg}. The bond strength sequence $S{-}Ag_{3a1} > S{-}Ag_{3a2}$ is also in agreement with **3a1** being more abundant than **3a2** (^{1}H NMR spectra, see below). For this reason, the most probable structure for the tetracoordinated isomer **3b1** is that with S[Ag] trans to aryl, as drawn in Scheme 4.

A ^{31}P-EXSY spectrum at 183 K (Figure 6a) still reveals exchange cross-peaks between **A1** and **A2**, showing that even at this very low temperature the exchange process P2 is active, although slow. Probably, this exchange occurs through a non-dissociative mechanism involving the momentary coordination of the Ag to both S atoms (Scheme 4; **3*** represents the transition state), as otherwise a complete dissociation of the [Ag] moiety would allow the exchange between tri- and tetracoordinated species (**A**⇔**B**, P3), which according to the ^{31}P NMR spectra clearly has a higher activation energy than process P2 (**A1**⇔**A2**). Below 213 K the pd **B** starts broadening and at 183 K only some humps are visible, suggesting the existence of additional dynamic processes involving **3b1** and other species (Scheme 4, **3bx**), which presumably

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[50] **A**(●): δ 13.4 ppm, $J(^{31}P,^{109}Ag)$ = 713 Hz, $J(^{31}P,^{107}Ag)$ = 634 Hz (at 253 K) and **B**(○): δ 12.2 ppm, $J(^{31}P,^{109}Ag)$ = 554 Hz, $J(^{31}P,^{107}Ag)$ = 484 Hz (at 243 K).

[51] Calhorda, M. J.; Costa, P. J.; Crespo, O.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Naranjo, M.; Quintal, S.; Shi, Y.-J.; Villacampa, M. D. *Dalton Trans.* **2006**, 4104. Carmona, D.; Oro, L. A.; Lamata, M. P.; Jimeno, M. L.; Elguero, J.; Belguise, A.; Lux, P. *Inorg. Chem.* **1994**, *33*, 2196. Santini, C.; Pettinari, C.; Lobbia, G. G.; Spagna, R.; Pellei, M.; Vallorani, F. *Inorg. Chim. Acta* **1999**, *285*, 81. Aguado, J. E.; Canales, S.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Villacampa, M. D. *Dalton Trans.* **2005**, 3005. Crespo, O.; Brusko, V. V.; Gimeno, M. C.; Tornil, M. L.; Laguna, A.; Zabirov, N. G. *Eur. J. Inorg. Chem.* **2004**, 423.

[52] Effendy; Lobbia, G. G.; Marchetti, F.; Pellei, M.; Pettinari, C.; Pettinari, R.; Santini, C.; Skelton, B. W.; White, A. *Inorg. Chim. Acta* **2004**, *357*, 4247.

[53] The presence of a second P-donor ligand usually results in lower J(Ag,P) values. Similarly, the presence of S-donor ligands also decreases the J(Ag,P) values. This effect is stronger as the number of P- or S- donor ligands increases.

[54] Santini, C.; Lobbia, G. G.; Pettinari, C.; Pellei, M.; Valle, G.; Calogero, S. *Inorg. Chem.* **1998**, *37*, 890. Canales, S.; Crespo, O.; Fortea, A.; Gimeno, M. C.; Jones, P. G.; Laguna, A. *J. Chem. Soc., Dalton Trans.* **2002**, 2250. Römbke, P.; Schier, A.; Schmidbaur, H. *Z. Naturforsch., Sect. B* **2003**, *58*, 168.

[55] ^{31}P NMR of complex **3** part **B** at 213 K in CD_2Cl_2: δ 14.3 ppm, $J(^{31}P,^{109}Ag)$ = 558 Hz, $J(^{31}P,^{107}Ag)$ = 485 Hz.

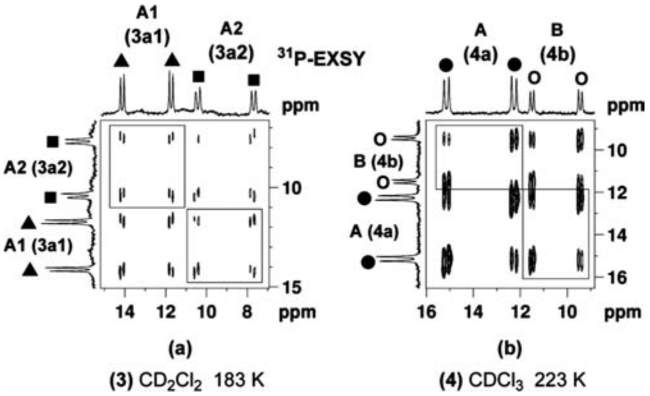

Figure 6. Section of the low-temperature ^{31}P-EXSY spectra (242.9 MHz) of complexes **3** (a) and **4** (b). The absence of mixed ^{31}P-^{109}Ag/^{31}P-^{107}Ag cross-peaks is an indication that the exchange occurs without phosphine dissociation.

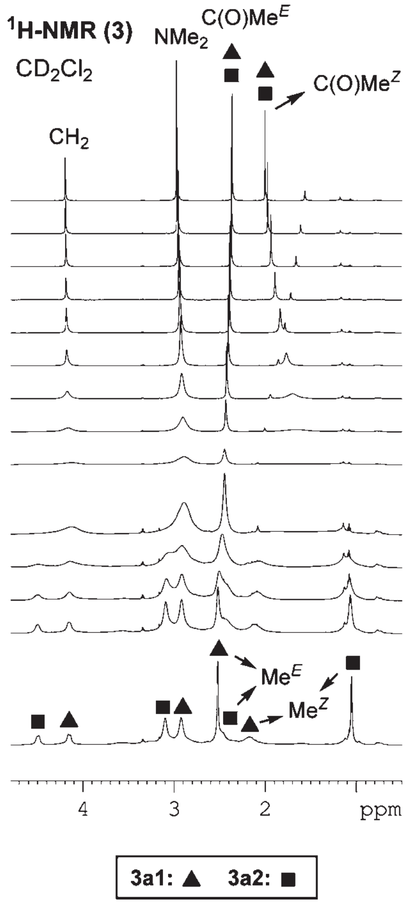

Figure 7. Section of the VT ^{1}H NMR spectra of **3** (600 MHz, CD_2Cl_2). The vertical scaling of the spectra is different in the upper (293−213K) and lower (213−183K) part of the figure.

would also be tetracoordinated. These dynamic processes should also be non-dissociative, as discussed for process P2.

Low Temperature ^{1}H NMR Spectra. Figure 7 and Supporting Information, Figure SI1 show the VT ^{1}H NMR spectra of **3**. As the temperature is decreased, the C(O)Me signal at lower frequency broadens faster than the rest of the spectrum. We assign this resonance to the Me^{Z} (pseudo-cis to the NMe_2 moiety, Scheme 4), which is more affected by the dynamic process P3. Below 213 K (Figure 7) we can observe a gradual splitting of the ^{1}H resonances into two major sets, in about 1.5:1 molar ratio, which we assign to **3a1**(▲) and **3a2**(■). Some additional very broad resonances would correspond to **3b1**/**3bx** (Supporting Information, Figure SI1). Interestingly, each of the two room temperature acetyl resonances resolves at 183 K into a narrow and a broad resonance. We assign the broad resonances to the Me groups cis to the [Ag] moiety in each of the isomers, that is, Me^{Z} in **3a1**(▲) and Me^{E} in **3a2**(■) (Scheme 4), as the rotation of these acetyl groups around the C−C(O)Me bonds should be slowed down by the presence of the bulky [Ag] fragment.

Complex 4. For the mixed (Au,Ag) nitrate complex **4** the room temperature ^{1}H and ^{13}C NMR spectra in $CDCl_3$ are almost identical to those of **3**, with two acetyl signals and single resonances for the NMe_2 and CH_2 groups. Supporting Information, Table SI1 provides a comparison of the NMR data of **1**, **3**, and **4**. However, the room temperature ^{1}H-EXSY spectrum of **4** (Supporting Information, Figure SI2a) does not show exchange cross-peaks[47] between the two C(O)Me groups, as opposed to **3** and in analogy with **1** (Figure 4). Nonetheless, when the temperature is increased to 333 K (Supporting Information, Figure SI2b) such cross-peaks appear, reflecting a slow exchange between the two acetyl groups and, correspondingly, a higher activation energy for this process in **4** than in **3**. This observation is in agreement with the stronger Ag−O bond expected for Ag−ONO_2 compared to Ag−$OClO_3$,[56] which would weaken the AuS−Ag bond in **4** and strengthen the Au−SAg bond, resulting in a higher activation energy for the exchange of the two acetyl groups in **4** with respect to **3**, according to the mechanism proposed for process P1 in Scheme 3.

The VT ^{31}P NMR spectra of **4** in $CDCl_3$ and CD_2Cl_2 are shown in Figure 8. At the higher temperatures the spectra are similar to those of **3**: two broad humps that resolve below 243 K into two pd's **A**(●) ($J_{\mathrm{P}^{109}\mathrm{Ag}}$ = 751 Hz) and **B**(○) ($J_{\mathrm{P}^{109}\mathrm{Ag}}$ = 536 Hz) ($CDCl_3$, 223 K). However, at the lower temperatures these ^{31}P resonances do not split or disappear (in contrast to **3**), although the pd **A** broadens below 220 K. The VT ^{1}H NMR spectra of **4** (Figure 8) are also similar to those of **3** for the higher temperatures but again, upon cooling, the resonances do not split, even at 168 K. These data agree with the mentioned weaker S−Ag bonds in **4** than in **3**, that decrease the activation energy for the [Ag] exchange within the tricoordinated isomers. A ^{31}P-EXSY spectrum of **4** at 223 K (Figure 6b) shows that the exchange between the 3- and 4-coordinated isomers (**4a** ⟺ **4b**, P3) also occurs without dissociation of the PPh_3 (similar to the site exchange process **3a1** ⟺**3a2**, P2, Scheme 4).

NMR Spectra of Palladium Complexes. In contrast to its analogous Au(III) complex **1** (and its derivatives **3** and **4**), the mononuclear Pd(II) complexes **5a**,**b** show only one C(O)Me resonance in the ^{1}H and ^{13}C NMR spectra at room temperature. This is because the Pd(II)−S bond is weaker than the Au(III)−S bond, which causes a faster exchange of the acetyl groups in **5a**,**b** with respect to **3** (process P1, Scheme 3). However, complexes **5a**,**b** resemble

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(56) Ashworth, R. S.; Prout, C. K.; Domenicano, A.; Vaciago, A. *J. Chem. Soc. A* **1968**, 93. Lin, C.-J.; Hwang, W.-S.; Chiang, M. Y. **2001**, *20*, 3275.

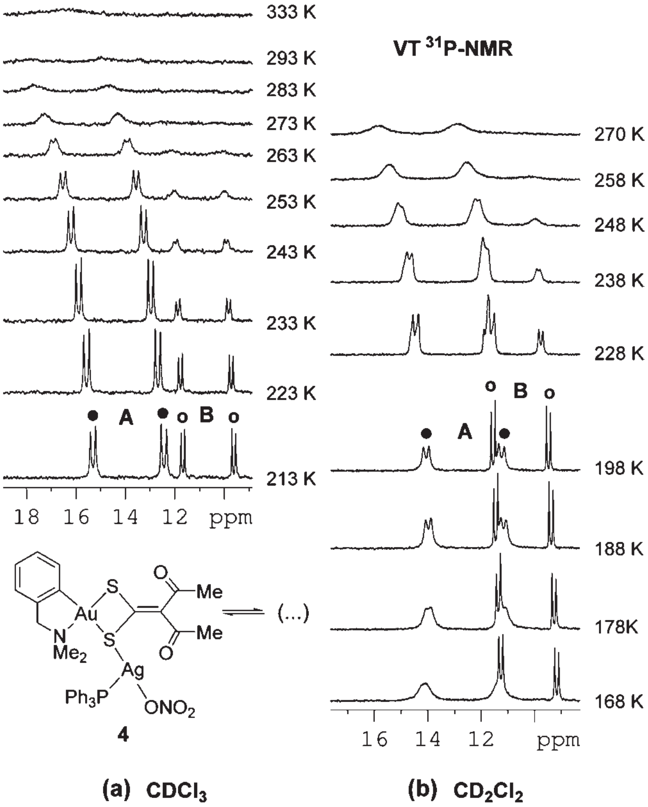


Figure 8. VT ^{31}P NMR spectra of complex **4** in CDCl$_3$ (a) and CD$_2$Cl$_2$ (b).

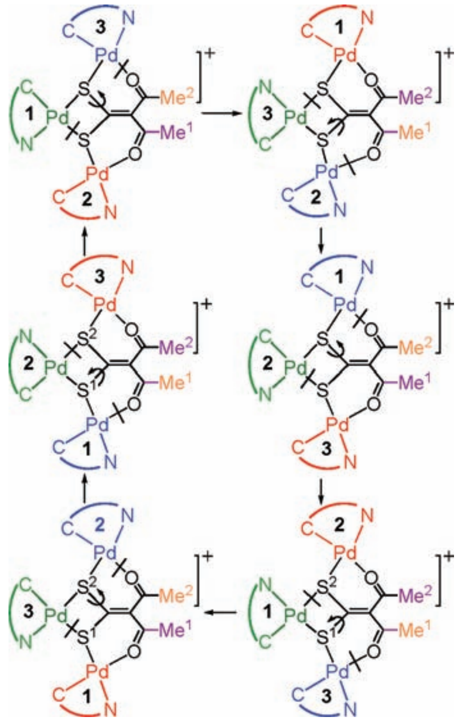
1 in showing CH$_2$ and NMe$_2$ singlets at room temperature, which proves the existence of sulfur inversion and free rotation around the C−C(O)Me bonds. A series of VT ^{1}H NMR spectra of **5b** (Supporting Information, Figure SI3) shows that below 218 K the exchange between the two acetyl groups is frozen (at 183 K there are two Me resonances), while the singlet (although broadened) CH$_2$ and NMe$_2$ resonances remain even at 183 K.

The NMR spectra of the di- and trinuclear complexes **6a** and **7a** have been measured in d^6-dmso because of their insolubility in other common deuterated solvents (Supporting Information, Figures SI6 and SI7). At 298 K the dinuclear complex **6a** shows two resonances for the C(O)Me, CH$_2$, and NH$_2$ groups. When the temperature is increased above 333 K (Supporting Information, Figure SI6), these two sets of ^{1}H resonances merge into a single set, showing that a dynamic process makes equivalent the pair of [Pd(C$_6$H$_4$CH$_2$NH$_2$)] fragments, as well as the two acetyl groups. For the trinuclear complex **7a** the ^{1}H NMR spectra in d^6-dmso are somewhat more complicated at room temperature (Supporting Information, Figure SI7), while at 363 K a single set of resonances is observed except for the three NH$_2$ groups, which afford a 1:2 pattern, probably caused by different NH-dmso hydrogen bond interactions. The high melting point of dmso prevents the further investigation of these complexes.

At room temperature, the dinuclear complex **6b** (CD$_2$Cl$_2$) shows the same ^{1}H NMR pattern as **6a** (two resonances for the C(O)Me, CH$_2$, and NH$_2$ groups). When the temperature is decreased the CH$_2$ and NMe$_2$ singlets broaden, although they do not resolve even at 168 K (see Supporting Information, Figure SI8). Above room temperature a broadening of the ^{1}H resonances is also observed, which results in the near-coalescence of the two sets of resonances at 323 K. We attribute this broadening to a dynamic process that would slowly make the pair of [Pd(C$_6$H$_4$CH$_2$NMe$_2$)] fragments equivalent, as well as the two acetyl groups, in the same way as for **6a**. Indeed, the ^{1}H EXSY spectrum of **6b** at room temperature (Supporting Information, Figure SI9) already shows exchange cross-peaks between the two sets of resonances. For this dynamic process we propose an equilibrium (Scheme 5) involving the cleavage of the Pd−O and Pd−S^1 bonds (both trans to the aryl groups), rotation around the C−S bonds and recoordination of the [Pd(C$_6$H$_4$CH$_2$NMe$_2$)] fragments to the dithiolene. This process is favored by the strong trans influence of the aryl groups, the weak Pd−O bond, and the μ^2 character of the S^1 atom. Indeed, in the X-ray structure of **6b** the Pd^1−S^1 distance (2.44 Å) is longer than for Pd^1−S^2 (2.29 Å).

Scheme 5. Proposed Dynamic Process in **6b**

Scheme 6. Proposed Mechanism for the Dynamic Process That Exchanges the Three [Pd(C$_6$H$_4$CH$_2$NMe$_2$)] Moieties, and Also the Two Acetyl Groups, in **7b**



We have already described in a preliminary communication[22] the dynamic behavior of the trinuclear complex **7b** in CD$_2$Cl$_2$. At room temperature we found a single set of ^{1}H resonances for the three [Pd(C$_6$H$_4$CH$_2$NMe$_2$)] groups, and a single resonance for the two acetyl groups (Supporting Information, Figure SI13). Scheme 6 shows our proposal to explain this behavior, which involves the cleavage of Pd−O and Pd−S bonds trans to the aryl

Table 2. Activation Parameters for the Fluxional Processes in **2**[a]

	5b		**6b**		**7b**	
process	PI	PII	PI	PII	PI	PII
E_{a}[b]	79(5)	*d*	54(3)	17.5	33.0(0.9)	30.9(1.5)
$\Delta H^{\ddagger}$[b]	77(4)	*d*	51(3)	16.0	31.0(0.7)	29.0(1.2)
$\Delta S^{\ddagger}$[c]	147(20)	*d*	−46(10)	*d*	−72(3)	−64(5)
$\Delta G^{\ddagger}_{298\mathrm{K}}$[b]	33.2(1.6)	*d*	64.7(0.0)	*d*	52.5(0.2)	48.1(0.3)

[a] Standard deviations in parentheses. [b] In $\mathrm{kJ \cdot mol^{-1}}$. [c] In $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. [d] Not determined.

groups, followed by rotation around a C−S bond and isomerization of one of the palladacycles before recoordination to the dithiolene. Thus, if we use colors to characterize the relative position of the groups in the molecule, in the six-step sequence each of the palladacycles (1, 2, or 3) is twice green, red, or blue, and each of the acetyl groups is three times orange or violet.

When the temperature is decreased (Supporting Information, Figure SI13) the ^{1}H resonances resolve as expected for a static situation: two C(O)Me, six NMe, and several methylenic and aromatic resonances. These have all been assigned with the help of 2D NMR spectroscopy at 178 K (Supporting Information, Figures SI14−16). Notably, the resonances of the CH_2NMe_2 protons at 178 K are still broad, most probably because sulfur inversion at this temperature is still slow.

Activation Parameters for Pd Complexes. As described above, we have found in the CD_2Cl_2 solutions of the Pd complexes **5b**, **6b**, and **7b** two types of dynamic processes: one of them (PI) makes the two acetyl groups equivalent, as well as (for **6b** and **7b**) all the palladacycles (Schemes 5 and 6); the second (PII) is a sulfur inversion process, that makes the two faces of the molecules equivalent. Supporting Information, Table SI3 compares the relative speed of these processes in the three complexes, as observed in the ^{1}H NMR spectra. A line shape analysis of some of the ^{1}H resonances has allowed the determination of the activation parameters shown in Table 2. The details of the calculations can be found in the Supporting Information.

For **5b** the activation energy for process PI is in agreement with Pd−S bond dissociation energies calculated for Pd complexes, which are between 60 and 100 $\mathrm{kJ \cdot mol^{-1}}$.[57] In the di- and trinuclear complexes **6b** and **7b**, the additional palladacycles would withdraw more electron density from the dithiolene, weakening the Pd−S and Pd−O bonds and thus resulting in lower E_{a} and $\Delta H^{\ddagger}$ values for PI as the nuclearity increases. The negative $\Delta S^{\ddagger}$ values in **6b** and **7b** are also in agreement with the proposed mechanisms, in which two palladacycles rotate simultaneously in a highly ordered and sterically crowded transition state. The steric interactions would be more important in **7b**. As for $\Delta G^{\ddagger}$ at 298 K, this parameter finds its largest value for the dinuclear complex **6b**, as a result of the balance between enthalpic and entropic effects. Indeed, **6b** is the only complex in the series for which process PI is still slow at room temperature, resulting in two C(O)Me resonances.

For the sulfur inversion process (PII), E_{a} and $\Delta H^{\ddagger}$ are low for **6b** and somewhat larger for **7b**, probably because of its more rigid structure. The negative $\Delta S^{\ddagger}$ value for **7b** is also in agreement with steric interactions in the transition state,[58] and the $\Delta G^{\ddagger}_{298\mathrm{K}}$ value of 48.1 $\mathrm{kJ \cdot mol^{-1}}$ is in very good agreement with the values reported for sulfur inversion processes in other Pd complexes, which are around 50 $\mathrm{kJ \cdot mol^{-1}}$.[46]

IR Spectra. The IR spectra of solid samples of complexes **1**−**7** show one or two bands in the 1700−1500 $\mathrm{cm^{-1}}$ region (see Experimental Section) previously assigned in related compounds to coupled ν(C=O) and ν(C=C) modes.[4] The energy lowering of the band above 1600 $\mathrm{cm^{-1}}$ can be related to conjugation within the acetyl and dithiolato moieties[5] or to coordination of the carbonyl oxygen to a metal center.[17] Two intense bands in the spectrum of **1** at 1636 and 1623 $\mathrm{cm^{-1}}$ show the extensive conjugation allowed by the moderate rotation of both acetyl groups out of the plane of the dithiolato ligand observed in the crystal structure (torsion angles of the planes C(2)−C(5)−O(2) and C(2)−C(3)−O(1) with respect to the C(2)=C(1)S(1)S(2) plane 23° and 31°, respectively). This data agrees with those of PPN[$AuCl_2$-{S_2C_2{C(O)Me}$_2$}][5] containing an almost planar dithiolato ligand and showing only one IR absorption at 1630 $\mathrm{cm^{-1}}$. The spectra of complexes **2**−**4** (see Experimental Section, $\Delta\nu$ = 18−35 $\mathrm{cm^{-1}}$) suggest somewhat larger torsion angles of both acetyl groups. In the palladium complexes **5** and **6** the great separation of the two very intense absorptions observed in the 1700−1500 $\mathrm{cm^{-1}}$ region ($\Delta\nu$ = 100 and 144 $\mathrm{cm^{-1}}$, respectively) suggests slight conjugation of the C=O and C=C bonds in the dithiolato ligand as confirmed in the crystal structure of **6a** with one of the acetyl groups rotated by 69° with respect to the C(2)=C(1)S(1)S(2) plane. The ν(C−S), ν(S−C−S),[59] and ν(Au−S)[60] bands, assigned in very few cases at 860−780, 670−712, and 380−362 $\mathrm{cm^{-1}}$, can not be unambiguously assigned in our complexes. Five perchlorato bands in the spectra of **2** and **3** are indicative of its coordination.

Conclusion

The reported complexes show the flexibility of the 2,2-diacetyl-1,1-ethylenedithiolato ligand to coordinate one, two, or three metal centers with different coordination modes. The presence of the 2-(aminomethyl)phenyl ligand produces the weakening of the M−S bond trans to the aryl carbon, which causes interesting fluxional processes in solution. Thus, we have found for the mixed (Au, Ag) complexes **3** and **4** three different dynamic processes in solution. P1 (Scheme 3): involving the exchange of the two acetyl groups, caused by the cleavage of the Au−S bond trans to aryl and the coordination to S of the [Ag] fragment. This process is only important above room temperature and easier in **3** than in **4**, that is, E_{a}(P1, **3**) < E_{a}(P1, **4**). P2 (Schemes 3 and 4): in which an exchange of the [$Ag(PPh_3)Y$] (Y = $OClO_3$, ONO_2) moiety between the two S atoms of the dithiolene takes place via a non-dissociative process. This process is very fast at room temperature and only becomes slow below 190 K; in addition, E_{a}(P2, **3**) > E_{a}(P2, **4**). P3 (Scheme 4): involving the change

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(57) Brust, D. J.; Gilbert, T. M. **2004**, *43*, 1116.

(58) Murray, R.; Story, P.; Kaplan, M. *J. Am. Chem. Soc.* **1966**, *88*, 526. Powell, J.; Jack, T. *Inorg. Chem.* **1972**, *11*, 1039.

(59) Chiari, B.; Piovesana, O.; Tarantelli, T.; Zanazzi, P. F. *Inorg. Chem.* **1985**, *24*, 366.

(60) Beurskens, P. T.; Blaauw, H. J. A.; Cras, J. A.; Steggerda, J. J. *Inorg. Chem.* **1968**, *7*, 805.

between 3- and 4- coordination for the Ag atom. This process is fast at room temperature, becomes slow around 250 K and E_a(P3, **3**) ≈ E_a(P3, **4**). For complexes **3** and **4**, E_a (P1) > E_a (P3) > E_a (P2). For the complexes **5b**, **6b**, and **7b** we have found two types of dynamic processes in solution: a sulfur inversion process (PII) and an exchange of positions between palladacycles (PI), which also makes the two acetyl groups equivalent.

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Supporting Information Available: CIF files for the crystal structures of **1**, **6b**·CH_2Cl_2 and **7b**·CH_2Cl_2, additional 2D and VT NMR spectra, tables with NMR data, details on the line shape analysis for complexes **5b**, **6b**, and **7b**, and proposed mechanism for the dynamic behavior of **7b**. This material is available free of charge via the Internet at http://pubs.acs.org.