Synthesis and Reactivity of Heteroleptic Complexes of Gold with 2-Thioxo-1,3-dithiole-4,5-dithiolate (dmit). X-ray Structure of [Au_2(μ-dmit)(PPh_3)$_2$], (NBu_4)[Au(dmit)(PPh_3)], and (PPN)[Au(dmit)(C_6F_5)$_2$]

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The reactions of Na_2dmit (dmit = 2-thioxo-1,3-dithiole-4,5-dithiolate) with AuClL in 1:2 ratios lead to [Au_2(dmit)L_2] [L = PPh_3 (**1**), PPh_2Me (**2**), $PPhMe_2$ (**3**), PMe_3 (**4**), CH_2PPh_3 (**5**), CH_2PPh_2Me (**6**), CH_2PPhMe_2 (**7**)]. Complexes **1**, **2**, and **5** react further with equimolecular amounts of [AuL(tht)]ClO_4 (tht = tetrahydrothiophene), affording trinuclear complexes [Au_3(dmit)L_3]ClO_4 (**8**−**10**). When the reactions of Na_2dmit with AuClL are carried out in 1:1 ratios and in the presence of NBu_4Br, mononuclear tricoordinated gold(I) complexes NBu_4[Au(dmit)L] [L = PPh_3 (**11**), PPh_2Me (**12**), PMe_3 (**13**)] are obtained. Other anionic derivatives such as (PPN)$_2$[Au_2(dmit)X_2] [X = C_6F_5 (**14**), Cl (**15a**), Br (**15b**)] can be obtained either by reaction of Na_2dmit with Q[Au(C_6F_5)X] in 1:2 ratio or by addition of (PPN)X to the recently reported [Au_2(dmit)($AsPh_3$)]. Oxidative reactions of **11**, **12**, and **14** or **15b** with excess (TTF)$_3$(BF_4)$_2$ afford (TTF)$_2$[Au(dmit)$_2$] (**16**), (TTF)[Au_2(dmit)(C_6F_5)$_2$] (**17**), and (TTF)$_3$[Au_2(dmit)Br_2] (**18**), respectively. Reaction of complex **14** with TCNQ gives the anionic gold(III) complex [Au(dmit)(C_6F_5)$_2$]$^-$ (**19**). Electrical conductivities of these complexes at room temperature in compacted pellets are 2×10^{-3} (**16**), 7×10^{-5} (**17**), and 2×10^{-2} (**18**) $S \cdot cm^{-1}$. Electrocrystallization of **1** and **11** affords [Au_2(dmit)$_2$(PPh_3)] (**20**) and the known NBu_4[Au(dmit)$_2$], respectively. X-ray structure determinations were performed for complexes **1**, **11**, and **19b**.

Introduction

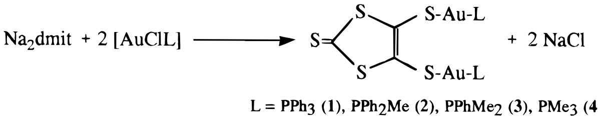
Metal complexes of the dmit [2-thioxo-1,3-dithiole-4,5-dithiolate ($C_3S_5^{2-}$)] ligand have received considerable attention in the last two decades,[1,2] because some of them were reported to exhibit high conductivities. After the discovery in 1986 of the first formally inorganic molecular superconductor[3] (TTF)-[Ni(dmit)$_2$] (TTF = tetrathiafulvalene), the research activity in this area was increased, and several (cation)$_x$[M(dmit)$_2$] compounds (cation = TTF, NMe_4)[3−8] have been synthesized that show superconducting properties, including the recently reported (α-EDT-TTF)[Ni(dmit)$_2$], which is superconducting at ambient pressure.[9]

Although nonplanar dmit−metal complexes are also expected to behave as conductors on the basis of multidimensional overlapping through the sulfur atoms of dmit ligands, few nonplanar dmit−metal complexes have been studied.[10−14] Furthermore many of the known dmit complexes are homoleptic; only a few dmit complexes containing other ligands have been reported, including [Au_2(dmit)(PPh_3)$_2$], [Au_3(dmit)(PPh_3)$_3$]ClO_4, and [Au_4(dmit)$_2$(dppm)$_2$] recently reported by us.[15]

This paper reports a synthetic study of heteroleptic gold(I) derivatives [Au_2(dmit)L_2], [Au_3(dmit)L_3]ClO_4, (NBu_4)[Au(dmit)L], and (PPN)$_2$[Au_2(dmit)X_2] and the products of reactions with (TTF)$_3$(BF_4)$_2$ and with TCNQ or electrochemical oxidation. The molecular structures of [Au_2(μ-dmit)(PPh_3)$_2$], (NBu_4)[Au(dmit)(PPh_3)], and (PPN)[Au(dmit)(C_6F_5)$_2$] have been established by single-crystal X-ray studies, showing that dmit can act as a bridging or chelate ligand in gold chemistry.

Results and Discussion

The reaction of a methanolic solution of Na_2dmit with chlorogold(I) complexes [AuClL] (L = phosphine or ylide) in a molar ratio of 1:2 leads to dinuclear complexes where the dmit ligand acts as a bridge between two gold centers (eq 1).



L = PPh_3 (**1**), PPh_2Me (**2**), $PPhMe_2$ (**3**), PMe_3 (**4**), CH_2PPh_3 (**5**), CH_2PPh_2Me (**6**), CH_2PPhMe_2 (**7**) (1)

Complexes **1**−**7** are dark yellow (**1**, **3**), red (**2**, **4**), and garnet (**5**−**7**) solids, air- and moisture-stable at room temperature. They

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(1) Cassoux, P.; Valade, L.; Kobayashi, H.; Kobayashi, A.; Clark. R. A.; Underhill, A. E. *Coord. Chem. Rev.* **1991**, *110*, 115.

(2) Olk, R. M.; Olk, B.; Dietzsch, W.; Kirmse, R.; Hoyer, E. *Coord. Chem. Rev.* **1992**, *117*, 99.

(3) Brossard, L.; Ribault, M.; Bousseau, M.; Valade, L.; Cassoux, P. *C. R. Acad. Sci. Paris, Ser. 2*, **1986**, *302*, 205.

(4) Kobayashi, A.; Kim, H.; Sasaki, Y.; Kato, R.; Kobayashi, H.; Moriyama, S.; Nishio, Y.; Kajita, K.; Sasaki, W. *Chem. Lett.* **1987**, 1819.

(5) Brossard, L.; Hundequint, H.; Ribault, M.; Valade, L.; Legros, J. P.; Cassoux, P. *Synth. Met.* **1988**, *27*, B157.

(6) Brossard, L.; Ribault, M.; Valade, L.; Cassoux, P. *J. Phys. Fr.* **1989**, *50*, 1521.

(7) Kobayashi, A.; Kobayashi, H.; Miyamoto, A.; Kato, R.; Clark, R. A.; Underhill, A. E. *Chem. Lett.* **1991**, 2163.

(8) Kobayashi, H.; Bun, K.; Naito, T.; Kato, R.; Kobayashi, A. *Chem. Lett.* **1992**, 1909.

(9) Tajima, H.; Inokuchi, M.; Kobayashi, A.; Ohta, T.; Kato, R.; Kobayashi, H.; Kuroda, H. *Chem. Lett.* **1993**, 1235.

(10) Matsubayashi, G.; Akiba, K.; Tanaka, T. *Inorg. Chem.* **1988**, *27*, 4744.

(11) Akiba, K.; Matsubayashi, G.; Tanaka, T. *Inorg. Chim. Acta* **1989**, *165*, 245.

(12) Broderick, W. E.; McGhee, E. M.; Cogfrey, M. R.; Hoffman, B. M.; Ibers, J. A. *Inorg. Chem.* **1989**, *28*, 2904.

(13) Matsubayashi, G.; Yokozawa, A. *J. Chem Soc., Chem. Commun.* **1991**, 68.

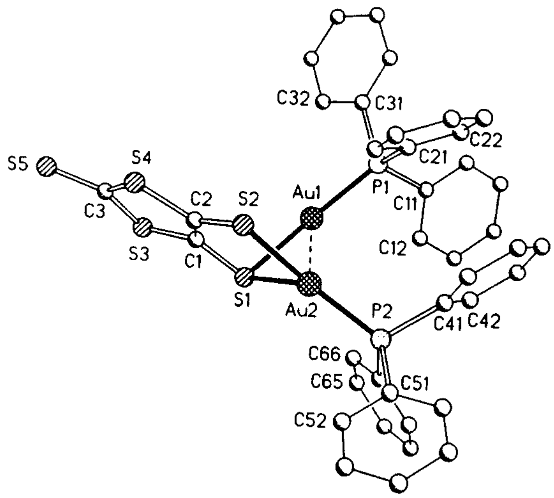


Figure 1. Molecule of complex **1** in the crystal (50% ellipsoids). H atoms are omitted.

are nonconducting in acetone solution ($\approx 5 \times 10^{-4}$ M). Their IR spectra show two bands at *ca.* 1050 (s) and 1034 (m) cm^{-1} that are assignable to v(C=S)[16] of the dmit ligand, a band at 1436 (s) cm^{-1} due to v(C=C), and a band at *ca.* 580 (m) cm^{-1} assignable to v(Au−C$_{\text{ylide}}$)[17] (**5**−**7**). Their ^{31}P{^{1}H} NMR spectra each show a singlet, consistent with the presence of two equivalent phosphorus atoms (see Table 1). The FAB$^+$ mass spectra for these complexes (NBA as matrix) show the [M$^+$] peak at *m/z* = 1114 (55%, **1**), 990 (15%, **2**), 865 (100%, **3**), 742 (100%, **4**), 1142 (40%, **5**), 1018 (13%, **6**), and 894 (28%, **7**). It is notable that peaks are present with higher *m/z* values corresponding to [M + AuL]: 1573 (16%, **1**), 1387 (20%, **2**), 1015 (18%, **4**), 1415 (45%, **5**), and 1265 (16%, **6**).

The structure of complex **1** has been established by X-ray diffraction. The molecule is shown in Figure 1. Selected bond lengths and angles are given in Table 3. As expected, the dmit ligand bridges the two gold atoms through the sulfur atoms; however, the mode of coordination is markedly nonsymmetric. The linear coordination at Au(1) is typical of Au(I) complexes [S(1)−Au(1)−P(1) = 174.86(3)°], but the angle S(2)−Au(2)−P(2) at Au(2) deviates considerably from linearity [159.32(4)°], associated with a pseudotrigonal geometry including an extra weak interaction Au(2)−S(1) = 2.823(1) Å; Au(2) lies only 0.04 Å out of the plane of P(2), S(1), and S(2). There is a intramolecular gold−gold contact of 3.0681(8) Å. The shorter Au−S distances [S(1)−Au(1) = 2.347(1), S(2)−Au(2) = 2.344(1) Å] are very similar to those found for other gold dithiolate complexes [$Au_2(\mu$-*i*-MNT)$(PPh_3)_2$] [2.321(4), 2.313(2) Å][18,19] and [$Au_2(\mu$-$S_2C_6H_4)(PPh_3)_2$] [2.322(4) Å].[18] Similar distorted three-coordinate structures have been reported by Fackler and Schmidbaur using other dithiolates.[18−21]

Although the molecular structure shows two different Au−PPh$_3$ fragments, the ^{31}P NMR spectrum consists of only one resonance, because of fluxional behavior involving the two Au−P units in solution, even at low temperature (−80 °C in HDA).

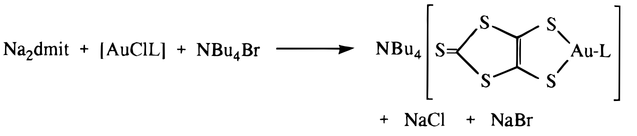
Mass spectrometry data for complexes **1**−**7** indicate that a further AuL unit could be incorporated into those complexes; thus, the reaction of complexes **1**, **2**, and **5** with "[AuPPh$_3$]$^+$" (generated *in situ* from AuClL and AgClO$_4$) or with [AuL(tht)]ClO$_4$ (tht = tetrahydrothiophene) leads[18b] to trinuclear complexes **8**−**10** (eq 2).

$$[Au_2(\mu\text{-dmit})L_2] + [AuL(tht)]ClO_4 \rightarrow [Au_3(\mu_3\text{-dmit})L_3]ClO_4 + \text{tht} \quad (2)$$
$$L = PPh_3\ (\mathbf{8}),\ PPh_2Me\ (\mathbf{9}),\ CH_2PPh_3\ (\mathbf{10})$$

^{31}P NMR spectra of these compounds at room temperature each show a broad signal, which is resolved into two singlets with a 2:1 intensity ratio at −80 °C. Complex **8** at low temperature shows a broad singlet with a shoulder.

The structure of complex **8** has been reported previously by us; it is very similar to that of complex **1**, with one extra Au−PPh$_3$ fragment bonded through the thione group of the dmit ligand.[15] Presumably complexes **9** and **10** are further examples of this μ_3-dmit coordination mode.

When reaction 1 is carried out in a 1:1 molar ratio, a new coordination mode of the dmit ligand is obtained: Na[Au(C$_3$S$_5$)L], where dmit chelates the gold center as part of a trigonal coordination (eq 3). Addition of NBu$_4$Br allows the isolation of anionic complexes. The reaction functions only in the case of L = phosphine; a mixture of compounds results when ylide is used instead, and complexes **5**−**7** can be detected in the reaction mixture.



L = PPh$_3$ (**11**), PPh$_2$Me (**12**), PMe$_3$ (**13**)

(3)

Complexes **11**−**13** are air- and moisture-stable red solids at room temperature. They behave as 1:1 electrolytes in acetone solution, and the IR spectra show bands characteristic of dmit and phosphine ligands. Their ^{31}P{^{1}H} NMR spectra each show a singlet from the single phosphine (see Table 1). The values are displaced downfield with respect to the dinuclear compounds, with the exception of that for L = PMe$_3$.

The trigonal coordination has been confirmed by X-ray diffraction of a single crystal of complex **11**. The structure contains two independent formula units; one anion is shown in Figure 2. Selected bond lengths and angles are given in Table 4. The gold atom displays regular three-coordination, with similar Au−S distances involving the sulfur atoms of the chelating dmit ligand [2.405(3), 2.476(3); 2.413(3), 2.483(3) Å], with narrow S−Au−S angles of 89.6(1), 89.9(1)°. The Au−S distances are slightly longer than those of complex **1**, presumably as a consequence of the more regular tricoordination. However the Au−P bond lengths [2.235(2), 2.243(2) Å] are slightly shorter than those in **1** [2.278(1), 2.257(1)Å].

Reaction 1 can be extended to ionic dinuclear compounds, starting from Q[Au(C$_6$F$_5$)X] (Q = NBu$_4$, N(PPh$_3$)$_2$ (PPN); X = Cl, Br), with which methanolic solutions of Na$_2$dmit give anionic complexes (eq 4).

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(14) Frisch, E.; Polborn, K.; Robl, C.; Sunkel, K.; Bock, W. *Z. Anorg. Allg. Chem.* **1993**, *619*, 2050.

(15) Cerrada, E.; Laguna, A.; Laguna, M.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1994**, 1325.

(16) Steimecke, G.; Sieler, H. J.; Kirmse R.; Hoyer, E. *Phosphorus Sulfur* **1979**, *7*, 49.

(17) Schmidbaur, H.; Franke, R. *Inorg. Chim. Acta* **1975**, *13*, 185; *Chem. Ber.* **1975**, *108*, 1321; *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 416.

(18) (a) Dávila, R. M.; Elduque, A.; Grant, T.; Staples, R. T.; Fackler, J. P., Jr. *Inorg. Chem.* **1993**, *32*, 1749. (b) Gimeno, M. C.; Jones, P. G.; Laguna, A.; Laguna, M.; Terroba, R. *Inorg. Chem.* **1994**, *33*, 3932.

(19) Ikhan, M. N.; Wang, S.; Heinrich, D. D.; Fackler, J. P., Jr. *Acta Crystallogr., C* **1988**, *44*, 822.

(20) (a) Nakamoto, M.; Hiller, W.; Schmidbaur, H. *Chem. Ber.* **1993**, *126*, 605. (b) Nakamoto, M.; Koijman, H.; Paul, M.; Schmidbaur, H. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1341.

(21) Dávila, R. M.; Staples, R. J.; Elduque, A.; Harlass, M. M.; Kyle, L.; Fackler, J. P., Jr. *Inorg. Chem.* **1994**, *33*, 5940.

$$\mathrm{Na_2dmit + 2Q[Au(C_6F_5)X] \rightarrow Q_2[Au_2(\mu\text{-}dmit)(C_6F_5)_2]} \quad \mathrm{Q = NBu_4\ (\mathbf{14a}),\ PPN\ (\mathbf{14b})} \tag{4}$$

These compounds can be isolated as dark pink (**14a**) or orange-pink (**14b**) solids, air- and moisture-stable at room temperature. They behave as 2:1 electrolytes in acetone solution. Their IR spectra show the bands characteristic of dmit and two bands at *ca.* 950 (s) and 790 (m) cm^{-1} due to C_6F_5 groups. The ^{19}F NMR spectra show three groups of signals with a pattern similar to those for other (pentafluorophenyl)-gold(I) fragments.

When Q[AuX_2] (X = halogen) is used in reaction 1, a mixture of complexes is obtained and the oxidation product, Q[Au(dmit)$_2$], can be isolated. For this reason, we have used an alternative procedure, starting from [Au_2(dmit)($AsPh_3$)]$_n$ (reported previously by us[15] in the presence of 2 equiv of (PPN)X (X = Cl, Br); triphenylarsine is replaced by the halide (eq 5).

$$\mathrm{[Au_2(dmit)(AsPh_3)] + 2(PPN)X \rightarrow (PPN)_2[Au_2(\mu\text{-}dmit)X_2] + AsPh_3} \quad \mathrm{X = Cl\ (\mathbf{15a}),\ Br\ (\mathbf{15b})} \tag{5}$$

These complexes are air- and moisture-stable pale brown solids. They behave as 2:1 electrolytes in acetone solution, and their IR spectra show bands at 326 (m) (**15a**) and 220 (m) (**15b**) cm^{-1} assignable to υ(Au−X).

Oxidation Reactions. We performed various oxidation reactions on the anionic derivatives, treating them with (TTF)$_3$(BF_4)$_2$ (TTF = tetrathiafulvalene) or TCNQ (7,7′,8,8′-tetracyanoquinodimethane), or on the neutral derivatives such as complex **1** by electrocrystallization procedures. Complexes **11**, **12**, **14**, and **15** react with an excess of (TTF)$_3$(BF_4)$_2$ in acetonitrile leading to the precipitation of dark solids, insoluble in common organic solvents, according to eqs 6−8.

$$\mathrm{(NBu_4)[Au(dmit)L] + (TTF)_3(BF_4)_2 \rightarrow \underset{\mathbf{16}}{(TTF)_2[Au(dmit)_2]}} \quad \mathrm{L = PPh_3,\ PPh_2Me} \tag{6}$$

$$\mathrm{Q_2[Au_2(\mu\text{-}dmit)(C_6F_5)_2] + (TTF)_3(BF_4)_2 \rightarrow \underset{\mathbf{17}}{(TTF)[Au_2(dmit)(C_6F_5)_2]}} \quad \mathrm{Q = NBu_4,\ PPN} \tag{7}$$

$$\mathrm{(PPN)_2[Au_2(\mu\text{-}dmit)Br_2] + (TTF)_3(BF_4)_2 \rightarrow \underset{\mathbf{18}}{(TTF)_3[Au_2(dmit)Br_2]}} \tag{8}$$

Because of the insolubility of complexes **16**−**18**, their stoichiometry can be given on the basis of only C, H, N, and gold anayses (see Table 1 and Experimental Section). The oxidation states of dmit and TTF cannot be accurately determined. The infrared spectra show absorptions (KBr pellets) at *ca.* 1437 cm^{-1} for complexes **16** and **18**, characteristic of $C_3S_5^{2-}$,[22] and at 1350 cm^{-1} in complex **17**, which can be assigned to $C_3S_5^{-}$.[23] The Raman spectra of **16**−**18** show bands at *ca.* 1440 cm^{-1}, which might be attributed to the stretching vibration of the central C=C bond of TTF, suggesting a partially oxidized moiety.[24−26] Complex **18** shows in addition an absorption at 1413 cm^{-1} characterictic of TTF^{+}.[25,26]

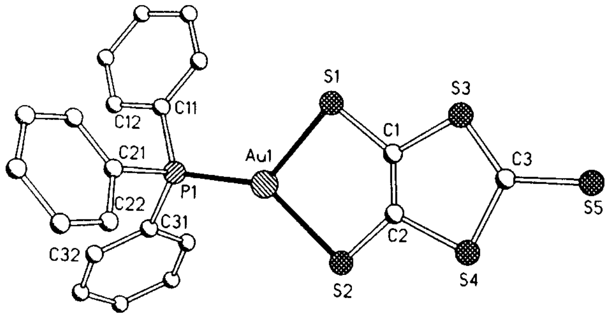
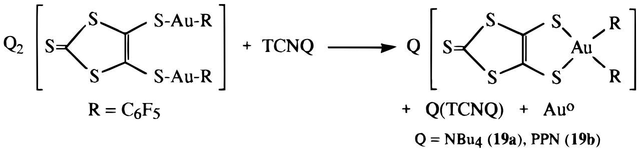


Figure 2. Molecule of complex **11** in the crystal (50% ellipsoids). H atoms are omitted.

The electron spin resonance (ESR) results measured at 300 K can be summarized as follows: $g_{\parallel} = 2.0080$, $g_{\perp} = 2.0037$, and half-width of 0.5 mT for **16**; $g = 2.0083$ and half-width of 1 mT for **17**; and $g = 2.0077$ and halfwidth of 2mT for **18**. The g values indicate that the resonance can be assigned to the presence of the TTF$^{\bullet+}$ radical.

Conductivity measurements were carried out at ambient pressures in the temperature range 295 −240 K using the two-probe method in compacted pellets. Complexes **16** and **17** showed semiconducting behavior in the whole temperature range with room-temperature values of 2×10^{-3} and 7×10^{-5} S•cm^{-1}, respectively, and activation energies of 0.06 and 0.59 eV. These values are similar to those of other reported gold complexes[28] but, in some cases, are lower that those reported for some (NR_4)$_x$[M(dmit)$_2$] complexes (M = Ni, Pd, Pt).[1,2] Complex **18** showed a conductivity value of 2×10^{-2} S·cm^{-1} at room temperature which increases in the temperature range studied, being 3.3×10^{-2} at 240 K. Because these data are measured on compresed pellets, we cannot conclude a metallic behavior.

The reaction of complex **14** with TCNQ in a 1:1 ratio leads to the oxidation of one gold atom of the compound, giving a gold(III) complex according to eq 9.



(9)

Complexes **19a**,**b** are air- and moisture-stable brown solids at room temperature. They behave as 1:1 electrolytes in acetone solution. The IR spectra show bands from the ligand [1443 (s) cm^{-1} (υ(C=C)) and 1028 (m), 1056 (s) cm^{-1} (υ(C=S))] and bands at 952 (m), 810 (m), and 780 (m) cm^{-1}, corresponding to the presence of two C_6F_5 groups. Their ^{19}F NMR spectra show three groups of signals characteristic of the presence of two pentafluorophenyl groups in *cis* positions related by a symmetry plane and with a free rotation around the ipso carbon (see Experimental Section).

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[22] Matsubayashi, G.; Akiba, K.; Tanaka, T. *Inorg. Chem.* **1988**, *27*, 4744.

[23] Sakamoto, Y.; Matsubayashi, G.; Tanaka, T. *Inorg. Chim. Acta* **1986**, *113*, 137.

[24] Bozio, R.; Girlando, A.; Pecile, D. *Chem. Phys. Lett.* **1977**, *52*, 503.

[25] Matsuzaki, S.; Moriyama, T.; Toyoda, K. *Solid State Commun.* **1980**, *34*, 857.

[26] Bozio, R.; Zanon, I.; Girlando, A.; Pecile, D. *J. Chem. Phys.* **1979**, *71*, 2282.

[27] (a) Jones, P. G.; Bembeneck, E. *Z. Kristallogr.* **1994**, *209*, 690. (b) Usón, R.; Laguna, A.; Vicente, J.; Garcia, J.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1981**, 655. (c) Usón, R.; Laguna, A.; Laguna, M.; Castilla, M. L.; Jones, P. G.; Meyer-Bäse, K. *J. Chem. Soc.* **1987**, *336*, 453.

[28] Matsubayashi, G.; Yokozawa, A. *J. Chem. Soc., Dalton Trans.* **1990**, 3535.

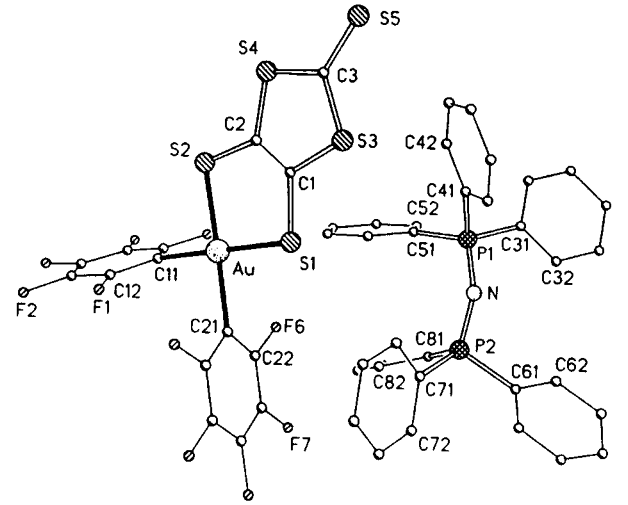

Figure 3. Formula unit of complex **19b** in the crystal (50% ellipsoids). H atoms are omitted.

The reaction with complexes **11**−**13** and **15** takes place in a similar way, and Q(TCNQ) can be detected, but we were not able to obtain the expected dmit derivatives in a pure form, because Q(TCNQ) was always present in the crude products.

The crystal structure of complex **19b** has been established by X-ray analysis. The formula unit is shown in Figure 3. Angles and distances are listed in Table 5. The anion shows the gold center in a square-planar geometry (mean deviation of five atoms 0.02 Å) typical of Au(III), with two C_6F_5 groups in *cis* positions and a chelating dmit ligand. Au−S bond lengths [2.322(2), 2.324(2) Å] are slightly shorter than those of equivalent moieties in complex **8**. Au−C distances involving the Au−C_6F_5 units [2.061(6), 2.059(5) Å] are similar to those in other gold(III) complexes $[Au(C_6F_5)_4]^-$ [2.054(7)−2.058-(8)Å][27a,b] and $[Au(C_6F_5)_2\{S_2CN(CH_2Ph)_2\}]$ [2.047(6), 2.049-(6) Å].[27c]

When complex **1** is subjected to a constant current in an H-tube (MeCN, $NBu_4[Au(C_6F_5)_2]$, or NBu_4ClO_4, $i = 1.3$ μA), black microcrystals form, for which elemental analysis indicates the formula $[Au_2(dmit)_2(PPh_3)]$ (**20**). The insolubility of the crystals in all common solvents precludes the recording of NMR data, and their poor quality makes X-ray analysis impossible. However, complex **11** under similar conditions gives the known gold(III) complex $NBu_4[Au(dmit)_2]$.[28] The electrical conductivity of complex **20** at room temperature in compacted pellets is 1.3×10^{-5} S·cm^{-1} and shows the behavior of a semiconductor with an activation energy of 0.56 eV. Complex **20** does not exhibit an electron spin resonance signal, showing that the dmit ligand is not oxidized in this complex.

Experimental Section

Materials. 4,5-Bis(benzoylthio)-1,3-dithiole-2-thione,[16,29] $[AuCl(PR_3)]$,[30] $[AuCl(CH_2PR_3)]$,[31] $Q[Au(C_6F_5)X]$,[30] $[Au_2(C_3S_5)(AsPh_3)]$,[15] and $(TTF)_3(BF_4)_2$[32] were obtained according to the literature procedures.

General Data. Infrared spectra were recorded on a Perkin-Elmer 559 or 883 spectrophotometer over the range 4000−200 cm^{-1} (Nujol mulls between polyethylene sheets), and ^{1}H and ^{31}P NMR spectra, on a Varian UNITY 300 in $CDCl_3$ solutions; chemical shifts are quoted relative to $SiMe_4$ (^{1}H) and H_3PO_4 (external ^{31}P). The C, H, N, and S analyses were performed with a Perkin-Elmer 2400 microanalyzer; Au was determined by ashing the samples with an aqueous solution of hydrazine. Conductivities were measured in acetone with a Philips PW 9509 apparatus, and mass spectra were recorded on a VG Autospec.

The ESR spectra were recorded at 300 K on a Bruker ESP 300 E spectrometer. The microwave frequency was measured using a 5350 B microwave frequency counter from Hewlett-Packard, and the magnetic field, with an ER 035 M NMR gaussmeter from Bruker. Estimated errors in the g values are better than ±0.0002.

The yields, elemental analyses, and ^{31}P{^{1}H} and some ^{1}H NMR data are listed in Table 1.

Safety Note. *Caution!* Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

Preparations. $[Au_2(\mu\text{-dmit})(L)_2]$ [L = PPh_3 (1), PPh_2Me (2), $PPhMe_2$ (3), PMe_3 (4), CH_2PPh_3 (5), CH_2PPh_2Me (6), CH_2PPhMe_2 (7)]. Sodium metal (9 mg, 0.4 mmol) and 4,5-bis(benzoylthio)-1,3-dithiole-2-thione (81 mg, 0.2 mmol) were dissolved under dinitrogen atmosphere in methanol (20 mL) to give a dark red solution of $Na_2[C_3S_5]$, to which was added $AuCl(PPh_3)$ (197 mg, 0.4 mmol), $AuCl(PPh_2Me)$ (173 mg, 0.4 mmol), $AuCl(PPhMe_2)$ (148 mg, 0.4 mmol), $AuCl(PMe_3)$ (123 mg, 0.4 mmol), $AuCl(CH_2PPh_3)$ (101 mg, 0.4 mmol), $AuCl(CH_2PPh_2Me)$ (89 mg, 0.4 mmol) or $AuCl(CH_2PPhMe_2)$ (80 mg, 0.4 mmol). Complexes **1**−**7** precipitated immediately [dark yellow (**1**, **3**), red (**2**, **4**), garnet (**5**−**7**)], were collected by filtration, washed with methanol, and dried *in vacuo*. Yields (%): 91 (**1**), 80 (**2**), 75 (**3**), 77 (**4**), 85 (**5**), 87 (**6**), 90 (**7**). ^{1}H NMR (in ppm): δ(Me) 1.96 (d, 9.7 Hz) (**2**), 1.72 (d, 12 Hz) (**3**), 1.58 (d, 10.7 Hz) (**4**), 2.3 (d, 11.7 Hz) (**6**), 2.03 (d, 12.6 Hz) (**7**); δ(−CH_2−) 1.96 (d, 12.2 Hz) (**5**), 1.7 (d, 11.7 Hz) (**6**), 1.52 (d, 12.6 Hz) (**7**).

$[Au_3(\mu_3\text{-dmit})(L)_3]ClO_4$ [L = PPh_3 (8), PPh_2Me (9), CH_2PPh_3 (10)]. To a dichloromethane solution of $[AuCl(PPh_3)]$ (49 mg, 0.1 mmol), $[AuCl(PPh_2Me)]$ (43 mg, 0.1 mmol), or $[AuCl(CH_2PPh_3)]$ (50 mg, 0.1 mmol) was added $AgClO_4$ (20 mg, 0.1 mmol). After 1 h of stirring, the suspension was filtered through 1 cm of Celite, and $[Au_2(\mu\text{-dmit})(PPh_3)_2]$ (111 mg, 0.1 mmol), $[Au_2(\mu\text{-dmit})(PPh_2Me)_2]$ (99 mg, 0.1 mmol), or $[Au_2(\mu\text{-dmit})(CH_2PPh_3)_2]$ (114 mg, 0.1 mmol) was added to the resulting solution. After 3 h of stirring, the solutions were concentrated by evaporation, and the addition of diethyl ether led to precipitation of dark garnet solids that were filtered off and dried *in vacuo*. Yields (%): 76 (**8**), 63 (**9**), 88 (**10**). ^{1}H NMR (in ppm): δ(Me) 1.96 (d, 9.8 Hz) (**9**); δ(−CH_2−) 1.9 (s, br) (**10**).

$(NBu_4)[Au(dmit)L]$ [L = PPh_3 (11), PPh_2Me (12), PMe_3 (13)]. 4,5-Bis(benzoylthio)-1,3-dithiole-2-thione (81 mg, 0.2 mmol) was dissolved under dinitrogen atmosphere in a methanol (20 mL) solution containing sodium metal (9 mg, 0.4 mmol), affording $Na_2[C_3S_5]$. A dichloromethane (5 mL) solution of $AuCl(PPh_3)$ (98 mg, 0.2 mmol), $AuCl(PPh_2Me)$ (86 mg, 0.2 mmol), or $AuCl(PPMe_3)$ (62 mg, 0.2 mmol) was added followed by a dichloromethane (5 mL) solution of $(NBu_4)Br$ (64 mg, 0.2 mmol) with stirring. The solutions turned red. After 12 h of stirring the solutions were evaporated to dryness, and acetone (15 mL) was added, affording a white solid (NaCl), which was filtered off. The solutions were concentrated to 5 mL. Addition of diethyl ether precipitated red solids (**11**−**13**). Yields (%): 87 (**11**), 76 (**12**), 50 (**13**). ^{1}HNMR (in ppm): δ(Me) 2.1 (d, 8.8 Hz) (**12**), 1.55 (d, 10.1 Hz) (**13**).

$Q_2[Au_2(\mu\text{-dmit})(C_6F_5)_2]$ [Q = NBu_4 (14a), $N(PPh_3)_2$ (PPN) (14b)]. Sodium metal (9 mg, 0.4 mmol) and 4,5-bis(benzoylthio)-1,3-dithiole-2-thione (81 mg, 0.2 mmol) were dissolved under dinitrogen atmosphere in methanol (20 mL) to give a dark red solution, to which was added $(NBu_4)[Au(C_6F_5)Br]$ (274 mg, 0.4 mmol) or $(PPN)[Au(C_6F_5)Cl]$ (375 mg, 0.4 mmol). Immediately pink complexes (**14a**,**b**) precipitated, were collected by filtration, washed with methanol, and dried *in vacuo*. Yields (%): 70 (**14a**), 80 (**14b**). ^{19}F NMR (in ppm): δ(**14a**) −115.6 (m, F_o), −163.4 (t, F_p), −164.6(m, F_m); δ(**14b**) −115.0 (m, F_o), −163.4 (t, F_p), −164.6 (m, F_m).

$(PPN)_2[Au_2(\mu\text{-dmit})(X)_2]$ [X = Cl (15a), Br (15b)]. To an acetone (20 mL) suspension of $[Au_2(C_3S_5)(AsPh_3)]$ (89 mg, 0.1 mmol) was added (PPN)Br (123 mg, 0.2 mmol) or (PPN)Cl (114 mg, 0.2 mmol). The solution turned orange. After being stirred for 12 h, the solution

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(29) Valade, L.; Legros, J. P.; Bousseau, M.; Cassoux, P.; Barbauskas, M.; Interrante, L. V. *J. Chem. Soc., Dalton Trans.* **1985**, 783.

(30) Usón, R.; Laguna, A. *Organomet. Synth.* **1985**, *3*, 325.

(31) Usón, R.; Laguna, A.; Laguna, M.; Usón, A.; Gimeno, M. C. *Inorg. Chim. Acta* **1986**, *114*, 91.

(32) Wuld, F. *J. Am. Chem. Soc.* **1975**, *79*, 1962.

Table 1. Analytical and Spectroscopic Data

		anal. (%)[a]					
no.	complex	C	H	N	S	Λ_M[b]	δ(^{31}P NMR[d])
1	$[Au_2(\mu\text{-dmit})(PPh_3)_2]$	42.15 (42.0)	2.55 (2.7)		14.05 (14.4)	8	36.5 (s)
2	$[Au_2(\mu\text{-dmit})(PPh_2Me)_2]$	35.15 (35.15)	3.45 (3.3)		15.7 (16.2)	2	19.4 (s)
3	$[Au_2(\mu\text{-dmit})(PPhMe_2)_2]$	26.05 (26.35)	2.45 (2.55)		18.09 (18.5)	5	7.4 (s)
4	$[Au_2(\mu\text{-dmit})(PMe_3)_2]$	15.0 (14.6)	2.4 (2.45)		21.6 (21.6)	2	-4.4 (s)
5	$[Au_2(\mu\text{-dmit})(CH_2PPh_3)_2]$	42.6 (43.1)	2.9 (3.0)		14.0 (14.0)	9	31.0 (s)
6	$[Au_2(\mu\text{-dmit})(CH_2PPh_2Me)_2]$	36.8 (36.55)	2.85 (2.95)		15.4 (15.7)	7	27.7 (s)
7	$[Au_2(\mu\text{-dmit})(CH_2PPhMe_2)_2]$	27.8 (28.2)	2.5 (2.9)		16.9 (17.9)	9	26.5 (s)
8	$[Au_3(\mu_3\text{-dmit})(PPh_3)_3]ClO_4$	41.1 (40.9)	2.5 (2.7)		9.8 (9.6)	113	35.7 (s,br)[e]
9	$[Au_3(\mu_3\text{-dmit})(PPh_2Me)_3]ClO_4$	34.05 (33.9)	2.3 (2.65)		10.2 (10.7)	124	19.2 (s,br)[e]
10	$[Au_3(\mu_3\text{-dmit})(CH_2PPh_3)_3]ClO_4$	42.0 (42.0)	3.15 (3.0)		9.2 (9.3)	97	30.7 (s,br)[e]
11	$(NBu_4)[Au(dmit)(PPh_3)]$	50.0 (49.5)	5.8 (5.7)	1.8 (1.55)	17.65 (17.85)	88	42.3 (s)
12	$(NBu_4)[Au(dmit)(PPh_2Me)]$	46.0 (46.0)	5.65 (5.9)	1.7 (1.7)	19.0 (19.2)	100	23.3 (s)
13	$(NBu_4)[Au(dmit)(PMe_3)]$	36.45 (37.1)	6.0 (6.4)	1.8 (2.0)	21.15 (22.5)	101	−6.5 (s)
14a	$(NBu_4)_2[Au_2(\mu\text{-dmit})(C_6F_5)_2]$	40.05 (40.05)	5.15 (5.15)	1.85 (2.0)	11.75 (11.4)	171	
14b	$(PPN)_2[Au_2(\mu\text{-dmit})(C_6F_5)_2]$	51.95 (52.2)	2.9 (3.0)	1.45 (1.4)	7.69 (8.0)	204	
15a	$(PPN)_2[Au_2(\mu\text{-dmit})Br_2]$	49.65 (49.3)	3.4 (3.3)	1.5 (1.55)	7.8 (8.8)	233	
15b	$(PPN)_2[Au_2(\mu\text{-dmit})Cl_2]$	51.7 (51.8)	3.6 (3.5)	1.7 (1.6)	10.1 (9.25)	205	
16	$(TTF)_2[Au(dmit)_2]$	21.45 (21.65)	0.9 (0.8)		56.65 (57.8)	*c*	
17	$(TTF)[Au_2(dmit)(C_6F_5)_2]$	22.35 (22.35)	0.55 (0.35)		26.8 (25.55)	*c*	
18	$(TTF)_3[Au_2(dmit)Br_2]$	18.65 (18.5)	0.85 (0.9)		40.5 (40.0)	*c*	
19a	$(NBu_4)[Au(dmit)(C_6F_5)_2]$	38.7 (38.4)	4.3 (4.05)	1.95 (1.45)	19.0 (19.9)	120	
19b	$(PPN)[Au(dmit)(C_6F_5)_2]$	48.75 (48.4)	2.15 (2.4)	1.35 (1.1)	15.7 (14.7)	121	
20	$[Au_2(dmit)_2(PPh_3)]$	27.5 (27.5)	1.35 (1.45)		30.2 (30.55)	*c*	

[a] Calculated values are given in parentheses. [b] In acetone; values in Ω^{-1} cm^2 mol^{-1}. [c] Low solubility. [d] δ in ppm. [e] At room temperature. **8**: 31.3, 31.5 (s, −80 °C). **9**: 18.3, 20.0 (s, −80 °C). **10**: 30.9, 31.4 (s, −60 °C).

Table 2. Crystallographic Data for Compounds **1**, **11**, and **19b**

	1	**11**	**19b**
formula	$C_{39}H_{30}Au_2P_2S_5$	$C_{37}H_{51}AuNPS_5$	$C_{51}H_{30}AuF_{10}NP_2S_5$
M_r	1114.80	898.02	1265.97
crystal habit	yellow prism	red-brown prism	orange prism
crystal size (mm)	0.5 × 0.3 × 0.2	0.4 × 0.3 × 0.2	0.4 × 0.35 × 0.3
temp (°C)	−100	−95	−95
crystal system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	Cc	$P2_1/c$
a (Å)	10.191(2)	17.134(4)	12.911(3)
b (Å)	12.550(3)	30.080(5)	34.194(7)
c (Å)	15.038(4)	17.048(4)	11.657(3)
α (deg)	85.36(2)	90	90
β (deg)	75.73(3)	115.76(2)	110.71(2)
γ (deg)	89.88(2)	90	90
V (Å^3)	1857.5	7913	4814
Z	2	8	4
D_x (Mg m^{-3})	1.993	1.508	1.747
μ (mm^{-1})	8.3	4.0	3.4
transm	0.63−0.99	0.72−0.89	0.74−0.86
F(000)	1064	3632	2488
$2\theta_{max}$ (deg)	55	50	50
no. of reflns			
measd	11 824	12 656	9221
indep	8578	12 218	8507
R_{int}	0.037	0.021	0.030
R_w (F^2, all reflns)[a]	0.063	0.103	0.086
$R(F, >4\sigma(F))$[b]	0.025	0.041	0.034
no. of params	434	431	631
no. of restraints	354	138	541
S[c]	1.04	1.01	1.02
max Δ/σ	<0.001	<0.001	<0.001
max $\Delta\rho$ (e Å^{-3})	1.32	1.10	1.48

[a] $R_w(F^2) = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and a and b are constants adjusted by the program. [b] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $S = [\sum\{w(F_o^2 - F_c^2)^2\}/(n - p)]^{0.5}$, where n is the number of data and p the number of parameters.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compound **1**

Au(1)−P(1)	2.2779(11)	S(4)−C(3)	1.732(4)
Au(1)−S(1)	2.3474(11)	S(4)−C(2)	1.756(4)
Au(1)−Au(2)	3.0681(8)	S(5)−C(3)	1.650(4)
Au(2)−P(2)	2.2569(12)	C(1)−C(2)	1.362(5)
Au(2)−S(2)	2.3435(12)	P(1)−C(11)	1.809(5)
Au(2)−S(1)	2.8226(14)	P(1)−C(31)	1.824(4)
S(1)−C(1)	1.749(4)	P(1)−C(21)	1.825(4)
S(2)−C(2)	1.740(4)	P(2)−C(51)	1.818(4)
S(3)−C(3)	1.725(5)	P(2)−C(61)	1.820(5)
S(3)−C(1)	1.745(4)	P(2)−C(41)	1.820(5)

P(1)−Au(1)−S(1)	174.86(3)	C(1)−C(2)−S(2)	129.4(3)
P(1)−Au(1)−Au(2)	113.75(4)	C(1)−C(2)−S(4)	114.6(3)
S(1)−Au(1)−Au(2)	61.12(4)	S(2)−C(2)−S(4)	116.0(2)
P(2)−Au(2)−S(2)	159.32(4)	S(5)−C(3)−S(3)	123.7(3)
P(2)−Au(2)−S(1)	115.05(4)	S(5)−C(3)−S(4)	124.6(3)
S(2)−Au(2)−S(1)	85.52(4)	S(3)−C(3)−S(4)	111.8(2)
P(2)−Au(2)−Au(1)	103.10(3)	C(11)−P(1)−C(31)	106.2(2)
S(2)−Au(2)−Au(1)	92.54(3)	C(11)−P(1)−C(21)	108.0(2)
S(1)−Au(2)−Au(1)	46.74(2)	C(31)−P(1)−C(21)	104.7(2)
C(1)−S(1)−Au(1)	102.39(13)	C(11)−P(1)−Au(1)	112.55(12)
C(1)−S(1)−Au(2)	93.36(13)	C(31)−P(1)−Au(1)	114.47(12)
Au(1)−S(1)−Au(2)	72.14(3)	C(21)−P(1)−Au(1)	110.35(12)
C(2)−S(2)−Au(2)	104.15(14)	C(51)−P(2)−C(61)	104.3(2)
C(3)−S(3)−C(1)	98.6(2)	C(51)−P(2)−C(41)	105.7(2)
C(3)−S(4)−C(2)	98.8(2)	C(61)−P(2)−C(41)	103.6(2)
C(2)−C(1)−S(3)	116.2(3)	C(51)−P(2)−Au(2)	112.10(13)
C(2)−C(1)−S(1)	127.3(3)	C(61)−P(2)−Au(2)	115.87(13)
S(3)−C(1)−S(1)	116.5(2)	C(41)−P(2)−Au(2)	114.23(14)

was concentrated to 5 mL; addition of diethyl ether (15 mL) led to the precipitation of brown solids (**15a**,**b**), which were filtered off and washed with diethyl ether. Yields (%): 50 (**15a**), 52 (**15b**).

$(TTF)_2[Au(dmit)_2]$ (16). An acetonitrile (20 mL) solution of $(TTF)_3(BF_4)_2$ (0.102 g, 0.13 mmol) was added to an acetonitrile (10 mL) solution of **11** (0.089 g, 0.1 mmol) or **12** (0.083 g, 0.1 mmol) to yield immediately a dark brown solid, which was filtered off and washed with acetonitrile. Anal. Calcd for $C_{18}H_8S_{18}Au$: Au, 19.7. Found: Au, 18.8.

$(TTF)[Au_2(dmit)(C_6F_5)_2]$ (17). An acetonitrile (20 mL) solution of $(TTF)_3(BF_4)_2$ (0.05 g, 0.065 mmol) was added to an acetonitrile (10 mL) solution of **14b** (0.1 g, 0.05 mmol) to yield immediately a dark garnet solid, which was filtered off and washed with acetonitrile. Anal. Calcd for $C_{21}H_4S_{14}F_{10}Au_2$: Au, 30.5. Found: Au, 29.6.

$(TTF)_3[Au_2(dmit)Br_2]$ (18). An acetonitrile (20 mL) solution of $(TTF)_3(BF_4)_2$ (0.078 g, 0.1 mmol) was added to an acetonitrile (10 mL) solution of **15a** (0.146 g, 0.08 mmol) to yield immediately a dark red solid, which was filtered off and washed with acetonitrile. Anal. Calcd for $C_{21}H_{12}S_{17}Br_2Au_2$: Au, 28.9. Found: Au, 27.8.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Compound **11**

Au(1)−P(1)	2.235(2)	Au(1′)−P(1′)	2.243(2)
Au(1)−S(2)	2.405(3)	Au(1′)−S(2′)	2.413(3)
Au(1)−S(1)	2.476(3)	Au(1′)−S(1′)	2.483(3)
P(1)−C(11)	1.809(10)	P(1′)−C(11′)	1.796(10)
P(1)−C(21)	1.846(10)	P(1′)−C(31′)	1.816(10)
P(1)−C(31)	1.849(9)	P(1′)−C(21′)	1.821(10)
S(1)−C(1)	1.715(10)	S(1′)−C(1′)	1.750(9)
S(2)−C(2)	1.748(10)	S(2′)−C(2′)	1.712(9)
S(3)−C(3)	1.727(10)	S(3′)−C(3′)	1.722(10)
S(3)−C(1)	1.759(10)	S(3′)−C(1′)	1.738(9)
S(4)−C(3)	1.749(10)	S(4′)−C(3′)	1.700(10)
S(4)−C(2)	1.761(9)	S(4′)−C(2′)	1.761(8)
S(5)−C(3)	1.632(9)	S(5′)−C(3′)	1.670(10)
C(1)−C(2)	1.352(13)	C(1′)−C(2′)	1.370(12)

P(1)−Au(1)−S(2)	142.78(9)	P(1′)−Au(1′)−S(2′)	138.33(9)
P(1)−Au(1)−S(1)	127.20(9)	P(1′)−Au(1′)−S(1′)	131.60(9)
S(2)−Au(1)−S(1)	89.57(8)	S(2′)−Au(1′)−S(1′)	89.91(9)
C(11)−P(1)−C(21)	104.6(4)	C(11′)−P(1′)−C(31′)	103.9(4)
C(11)−P(1)−C(31)	101.3(4)	C(11′)−P(1′)−C(21′)	105.3(4)
C(21)−P(1)−C(31)	105.0(4)	C(31′)−P(1′)−C(21′)	101.3(4)
C(11)−P(1)−Au(1)	117.3(3)	C(11′)−P(1′)−Au(1′)	115.2(3)
C(21)−P(1)−Au(1)	109.9(3)	C(31′)−P(1′)−Au(1′)	113.2(3)
C(31)−P(1)−Au(1)	117.4(3)	C(21′)−P(1′)−Au(1′)	116.2(3)
C(1)−S(1)−Au(1)	97.8(4)	C(1′)−S(1′)−Au(1′)	97.1(3)
C(2)−S(2)−Au(1)	98.4(3)	C(2′)−S(2′)−Au(1′)	98.4(3)
C(3)−S(3)−C(1)	100.4(5)	C(3′)−S(3′)−C(1′)	98.2(5)
C(3)−S(4)−C(2)	99.3(5)	C(3′)−S(4′)−C(2′)	99.7(5)
C(2)−C(1)−S(1)	126.7(9)	C(2′)−C(1′)−S(3′)	116.7(7)
C(2)−C(1)−S(3)	114.5(8)	C(2′)−C(1′)−S(1′)	125.3(7)
S(1)−C(1)−S(3)	118.6(6)	S(3′)−C(1′)−S(1′)	117.9(5)
C(1)−C(2)−S(2)	127.3(8)	C(1′)−C(2′)−S(2′)	128.9(7)
C(1)−C(2)−S(4)	115.6(8)	C(1′)−C(2′)−S(4′)	113.0(7)
S(2)−C(2)−S(4)	117.0(6)	S(2′)−C(2′)−S(4′)	118.0(6)
S(5)−C(3)−S(3)	126.2(6)	S(5′)−C(3′)−S(4′)	123.1(6)
S(5)−C(3)−S(4)	123.9(6)	S(5′)−C(3′)−S(3′)	124.6(6)
S(3)−C(3)−S(4)	109.8(5)	S(4′)−C(3′)−S(3′)	112.3(5)

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Compound **19b**

Au−C(21)	2.059(5)	S(3)−C(3)	1.731(6)
Au−C(11)	2.061(6)	S(3)−C(1)	1.750(5)
Au−S(1)	2.3215(14)	S(4)−C(3)	1.739(6)
Au−S(2)	2.324(2)	S(4)−C(2)	1.739(5)
S(1)−C(1)	1.747(5)	S(5)−C(3)	1.647(6)
S(2)−C(2)	1.752(5)	C(1)−C(2)	1.340(7)

C(21)−Au−C(11)	90.4(2)	C(2)−C(1)−S(1)	125.1(4)
C(21)−Au−S(1)	89.19(13)	S(3)−C(1)−S(1)	118.4(3)
C(11)−Au−S(1)	178.9(2)	C(1)−C(2)−S(4)	115.7(4)
C(21)−Au−S(2)	178.61(11)	C(1)−C(2)−S(2)	124.3(4)
C(11)−Au−S(2)	88.79(14)	S(4)−C(2)−S(2)	120.0(3)
S(1)−Au−S(2)	91.68(5)	S(5)−C(3)−S(3)	124.0(3)
C(1)−S(1)−Au	99.4(2)	S(5)−C(3)−S(4)	124.3(3)
C(2)−S(2)−Au	99.5(2)	S(3)−C(3)−S(4)	111.7(3)
C(3)−S(3)−C(1)	97.8(3)	C(16)−C(11)−C(12)	116.4(5)
C(3)−S(4)−C(2)	98.4(3)	C(22)−C(21)−C(26)	115.5(5)
C(2)−C(1)−S(3)	116.4(4)		

Q[Au(dmit)(C_6F_5)$_2$] [Q = NBu_4 (19a), N(PPh_3)$_2$ (PPN) (19b)]. To a dichloromethane (15 mL) solution of complex **14** [(NBu_4)$_2$[Au_2(μ-C_3S_5)(C_6F_5)$_2$] (84 mg, 0.06 mmol) or (PPN)$_2$[Au_2(μ-C_3S_5)(C_6F_5)$_2$] (120 mg, 0.06 mmol)] was added a dichloromethane solution of TCNQ (12 mg, 0.06 mmol). The solutions turned dark green. After 3 h of stirring, the solutions were concentrated to 1 mL, and the addition of diethyl ether (20 mL) precipitated a green solid [Q(TCNQ)], which was filtered off and washed with diethyl ether. The remaining solutions were concentrated to 5 mL, whereupon addition of hexane (15 mL) precipitated brown solids (**19a**,**b**). Yields (%): 55 (**19a**), 80 (**19b**). ^{19}F NMR: δ(**19a**) −115.6 (m, F_o), −161.6 (t, F_p), −163.4 (m, F_m); δ(**19b**) −115.4 (m, F_o), −163.2 (t, F_p), −164.6 (m, F_m).

[Au_2(dmit)$_2$(PPh_3)] (20) by Electrolysis. An acetonitrile (10 mL) solution containing complex **1** (0.044 g, 0.04 mmol) and (NBu_4)[Au(C_6F_5)$_2$] (0.077 g, 0.1 mmol) or (NBu_4)ClO_4 (0.068 g, 0.1 mmol) was subjected to a controlled-current (1.3 μA) electrolysis under a nitrogen atmosphere for 15 d at room temperature in an H-type glass cell with platinum wires as anode and cathode. Black microcrystals of complex **20** formed on the anode and were collected and dried *in vacuo*.

Crystal Structure Analyses. Crystal data are presented in Table 2. Data collection: Data were collected with Mo Kα radiation on a Siemens R3 diffractometer equipped with an LT-2 low-temperature device; scan type ω. Cell constants were refined from setting angles of *ca.* 50 reflections in the 2θ range 20−23°. Absorption corrections based on ψ scans were applied. Structure solution: heavy-atom method. Structure refinement: anisotropic refinement on F^2,[33] H atoms as rigid methyls or with a riding model, weighting scheme $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $3P = (2F_c^2 + F_o^2)$, and *a* and *b* are constants optimized by the program. A variety of restraints were applied to light-atom displacement parameters (DELU) and aromatic rings (FLAT, SAME).

Special features of refinement: For **11**, the absolute structure was determined by an *x* refinement[34] and the origin was fixed in terms of a weighted sum of coordinates;[35] C and N atoms were refined isotropically.

Final atomic coordinates are given in the Supporting Information, and selected bond lengths and angles are given in Tables 3−5.

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Supporting Information Available: Tables of crystal data, data collection and solution and refinement parameters, all atomic coordinates, bond distances and angles, and thermal parameters (20 pages). Ordering information is given on any current masthead page.

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(33) Sheldrick, G. M. SHELXL-93, a program for refining crystal structures. University of Göttingen, 1993.

(34) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.

(35) Flack, H. D.; Schwarzenbach, D. *Acta Crystallogr.* **1988**, *A44*, 499.