Charge-transfer salts with mononuclear and dinuclear ylide gold(I) complexes: x-ray structure of $[Au(CH_2PPh_3)_2](TCNQ)$ ($TCNQ = 7,7',8,8'$-tetracyanoquinodimethane)

Elena Cerrada [a], M. Concepción Gimeno [a], Antonio Laguna [a], Mariano Laguna [a,*],
Victor Orera [a], Peter G. Jones [b]

[a] *Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza, Consejo Superior de Investigaciónes Científicas,
50009 Zaragoza, Spain*
[b] *Institut für Anorganische und Analytische Chemie, Technische Universität, Postfach 3329, 38023 Braunschweig, Germany*

Abstract

The reaction of $[Au_2(CH_2PPh_2CH_2)_2]$ with $7,7',8,8'$-tetracyanoquinodimethane (TCNQ) or 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) led to the charge-transfer complexes $[Au_2(CH_2PPh_2CH_2)_2]_2(TCNQ)$ (1) and $[Au_2(CH_2PPh_2CH_2)_2](DDQ)$ (2). In a similar way $[Au_2(NC_5H_4S)_2]$ reacts with TCNQ forming $[Au_2(NC_5H_4S)_2](TCNQ)$ (3). All these complexes show conductivities of about 10^{-5} S cm^{-1} in pressed pellet samples. The reaction of $[Au(CH_2PR_3)_2]ClO_4$ ($PR_3 = PPh_3$, PPh_2Me or $PPhMe_2$) with LiTCNQ led to cationic complexes $[Au(CH_2PR_3)_2](TCNQ)$ which react further with TCNQ to give $[Au(CH_2PR_3)_2](TCNQ)_2$. The structure of $[Au(CH_2PPh_3)_2](TCNQ)$ has been established by X-ray crystallography. The cation shows a linear coordination of gold. Two independent TCNQ molecules are related by a crystallographic inversion symmetry.

Keywords: Gold; Ylide; Charge–transfer salts; Crystal structure

1. Introduction

Gold complexes have been widely used as counter-ions in the synthesis of conducting or superconducting ion radical salts of bis-ethylenedithiotetrathiafulvalene (ET) and related organic donors (e.g. $(ET)_2[AuX_2]$ (X = Cl [1], Br [2], I [3] or CN [4])). In contrast, only a few gold compounds have been used in charge-transfer complexes with $7,7',8,8'$-tetracyanoquinodimethane (TCNQ) or related electron acceptors, namely $[Au(S_2NCR_2)_2](TCNQ)_n$ where R represents various alkyl groups and $n = 1$, or $R = CH_2Ph$ and $n = 2$ or 4 [5], or $[Au(PPh_3)_2](TCNQ)$ [6].

Other approaches to charge-transfer derivatives consist of the reaction of donor molecules such as tetrathiafulvalene (TTF) with acceptors such as TCNQ to give donor–acceptor salts (e.g. TTF–TCNQ). The reaction of organometallic gold complexes, which can act as

electron donors with organic electron acceptors could be a way to metal-containing charge-transfer complexes.

We have recently shown that some mononuclear and dinuclear ylide gold complexes can act as electron donors in polynuclear complexes. For example, in $[Au_2Ag_2(CH_2PPh_3)_4(ClO_4)_4]$ (a) two donor–acceptor gold–silver bonds are formed whereby the species $[Au(CH_2PPh_3)_2]$ transfer electron density to silver [7]. In a similar way, complexes $[\{Au_2(CH_2PPh_2-CH_2)_2\}Au(C_6F_5)_3]$ (b), $[\{Au_2(CH_2PPh_2CH_2)_2\}-(SO_2)_2]$ (c) and $[\{RAu(CH_2PPh_2CH_2)_2Au\}_2\{Au_2(CH_2-PPh_2CH_2)_2\}]$ (d) can be rationalized if the dinuclear $[Au_2(CH_2PPh_2CH_2)_2]$ units transfer electron density either to the $Au(C_6F_5)_3$ moeity [8], to the SO_2 molecules [9] or to the $[RAu(CH_2PPh_2CH_2)_2Au]$ fragments [10].

We have studied the reactivity of $[Au_2(CH_2PPh_2-CH_2)_2]$, $[Au_2(S_2CNR_2)_2]$, $[Au_2(NC_5H_4S)_2]$ and $[Au(CH_2PR_3)_2]ClO_4$ as donors with the electron acceptors TCNQ or 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ). Only in the cases of $[Au_2(CH_2PPh_2-CH_2)_2]$ and $[Au_2(NC_5H_4S)_2]$ does the reaction with the

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* Corresponding author.

a

b

c

d
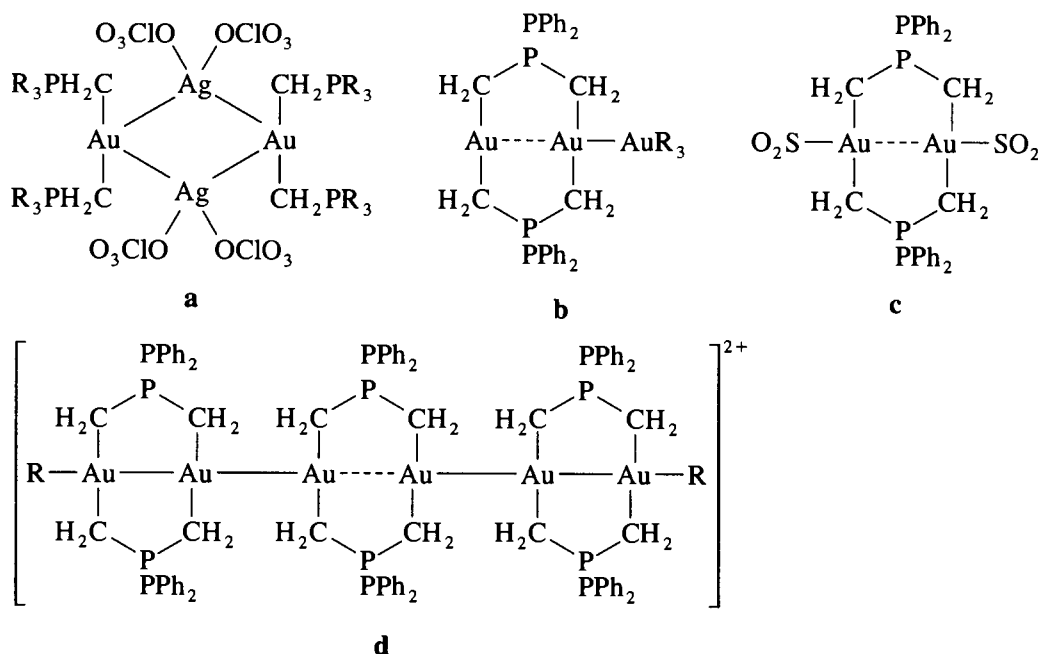
neutral species lead to the charge-transfer salts $[Au_2(CH_2PPh_2CH_2)_2]_2(TCNQ)$ (1), $[Au_2(CH_2PPh_2-CH_2)_2]$ (DDQ) (2) and $[Au_2(NC_5H_4S)_2](TCNQ)$ (3). With $[Au(CH_2PR_3)_2]ClO_4$, only reaction with LiTCNQ or TCNQ/LiTCNQ gives the charge-transfer salts $[Au(CH_2PR_3)_2](TCNQ)_n$. To the best of our knowledge, these complexes are the first examples of organometallic charge-transfer derivatives involving gold.

The molecular structure of $[Au(CH_2PPh_3)_2](TCNQ)$ has been established by a single-crystal X-ray analysis, which shows a linear coordination at gold without any interaction between gold and the TCNQ moeities, in contrast with the recently reported $[Au(PPh_3)_2](TCNQ)$ [6].

2. Results and discussion

The addition of the dinuclear gold complex $[Au_2(CH_2PPh_2CH_2)_2]$ to dichloromethane solutions of the organic acceptors TCNQ or DDQ affords dark solutions from which complexes $[Au_2(CH_2PPh_2-CH_2)_2]_2(TCNQ)$ (1) or $[Au_2(CH_2PPh_2CH_2)_2](DDQ)$ (2) can be isolated. The stoichiometry varies with the acceptor used but is independent of the gold complex-to-acceptor ratio.

Complexes 1 and 2 are dark-green or dark-brown solids respectively, stable to air and moisture at room temperature. Only 1 is (sparingly) soluble in organic solvents such as dichloromethane and acetone. The $^{31}P\{^1H\}$ NMR spectrum of 1 shows a singlet at 32.5 ppm, displaced slightly upfield from the starting bis(ylide) (34.2 ppm) [8] and the methylene protons appear as a pseudodoublet at 1.84 ppm, with a separation of $N = 9.7$ Hz, displaced downfield from that in the starting material. Both shifts are in the same sense as those observed when $[Au_2(CH_2PPh_2CH_2)_2]$ acts as an electron donor to other metals [8,10].

The IR spectrum of 1 shows two absorptions (KBr pellet) in the $\nu(C{\equiv}N)$ region at 2180(s) and 2148(s)

Table 1
Analytical data for products

Complex	Analysis [a] (%)			Λ_M [b] $(\Omega^{-1}\ cm^2\ mol^{-1})$	Melting point (°C)	^{31}P NMR, δ (ppm)	IR, δ(C–H) (cm^{-1})
	C	H	N				
1 $[Au_2(CH_2PPh_2CH_2)_2]_2(TCNQ)$	44.1 (44.3)	3.4 (3.3)	3.05 (3.05)	c	172	32.5(s)	848
2 $[Au_2(CH_2PPh_2CH_2)_2](DDQ)$	41.4 (41.3)	2.55 (2.7)	2.45 (2.7)	c	185	c	848
3 $[Au_2(NC_5H_4S)_2](TCNQ)$	26.4 (26.8)	1.3 (1.4)	7.7 (7.8)	c	205	c	861, 834
4 $[Au(CH_2PPh_3)_2](TCNQ)$	62.55 (62.95)	3.9 (4.0)	5.9 (5.9)	116	162	32.0(s)	831
5 $[Au(CH_2PPh_2Me)_2](TCNQ)$	58.25 (57.9)	4.25 (4.15)	6.7 (6.75)	74	155	28.5(s)	829
6 $[Au(CH_2PPhMe_2)_2](TCNQ)$	51.25 (51.1)	4.2 (4.3)	8.0 (7.95)	86	148	28.4(s)	823
7 $[Au(CH_2PPh_3)_2](TCNQ)_2$	64.1 (64.3)	4.3 (3.65)	10.2 (9.7)	117	164	31.95(s)	860, 831
8 $[Au(CH_2PPh_2Me)_2](TCNQ)_2$	60.85 (60.4)	3.4 (3.7)	10.2 (10.85)	87	160	28.5(s)	860, 829

[a] Calculated values are given in parentheses.
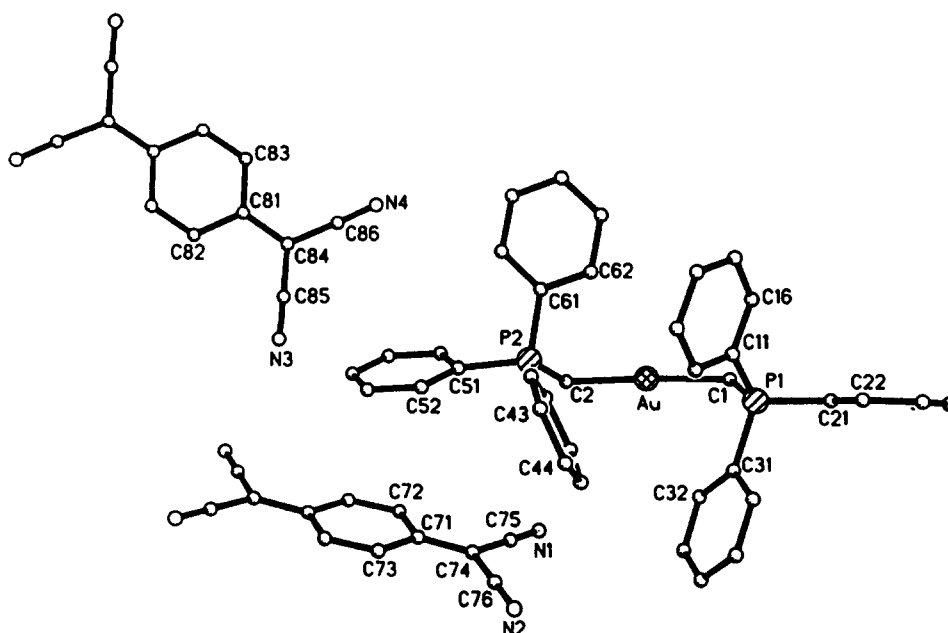[b] In acetone.
[c] Low solubility.

Fig. 1. The structure of **4** in the crystal. Both TCNQ moieties are complete (they display inversion symmetry), so that the figure does not correspond to the true stoichiometry (1 : 1).

cm^{-1} and one assignable to δ(C–H) at 848(m) cm^{-1}, which are characteristic [11] of $(TCNQ)_2^-$. Complex **2** shows two absorptions (KBr pellet) at 2200(m) and 848(m) cm^{-1}, assignable to ν(C≡N) and δ(C–H) modes of the DDQ which may indicate the presence of DDQ^- in **2** [12]. Consistent with these data, partial oxidation of the original gold-containing materials occurs, leading to an average oxidation state of gold of 1.25 in **1** or 1.5 in **2**. Complexes (Au_3^{5+}) [8,13], (Au_5^{9+}) [14] or (Au_6^{10+}) [10] involving linear chains of gold

atoms (see **b** and **c**) with non-integral oxidation states have been described recently. Unfortunately we were not able to grow crystals of sufficient quality for X-ray study.

Other neutral dinuclear gold(I) complexes such as $[Au_2(S_2CNR_2)_2]$ [15] do not react with TCNQ and the starting materials are recovered unchanged after stirring for 2 days in dichloromethane. However, if $[Au_2-(NC_5H_4S)_2]$ [16] (NC_5H_4S = 2-pyridinthiolate) is used a black solid of stoichiometry $[Au_2(NC_5H_4-$
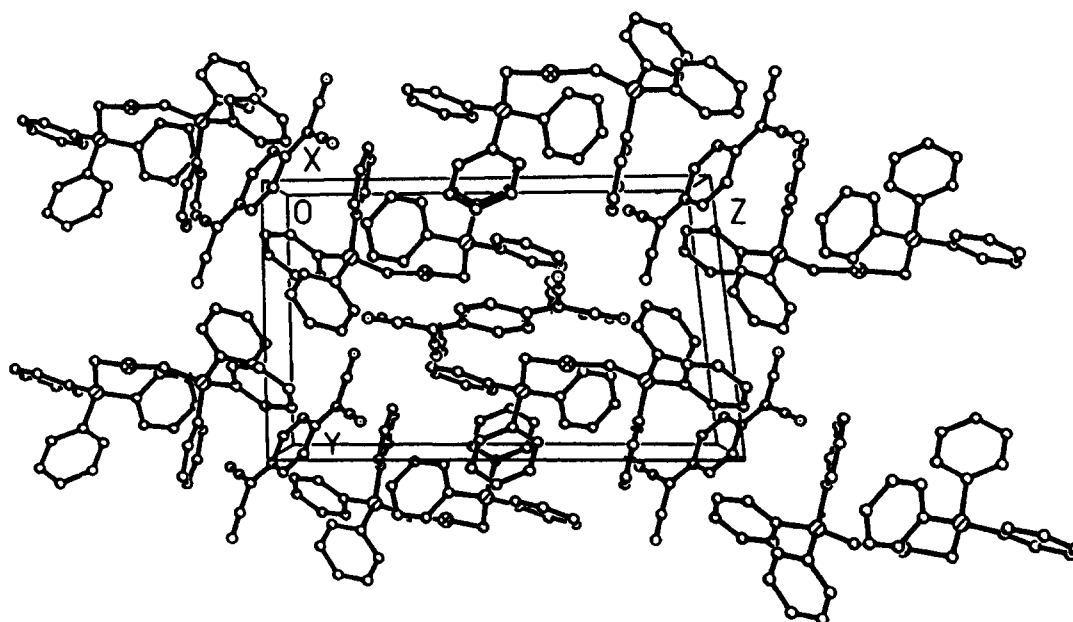

Fig. 2. Packing diagram for **4**, looking down the *a* axis.

S)₂](TCNQ) (**3**) is formed. The insolubility of **3** in common organic solvents precludes the recording of its solution NMR data. Its IR spectra (KBr pellet) shows two absorptions in the $\nu(C\equiv N)$ region at 2180(m) and 2140(m) cm⁻¹ and two in the $\delta(C–H)$ region at 861(m) and 834(m) cm⁻¹, which may indicate the existence of two kinds of TCNQ molecule, as in other complexes described in this work (see below and Table 1). Again, the oxidation states of the gold atoms in **3** are not obvious because two types of TCNQ molecule are present, and the lack of good crystals precludes an X-ray study.

The pressed pellet samples of these complexes have electrical conductivities of 5×10^{-5} S cm⁻¹ (**1**), 2×10^{-5} S cm⁻¹ (**2**) and 10^{-5} S cm⁻¹ (**3**) at room temperature.

Mononuclear complexes [Au(CH₂PR₃)₂]ClO₄ (PR₃ = PPh₃, PPh₂Me or PPhMe₂) do not react with neutral TCNQ but they do react with the lithium salt in ethanol:

$$[Au(CH_2PR_3)_2]ClO_4 + LiTCNQ$$

$$\rightarrow [Au(CH_2PR_3)_2](TCNQ) + LiClO_4 \qquad (1)$$
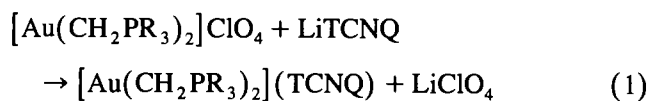
where PR₃ = PPh₃ (**4**), PPh₂Me(**5**) or PPhMe₂ (**6**).

Complexes **4–6** are green solids, stable to air and moisture at room temperature. Their analyses and conductivities confirm their ionic nature. Their IR spectra show absorptions assignable to $\nu(C\equiv N)$ and $\delta(C–H)$, the latter at about 830 cm⁻¹ consistent with the mononegative TCNQ ion [17,18], and, as expected, lack the absorptions of the ClO₄⁻ group. The ³¹P{¹H} and ¹H NMR data are very similar to those of the starting materials [Au(CH₂PR₃)₂]ClO₄ [7,19], showing that in these cases that the TCNQ is a counter-ion.

The crystal structure of **4** has been established by X-ray diffraction. The molecular structure of **4** is shown in Fig. 1 and a packing diagram in Fig. 2. Atomic coordinates are found in Table 2 and selected bond lengths and angles in Table 3. Details of data collection and structure refinement for complex **4** are shown in Table 4.

The asymmetric unit contains one cation [Au(CH₂-PPh₃)₂]⁺ and two independent half TCNQ moieties, which lie across symmetry centres. In the cation the geometry around the gold atom is slightly distorted from linear, with the angle C(2)–Au–C(1) 175.8(2)°. The Au–C distances are 2.087(5) and 2.077(5) Å and are very similar to those found in [Au₂Ag₂-(CH₂PPh₃)₄(ClO₄)₄] [7], where two units of [Au(CH₂PPh₃)₂]⁺ act as Lewis bases to silver. The H₂C–P bond lengths are 1.749(5) and 1.752(4) Å and are comparable with those in ylide [7] and methanide [20] complexes but shorter than in diphosphine [21] complexes. The bond lengths in the two independent TCNQ moieties are very similar to those found in RbTCNQ [21], as one would expect for TCNQ⁻.

Table 2
Atomic coordinates for **4**

	x ($\times 10^{-4}$)	y ($\times 10^{-4}$)	z ($\times 10^{-4}$)
Au	5493.9(2)	6689.5(2)	6546.9(1)
P(1)	5491.0(12)	7320.6(11)	8290.6(7)
P(2)	2914.6(12)	7756.7(11)	5505.8(7)
C(1)	6563(5)	6730(4)	7466(3)
C(2)	4520(4)	6509(4)	5633(3)
C(11)	4222(5)	8901(4)	8059(3)
C(12)	2875(5)	9238(4)	8058(3)
C(13)	1965(5)	10467(5)	7859(3)
C(14)	2411(6)	11339(5)	7664(3)
C(15)	3763(5)	11005(4)	7668(3)
C(16)	4665(5)	9782(4)	7866(3)
C(21)	6355(5)	7422(4)	9097(3)
C(22)	7733(5)	6681(5)	9130(3)
C(23)	8398(6)	6733(5)	9754(3)
C(24)	7692(6)	7503(5)	10358(3)
C(25)	6321(6)	8247(5)	10326(3)
C(26)	5657(6)	8216(5)	9703(3)
C(31)	4696(5)	6369(4)	8636(3)
C(32)	4935(5)	5323(4)	8250(3)
C(33)	4354(6)	4577(5)	8534(3)
C(34)	3517(6)	4882(5)	9194(3)
C(35)	3275(6)	5903(5)	9581(3)
C(36)	3860(6)	6645(5)	9315(3)
C(41)	1847(5)	8018(4)	6383(3)
C(42)	705(5)	9143(4)	6461(3)
C(43)	−182(5)	9323(5)	7107(3)
C(44)	98(6)	8373(5)	7678(3)
C(45)	1248(6)	7253(5)	7615(3)
C(46)	2128(5)	7065(4)	6964(3)
C(51)	2081(4)	7499(4)	4747(3)
C(52)	736(5)	7781(4)	4818(3)
C(53)	148(5)	7603(4)	4195(3)
C(54)	884(5)	7150(4)	3510(3)
C(55)	2220(5)	6858(5)	3441(3)
C(56)	2827(5)	7017(5)	4059(3)
C(61)	3011(4)	9180(4)	5223(3)
C(62)	3382(5)	9730(4)	5760(3)
C(63)	3520(5)	10794(4)	5534(3)
C(64)	3289(5)	11297(5)	4781(4)
C(65)	2912(6)	10766(5)	4249(4)
C(66)	2769(5)	9706(5)	4461(3)
N(1)	3932(5)	3643(5)	6359(4)
N(2)	210(6)	5043(6)	7753(4)
C(71)	684(5)	4834(5)	5693(4)
C(72)	1381(6)	4507(5)	4953(4)
C(73)	−731(5)	5335(5)	5710(4)
C(74)	1366(5)	4607(5)	6382(4)
C(75)	2791(6)	4072(5)	6374(4)
C(76)	714(6)	4860(6)	7137(4)
N(3)	1714(5)	6336(4)	1601(3)
N(4)	3409(5)	8910(5)	1751(3)
C(81)	897(5)	9183(4)	569(3)
C(82)	−53(5)	8914(5)	254(3)
C(83)	904(5)	10314(4)	287(3)
C(84)	1770(5)	8373(4)	1141(3)
C(85)	1743(5)	7253(5)	1409(3)
C(86)	2682(5)	8654(5)	1486(3)

The TCNQ molecules do not approach each other closely. The shortest contact corresponds to the short axis and thus interactions between the TCNQ can be

Table 3
Selected bond lengths (Å) and angles (°) for **4**

Bond lengths

Au–C(2)	2.077(5)	Au–C(1)	2.087(5)
P(1)–C(1)	1.749(5)	P(1)–C(31)	1.804(5)
P(1)–C(21)	1.807(5)	P(1)–C(11)	1.813(5)
P(2)–C(2)	1.752(4)	P(2)–C(41)	1.799(5)
P(2)–C(51)	1.801(5)	P(2)–C(61)	1.806(5)
N(1)–C(75)	1.141(7)	N(2)–C(76)	1.147(8)
C(71)–C(74)	1.404(9)	C(71)–C(73)	1.418(7)
C(71)–C(72)	1.421(8)	C(72)–C(73)#1	1.359(9)
C(74)–C(76)	1.419(9)	C(74)–C(75)	1.425(8)
N(3)–C(85)	1.149(6)	N(4)–C(86)	1.144(6)
C(81)–C(84)	1.412(7)	C(81)–C(82)	1.419(6)
C(81)–C(83)	1.420(6)	C(82)–C(83)#2	1.349(7)
C(84)–C(85)	1.411(7)	C(84)–C(86)	1.415(7)

Bond angles

|			
C(2)–Au–C(1)	175.8(2)	C(1)–P(1)–C(31)	111.7(2)
C(1)–P(1)–C(21)	112.4(2)	C(31)–P(1)–C(21)	107.4(2)
C(1)–P(1)–C(11)	109.7(2)	C(31)–P(1)–C(11)	109.7(2)
C(21)–P(1)–C(11)	105.7(2)	C(2)–P(2)–C(41)	112.4(2)
C(2)–P(2)–C(51)	111.6(2)	C(41)–P(2)–C(51)	107.1(2)
C(2)–P(2)–C(61)	110.7(2)	C(41)–P(2)–C(61)	107.7(2)
C(51)–P(2)–C(61)	107.1(2)	C(62)–C(61)–C(66)	119.5(5)
C(62)–C(61)–P(2)	119.6(4)	C(66)–C(61)–P(2)	120.8(4)
C(61)–C(62)–C(63)	119.8(5)	C(64)–C(63)–C(62)	120.1(5)
C(65)–C(64)–C(63)	120.4(5)	C(64)–C(65)–C(66)	120.4(5)
C(65)–C(66)–C(61)	119.7(5)	C(74)–C(71)–C(73)	121.4(6)
C(74)–C(71)–C(72)	121.7(5)	C(73)–C(71)–C(72)	116.8(6)
C(73)#1–C(72)–C(71)	122.0(5)	C(72)#1–C(73)–C(71)	121.2(6)
C(71)–C(74)–C(76)	123.5(5)	C(71)–C(74)–C(75)	121.9(5)
C(76)–C(74)–C(75)	114.6(6)	N(1)–C(75)–C(74)	179.2(8)
N(2)–C(76)–C(74)	178.5(8)	C(84)–C(81)–C(82)	121.5(4)
C(84)–C(81)–C(83)	122.1(4)	C(82)–C(81)–C(83)	116.5(4)
C(83)#2–C(82)–C(81)	122.1(5)	C(82)#2–C(83)–C(81)	121.5(4)
C(85)–C(84)–C(81)	120.8(4)	C(85)–C(84)–C(86)	117.0(4)
C(81)–C(84)–C(86)	122.2(4)	N(3)–C(85)–C(84)	177.7(5)
N(4)–C(86)–C(84)	178.0(6)		

Symmetry transformations used to generate equivalent atoms: #1, $-x, -y+1, -z+1$; #2, $-x, -y+2, -z$.

ruled out. Both are planar with a mean deviation of 0.02 and 0.01 Å (maximum, 0.07 Å for N(2)). In **4** there is no short interaction between TCNQ and the gold, in contrast with the structure of [Au(PPh$_3$)$_2$](TCNQ) [6], recently reported by us in which the shortest Au $\cdots$ C is 3.9 and Au $\cdots$ N is 4.7 Å.

Complexes **4** and **6** react further with TCNQ leading to the cationic complexes **7** and **8** with two TCNQ in the molecule.

$$[Au(CH_2PR_3)_2](TCNQ) + TCNQ$$
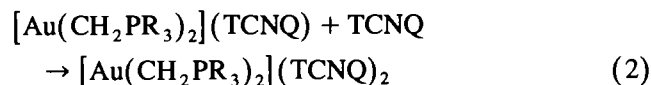
$$\rightarrow [Au(CH_2PR_3)_2](TCNQ)_2 \quad (2)$$

where PR_3 = PPh$_3$ (**7**) or PPh$_2$Me (**8**). Complexes **7** and **8** can also be obtained by reaction of [Au(CH$_2$PR$_3$)$_2$]ClO$_4$ with a mixture of LiTCNQ and TCNQ:

$$[Au(CH_2PR_3)_2]ClO_4 + LiTCNQ + TCNQ$$

$$\rightarrow [Au(CH_2PR_3)_2](TCNQ)_2 + LiClO_4 \quad (3)$$
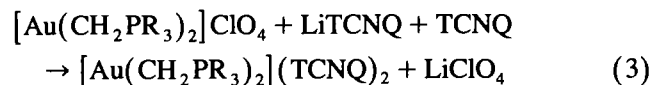
where PR_3 = PPh$_3$ (**7**) or PPh$_2$Me (**8**).

Complexes **7** and **8** resemble **4** and **5**, showing very similar ^{31}P and ^{1}H NMR spectra and only minor changes in colour (**7** and **8** are green, but darker than **4** and **5**). The main differences are in the analyses and IR spectra. The former are consistent with the presence of a further TCNQ molecule, and the IR spectra in the δ(C–H) region of TCNQ (870–820 cm^{-1}) show two absorptions at 860 and 830 cm^{-1} for **7** and **8**, in contrast with only one (about 830 cm^{-1}) in **4** and **5**. In addition, the ν(C≡N) region (2100–2200 cm^{-1}) is different in the shape, showing broader bands in **7** and **8** than in **4** and **5**. Because the absorption at 860 cm^{-1} has been assigned to a neutral TCNQ molecule [22] these data imply that **7** and **8** contain two types of TCNQ molecule.

The pressed pellets of **4**–**8** do not show electrical conductivity greater than 10^{-9} S cm^{-1}, which is the lower limit of our instrument. These data are consistent with the non-packing column structure of TCNQ moieties in **4** and the lack of black colour in **4**–**8**.

Table 4
Details of data collection and structure refinement for **4**

Chemical Formula	$C_{50}H_{38}AuN_4P_2$
Crystal habit	Green plate
Crystal size (mm)	0.40 × 0.40 × 0.10
Space group	$P\bar{1}$
a (Å)	11.299(3)
b (Å)	12.161(3)
c (Å)	17.175(6)
α (°)	84.81(3)
β (°)	85.02(3)
γ (°)	67.02(6)
V (Å^3)	2073.7(10)
Z	2
D_c (Mg m^{-3})	1.527
M	953.75
$F(000)$	950
T(°C)	−95
$2\theta_{max}$ (°)	50
μ (Mo Kα) (mm^{-1})	3.66
Transmission	0.55–1.0
Number of reflections measured	7737
Number of unique reflections	7334
Number of reflections used	7326
R_{int}	0.028
R [a] $(F, I > 2\sigma(I)$, 6397 reflections)	0.031
wR [b] $(F^2$, all reflections)	0.078
Number of parameters	514
Number of restraints	497
S [c]	1.074
Maximum $\Delta\rho$ (electrons Å^{-3})	2.05

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

3. Electron spin resonance results

The results of the electron spin resonance (ESR) measurements are summarized in Table 5. The powder spectrum of 2 consists of a single relatively broad line the g value of which is typical of isolated $[DDQ]^-$ ions, confirming the presence of this radical [12a].

The presence of $[TCNQ]^-$ counter-ions in all the other compounds is shown by ESR measurements. In some of the mononuclear complexes 4, 5, 7 and 8 the ESR lines are very narrow, implying relatively strong magnetic exchange interaction between $[TCNQ]^-$ radicals. To support this, we also measured frozen solutions of the 4, 5 and 8 in CH_2Cl_2 at the same temperature. The lines broaden by a factor between 5 and 10 with respect to the solid, indicating that magnetic exchange takes place in the former.

In contrast, 5 and 8 show slightly anisotropic, nearly axial ESR line shapes. We think that this anisotropy resides in the asymmetry of the metal cation. Complex 6 shows an isotropic ESR line but its half-width is large enough for us to exclude magnetic exchange in that case. Lacking any crystal structure determination for this compound, we speculate that $[TCNQ]^-$ radicals are far enough apart owing to the extra methyl group to prevent exchange.

The possibility of exchange coupling between $[TCNQ]^-$ ions in a low conducting compound merits some discussion. Electronic transport in [TCNQ] complexes takes place along the stacks of π rings, which in our compounds are too far away for it to be effective. However, the magnetic exchange interaction requires intermolecular electronic wavefunction overlap. A possible mechanism would be through cyanide groups of contiguous $[TCNQ]^-$ molecules, which in these mononuclear complexes would take place along chains, thus allowing electronic intermolecular overlap with very low electron transport.

Table 5
Electron spin resonance measured at 77 K in powder and solution samples

Compound	g [a]	ΔH_{pp} (solid) (mT)	ΔH_{pp} (frozen sol) (mT)
1	2.0022	0.57	–
2	2.0051	1.05	–
3	2.0024	0.2	–
4	2.0018	0.05	0.5
5	2.0030(∥)	≈ 0.06	0.28
	2.0022(⊥)		
6	2.0025	0.75	–
7	2.0020	0.05	–
8	2.0028(∥)	≈ 0.05	0.25
	2.0023(⊥)		

[a] Powder samples.

4. Experimental details

The starting materials $[Au_2(CH_2PPh_2CH_2)_2]$ [23], $[Au(CH_2PR_3)_2]ClO_4$ [7] and LiTCNQ [24] were prepared as described previously. All other reagents were obtained commercially.

The C, H, N analyses were carried out on a Perkin–Elmer 2400 microanalyser. Conductivities were measured in approximately 5×10^{-4} mol dm^{-3} acetone solutions, with a Jenway 4010 conductimeter. Melting points were measured on a Gallenkamp apparatus. IR spectra were recorded (4000–200 cm^{-1}) on Perkin–Elmer 883 and Perkin–Elmer 3700 spectrophotometers, using Nujol mulls between polyethylene sheets, and KBr pellets. The NMR spectra were recorded on a Varian XL 300 spectrometer in CDCl$_3$. Chemical shifts are relative to SiMe$_4$ (external ^{1}H) and 85% H$_3$PO$_4$ (external ^{31}P). The elemental analyses, conductivities, melting points, ^{31}P NMR and some IR data of the new complexes are listed in Table 1.

4.1. Electron spin resonance

The ESR spectra were recorded at 77 K using 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.

4.2. Synthesis of $[Au_2(CH_2PPh_2CH_2)_2]_n(acceptor)$ $(acceptor = TCNQ, n = 2 (1))$ $(Acceptor = DDQ, n = 1 (2))$

To a dichloromethane solution (15 cm^3) of $[Au_2(CH_2PPh_2CH_2)_2]$ (0.082 g, 0.1 mmol) was added the acceptor TCNQ (0.020 g, 0.1 mmol) or DDQ (0.022 g, 0.1 mmol). After stirring for 2 h the solution of 1 was concentrated to 5 cm^3, whereupon the addition of diethyl ether precipitated 1 as a green solid. The compound with DDQ precipitated without addition of ether. After stirring for 3 h the solid was filtered off and washed thoroughly with CH_2Cl_2. Yield, 91% (1), 92% (2). 1: ^{1}H NMR: $\delta = 1.84$ (d, 8H, CH_2–P, $^2J_{P-H} = 9.7$ Hz), 7.6–7.2 (m, 44 H, Ph) ppm.

4.3. $[Au_2(NC_5H_4S)_2](TCNQ)$

To a dichloromethane suspension (15 cm^3) of $[Au_2(NC_5H_4S)_2]$ (0.061 g, 0.1 mmol) was added TCNQ (0.020 g, 0.1 mmol). A black solid 3 appeared immediately, which was filtered off and washed with CH_2Cl_2 (yield, 82%).

4.4. [Au(CH₂PR₃)₂](TCNQ) (PR₃ = PPh₃ (4), PPh₂Me (5) or PPhMe₂ (6))

4.4. $[Au(CH_2PR_3)_2](TCNQ)$ $(PR_3 = PPh_3$ (4), PPh_2Me (5) or $PPhMe_2$ (6))

To an ethanol solution (15 cm³) of the perchlorates [Au(CH₂PR₃)₂]ClO₄ (0.1 mmol)(PR₃ = PPh₃ (0.084 g), PPh₂Me (0.072 g) or PPhMe₂ (0.060 g)) was added LiTCNQ (0.021 g, 0.1 mmol). Green solids precipitated after 5 min. After stirring for 4 h, the solids were filtered off, washed with ethanol and dried with OEt₂ (yield, 62% (4), 50% (5), 57% (6)).

4.5. $[Au(CH_2PR_3)_2](TCNQ)_2$ $(PR_3 = PPh_3$ (7) or $PPh_2Me(8))$

(a) To a dichloromethane solution (15 cm³) of **4** and **5** (**4**, 0.095 g; **5**, 0.082 g, 0.1 mmol) was added TCNQ (0.020 g, 0.1 mmol). The solutions turned dark green. After stirring for 2 h, the solutions were concentrated to 5 cm³. Addition of diethyl ether (10 cm³) precipitated the dark-green solids **7** and **8**.

(b) To a methanol (10 cm³) and acetonitrile (5 cm³) solution of the perchlorates [Au(CH₂PR₃)₂]ClO₄ (0.1 mmol) (PR₃ = PPh₃ (0.084 g) or PPh₂Me (0.072 g)) under dinitrogen was added a mixture of LiTCNQ (0.021 g, 0.1 mmol) and TCNQ (0.020 g, 0.1 mmol). The solutions turned dark green. After stirring for 4 h the solutions were concentrated to 5 cm³. Addition of diethyl ether (10 cm³) precipitated dark-green solids which were washed with water and dried with OEt₂ (yield, 81% (7), 61% (8)).

4.6. Crystal structure determination of 4

The crystal was mounted in inert oil on a glass fibre. Data were collected using monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) on a Siemens P3 diffractometer with an LT-2 low temperature attachment. The scan type was ω. Cell constants were refined from setting angles of 48 reflections in the range of $2\theta = 20$–23°. Absorption corrections were applied on the basis of Ψ scans.

The structure was solved by the heavy-atom method and refined anisotropically on F^2 using the program SHELXL 93 [25]. Hydrogen atoms were included using a riding model. To stabilize the refinement of the light atoms, 497 restraints were applied; ring atoms were restrained to be planar, anisotropic displacement parameter components of neighbouring atoms to be similar, and the TCNQ moieties to be similar (free refinement led to no significant differences). Other data are listed in Table 4.

5. Supplementary material available

Full details of the structure determination have been deposited at the Fachinformationszentrum Karlsruhe,

Gessellschaft für Wissenschaftlich-technische Information mbH, 76344 Eggenstein-Leopoldshafen, Germany. Any request for this material should quite a full literature citation and the reference number CSD 1.

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