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Solid state and solution studies of a T-shaped gold(I) complex: $Au[(C_6H_5)_2PCH_2N(C_6H_5)_2]_2Cl$

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Abstract

The addition of the ligand NPm (diphenylphosphino diphenylamino methane) to the $Na[AuCl_4]$ salt reduced by thiodiglycol or directly to Ph_3PAuCl leads to the same product of general formula $(NPm)_2AuCl$. The structure of this complex has been determined by X-ray crystallography. The colorless orthorhombic compound crystallizes in the space group *Fdd*2, $Z=8$, $a=24.941(4)$, $b=32.576(4)$, $c=10.299(1)$ Å, with R and R_w values of 2.5 and 2.0%, respectively. The ligand is P-bonded to gold. The ionic or covalent character of the Au–Cl bond is discussed in regard to the bond length and the conductivity data. ^{31}P NMR solution studies are reported.

Keywords: Crystal structures; Gold complexes; Bidentate phosphine complexes

1. Introduction

Although gold is certainly the most famous of all metals, its coordination chemistry has not been studied as much as that of other precious metals like platinum for example. However during the last decade the number of papers dealing with gold chemistry has greatly increased. This new interest in gold complexes is partly related to its use for the treatment of arthritis and cancer.

Bidentate or polydentate phosphines give rise to a variety of interesting species, the structures of which are a function of the ligand and also of the preparation scheme. Moreover the well known cytotoxicity and antitumor activity of ddpe and related diphosphines is often enhanced when these ligands are metal complexed [1–3]. A number of bis(diphosphino) gold(I) complexes have been recently tested for their antitumor activity and found to be active against P388, M5076 and sarcoma [4]. A mixed-donor dibasic ligand which may bond either by phosphorus or by nitrogen may allow a new kind of complex to be elaborated.

We describe here the synthesis, characterization in solution and in the solid state of a monomeric complex of general formula L_2AuX obtained from NPm (diphenylphosphino diphenylamino methane, $(C_6H_5)_2PCH_2N(C_6H_5)_2$.

2. Experimental

IR spectra were recorded on a Perkin-Elmer 983 G spectrophotometer in the solid state (in polyethylene or CsBr mulls). NMR spectra were recorded on WHM 200, WHM 250 and ARX 400 Bruker Fourier-transform spectrometers in $CDCl_3$ solution. Chemical shifts for ^{31}P NMR spectra were referenced to external H_3PO_4/D_2O (85/15 vol.) and recorded from 323 to 213 K. ^1H and ^{13}C spectra were referenced to Me_4Si and recorded at room temperature. Analyses were carried out by the Interuniversity Microanalytical Services.

All the compounds were prepared using a vacuum line under an atmosphere of argon. Solvents were deoxygenated by bubbling nitrogen and degased immediately before use. Commercially available reagent-grade chemicals were used.

2.1. *$(C_6H_5)_2PCH_2N(C_6H_5)_2(NPm)$*

The ligand was prepared as previously described [5] and recrystallized from CH_2Cl_2/C_2H_5OH.

Abbreviations: NPm = $Ph_2PCH_2NPh_2$; etu = ethylenethiourea; Cy_3P = tricyclohexylphosphine; Ph_2MeP = diphenylmethylphosphine; Me_2PhP = dimethylphenylphosphine; PP = 2,11-bis(diphenylphosphinomethyl) benzo(c) phenanthrene); dppe = (1,2-bis(diphenylphosphino)ethane.

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2.2. $(NPm)_2AuCl$

Method a. $Na[AuCl_4]\cdot 2H_2O$ (0.2 g) was reduced to Au(I) using thiodiglycol $[S(CH_2CH_2OH)_2]$ (0.123 g) in a mixture acetone/water (1/3, 20 ml). After stirring until the solution became colorless (1 h) the ligand NPm (0.368 g in 40 ml $CHCl_3$) was added dropwise. The mixture was stirred for 2 h and a white solid was obtained by addition of diethyl ether. The precipitate was filtered off, washed with diethyl ether and dried in vacuo.

Method b. Ph_3PAuCl was prepared as previously described [6].

A solution of Ph_3PAuCl (0.16 g) in toluene (20 ml) was added to a large excess of NPm (0.48 g) dissolved in acetone (20 ml). Four hours of stirring followed by addition of hexane gave white crystals after one day at 4 °C. They were filtered off and dried in vacuo.

The physical characterization and elemental analysis are identical for the products obtained from methods a and b. *Anal.* Calc. for $AuC_{50}H_{44}ClN_2P_2$: C, 62.31; H, 4.58; N, 2.64; Au, 17.68. Found (method b): C, 61.20; H, 4.55; N, 2.76; Au, 16.64%.

2.3. X-ray crystal structure determination

Crystal data, intensity measurements and structure refinements are summarized in Table 1. Unit cell parameters and diffracted intensities were measured at room temperature on a STOE STADI 4 diffractometer using graphite monochromated Mo Kα radiation. Data were corrected for Lorentz and polarization effect and for absorption [7]. The structure was solved by direct methods (MULTAN87) [8] and refined by the XTAL program [9]. Atomic scattering factors and anomalous dispersion terms are taken from Ref. [10]. The chirality/polarity [11] of the structure was refined and converges to $x=0.01(1)$. All coordinates of the H atom have been calculated. An ORTEP plot of the molecule is shown in Fig. 1 along with the labeling scheme, and a stereoscopic view is given in Fig. 2. Selected interatomic distances and angles are listed in Table 2. See also Section 4.

Table 1
Summary of crystal data, intensities measurements and structure refinement

Formula	$Au[(C_6H_5)_2PCH_2N(C_6H_5)_2]_2Cl$
Molecular weight	967.3
Crystal size (mm)	0.13×0.13×0.30
Crystal system	orthorhombic
Space group	*Fdd*2
a (Å)	24.941(4)
b (Å)	32.576(4)
c (Å)	10.299(1)
V (Å^3)	8368(2)
Z	8
D_c (g cm^{-3})	1.54
$F(000)$	3872
μ(Mo Kα) (mm^{-1})	3.685
A*, min., max.	1.478, 1.768
2θ Range (°)	6–44
No. measured reflections	2776
No. observed reflections	2355
Criterion for observed reflections	$\lvert F_o\rvert > 4\sigma(F_o)$
Weighting scheme, ω	$1/\sigma^2(F_o)$
Max. and min. $\Delta\rho$ (e Å^{-3})	+0.46, −0.47
R, R_w (%)	2.5, 2.2
No. parameters	254
Absolute structure parameter, x	0.01(1)
S	3.58

3. Results and discussion

3.1. Chemistry

The addition of the ligand NPm to the $Na[AuCl_4]$ salt (reduced by thiodiglycol) in a 2/1 ratio or directly to an Au(I) complex, i.e. Ph_3PAuCl, leads to the same product of general formula $(NPm)_2AuCl$.

3.2. Physical data

Conductivities measurements indicate that the complex does not dissociate appreciably at room temperature in $CHCl_3$ (1.2 Ω^{-1} cm^2 mol^{-1}) but exhibits a quite large dissociation in CH_3CN (62 Ω^{-1} cm^2 mol^{-1}). In the range 600–200 cm^{-1}, the solid state IR spectra of the complex compared with the spectra of the free ligand, exhibit a characteristic absorption at 345 cm^{-1} which was attributed to ν(Au–P).

3.3. Solid state studies

Selected interatomic distances and bond angles are given in Table 2. The structure consists of molecules of $[(C_6H_5)_2PCH_2N(C_6H_5)_2]_2AuCl$. The metal atom is tri-coordinated to two phosphorus atoms and to one chlorine. The molecule unit is located on a C_2 axis with the Au and Cl atoms in special position 8a. Consequently, the coordination about the gold is planar. It should be noted that the two phenyl substituents are almost coplanar (0.4(3)°) with the coordination plane leading to a short contact distance between two C_2 related H atoms (H8...H8′ = 2.23 Å). Although the NPm ligand may act as either a P or an N donor, we did not observe N-coordination. A number of complexes of gold with nitrogen donor ligands are known today [12], but when it competes with phosphorus, nitrogen is too hard to coordinate to gold(I) and the NPm ligand is therefore P-monodentate.

X-ray structural studies have largely demonstrated that the most common stereochemistry of gold(I) complexes is linear, the coordination number of the metal

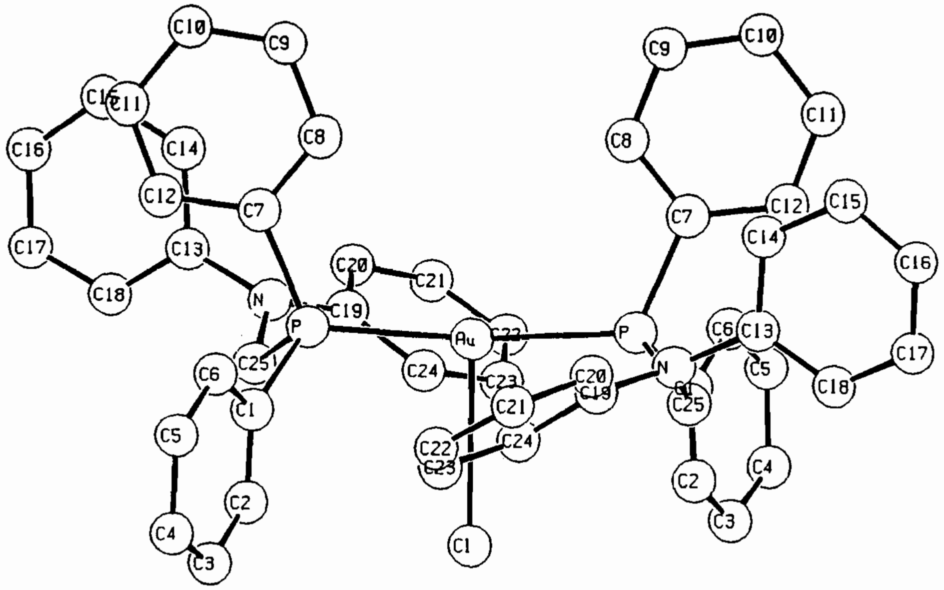

Fig. 1. Structure of Au(NPm)$_2$Cl with atom numbering.

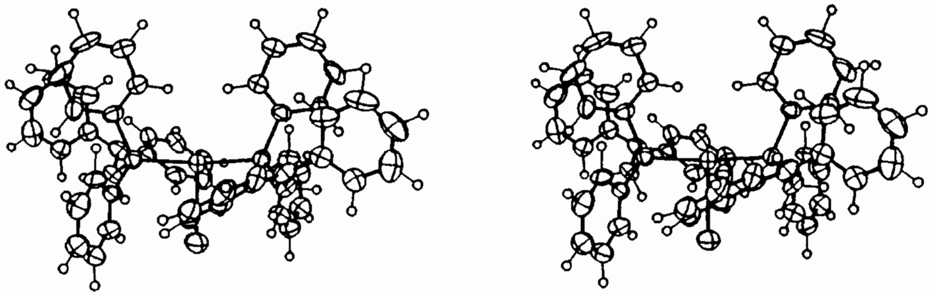

Fig. 2. A stereoscopic view of Au(NPm)$_2$Cl. Ellipsoids are represented with 50% probability.

Table 2
Selected interatomic distances (Å) and bond angles (°) with e.s.d.s in parentheses

Metal environment			
Au–P	2.300(3)	Au–Cl	2.951(4)
Cl–Au–P	93.4(1)	P–Au–P′	173.2(1)
Ligand			
P–C1	1.83(1)	P–C7	1.82(1)
P–C25	1.86(1)	N–C13	1.44(2)
N–C19	1.37(1)	N–C25	1.44(1)
Angles			
Au–P–C1	111.5(4)	Au–P–C7	115.9(5)
Au–P–C25	113.6(4)	C1–P–C7	107.8(6)
C1–P–C25	100.9(5)	C7–P–C25	105.9(5)
C13–N–C19	119.7(9)	C13–N–C25	116.0(9)
C19–N–C25	121(1)	P–C25–N	114.8(8)

P′ refers to a symmetry-generated atom.

atom being two; such complexes may be cationic such as [(Ph$_3$P)$_2$Au]$^+$, neutral such as [(Ph$_3$P)AuCN] or anionic such as [AuCl$_2$]$^-$. Higher coordination numbers are also known for gold(I), and tri- or tetra-coordinated gold complexes have been described.

LAuX complexes invariably have linear two-coordination at the gold(I) but complexes of the type L$_2$AuX (where X is an anion which can also act as a ligand) could a priori exhibit three-coordination; however due to the preponderant tendancy of gold to di-coordination, several species of these types do not achieve three-coordination and thus the X anion may be ionic rather than coordinated. This is the case of [etu$_2$Au]$^+$Cl$^-$ [13] and [(Cy$_3$P)$_2$Au]$^+$SCN$^-$ [14]. In [(PhMe$_2$P)$_2$Au]SnCl$_3$ [15] the SnCl$_3$$^-$ anion appeared to be uncoordinated although the P–Au–P angle was 158.3°. [(Ph$_2$MeP)$_2$Au]PF$_6$ was the first L$_2$Au$^+$ structure to be determined and is exactly linear at Au [16]. The ability of L$_2$AuX complexes to be di- or tri-coordinated certainly depends on the nature of L but also on the coordinating power of the X anion; when X is a poor ligand such as nitrate or PF$_6$ the ionic [L$_2$Au]$^+$ is formed exclusively.

As our ligand is only coordinated by phosphorus, its geometry may be tentatively compared to that of (Ph$_3$P)$_2$AuCl [17]. This last complex may be described as almost trigonal planar although the angles deviate somewhat from the idealized geometry of 120° (132.1° for P–Au–P′, 118.7° for P–Au–Cl). In (NPm)$_2$AuCl the geometry is quite different having a T-shaped form and a C_2 symmetry axis. The P–Au–P′ and P–Au–Cl angles are 173.2(1) and 93.4(1)°, respectively. This geometry may be compared to that observed in the complex PPAuCl (PP = 2,11-bis(diphenylphosphinomethyl) benzo(c) phenanthrene) [18] where the P–Au–P and P–Au–Cl angles are 175.7(1) and 90.4(1)°, respectively. However it should be noted that in this case the steric requirements of the ligand undoubtedly impose the geometry since the bidentate phosphine ligand bridges *trans* coordination sites.

The different nature of the covalent or ionic character of the complex may be supported by the observed Au–Cl bond length. Etu_2AuCl [13] was originally formulated as ionic since it is water soluble and the Au–Cl distance of 3.62 Å confirms this ionic nature. In $(NPm)_2AuCl$ the Au–Cl bond distance of 2.951(4) Å is considerably longer than that previously reported [19]. It greatly exceeds the standard distance obtained by the sum of the covalent radii of chlorine and gold (1 and 1.5 Å, respectively) but is shorter than the sum of the ionic radii (1.81 and 1.37 Å, respectively) [20]. For ease of comparison we have collected in Table 3 bond angles and bond distances observed in some mono-, di- or tri-coordinated gold(I) compounds. In tri-coordinated complexes, the Au–Cl bond lengths correlate with the P–Au–P bond angles. These results are consistent with the trend that in trigonal species the widest angle is opposite to the weakest bond. However it should be noted that, except for the Ph_3PAuCl complex (Au–Cl = 2.279(3) Å), Au–Cl bonds are generally long in molecular complexes, due to the great dissociation process observed in gold complexes; the extreme case being a diagonal geometry around Au with an ionic Au–X bond.

Studies of gold–ligand IR stretching and other vibrations can yield useful informations about the metal–ligand bond strength and the degree of covalency in the metal–ligand bond. There have been several studies of LAuCl complexes, underlining that the Au–X stretching frequencies show only a slight dependance on the nature of the other ligands. In Ph_3PAuCl, ν(Au–Cl) is reported at 330 cm^{-1} by Westland [27], at 326 cm^{-1} for $(MeO)_3PAuCl$ [28], 366 and 340 cm^{-1} for Ph_3PAuCl_3 [29] while 349 cm^{-1} is attributed to the stretching frequency of the Au–Cl bond in $K[AuCl_4]$ [30]. In general, gold–halogen bridging stretching frequencies are slightly lower than the terminal ones. In $(NPm)_2AuCl$ ν(Au–Cl) does not appear when recorded in polyethylene mulls. This band may be hidden by the Au–P stretching which occurs in the same frequency area. In CsBr mulls, the chlorine is substituted by bromine and ν(Au–Br) is observed at 260 cm^{-1} [30, 31].

Au–P bonds vary in length considerably, as expected for a bond between a soft ligand and a soft metal at a low oxidation state. It has previously been reported [17] that an Au–L bond lengthening occurs on going from a linear gold complex to a trigonal planar gold complex. In linear complexes, gold(I) in sp-hybridized while in the trigonal planar complexes gold(I) is sp^2-hybridized; thus increasing the s-character in the Au–P bond leads to the formation of a stronger σ bond. The Au–P distance is 2.235(3) Å in Ph_3PAuCl [21] and

Table 3
Geometries around gold in some phosphine–gold(I) complexes

Compound	Au–Cl	P–Au–P′	P–Au–Cl	Au–P	Ref.
Regular or not di-coordination					
Ph_3PAuCl	2.279(3)		179.63(8)	2.235(3)	[21]
$[(Ph_2MeP)_2Au](PF_6)^-$		180		2.316(4)	[16]
$[(Cy_3P)_2Au]^+(SCN)^-$		177.2		2.305 (av.)	[14]
Regular or not tri-coordination					
PPAuCl	2.818(3)	175.7(1)	90.4(1) 94.4(1)	2.307(2) 2.310(2)	[18]
PNm_2AuCl	2.951(4)	173.2(1)	93.4(1)	2.300(3)	this work
$[(Ph_2P)_2CH_2AuCl]_2$	2.771(4)	155.9(1)	88.4 115.7	2.307 (av.)	[22]
$(Ph_3P)_2AuCl$	2.500(4)	132.1(1)	118.7(1)	2.33(9) 2.32(3)	[17]
$[(Ph_3P)_3Au]^+(B_9H_{12}S)^-$		119.3 (av.)		2.382 (av.)	[23]
$[(Ph_3P)_3Au]^+(Ph_4B)^-$		119.9 (av.)		2.384 (av.)	[24]
Tetra-coordination					
$(Ph_3P)_3AuCl$	2.710	117.4 (av.)	99.3 (av.)	2.410 (av.)	[25]
$[(Ph_2MeP)_4Au]^+(PF_6)^-$		105.24(4) 118.32(4)		2.449(1)	[26]

2.325 (av.) Å in $(Ph_3P)_2AuCl$ [17]. In $[(Ph_3P)_3Au]^+$ [23,24] an averaged distance of 2.38 Å is found, and 2.449(1) Å is observed in $[(Ph_3P)_4Au]^+$ [26]. The Au–P distance of 2.300(3) Å observed here lies between those observed in di- and tri-coordinated complexes.

The assignment of ν(Au–P) is not straightforward due to the fact that there are wide variations. In trimethylphosphine complexes of gold, ν(Au–P) is considered to occur in the region 335–381 cm^{-1}. It is significant that ν(Au–P) is lower in the tetrahedral $[(PMe_3)_4Au]^+$ (335 cm^{-1}) than in the linear $[(PMe_3)_2Au]^+$ (353 cm^{-1}) [28], according to the weakening of the Au–P bond with increasing coordination number; we attributed the observed band at 345 cm^{-1} to Au–P stretching, data which are coherent with the determined bond length.

Considering the measured P–Au–P angle and the Au–P and Au–Cl distances, the coordination of gold(I) in $(NPm)_2AuCl$ is found to be intermediate between the two extremes, i.e. a trigonal planar coordination and a linear two-fold coordination. However the particularly long Au–Cl bond distance prompts us to suggest that there is more ionic form $[L_2Au]^+Cl^-$ than covalent character in the Au–Cl bond. Geometries within the phosphine ligand are standard.

Gold(I) differs from silver(I) and copper(I) which have a greater tendency to form complexes with higher coordination numbers. For example as previously mentioned the complexes Ph_3PAuCl and $(Ph_3P)_2AuCl$ are linear and trigonal, respectively. By contrast while $(Ph_3P)_2CuX$ (X = Cl, Br, I, NO_3) are structurally identified as trigonal monomer units [32], with the same triphenylphosphine ligand the 1/1 complexes Ph_3PCuX (X = Cl, Br, I) have previously been characterized as tetrameric with a cubane or chair form according to the size of X [33–35], the copper atoms having a coordination number of four. We have recently prepared and structurally identified [36], with the same NPm ligand, a copper(I) complex of general formula $(NPm)_2CuCl$. This complex differs strongly from the gold complex since the structure may be described as almost trigonal planar with the Cl–Cu–P1 and Cl–Cu–P01 angles of 109.24(8) and 117.84(8)°, respectively, the value of P1–Cu–P01 being 132.64(8)°. The Cu–Cl bond distance is 2.257(2) Å which is a normal length for a covalent bond [37], moreover conductivity measurements yield complementary information since the copper complex is a non-electrolyte ($5\ \Omega^{-1}\ cm^2\ mol^{-1}$). Tri-coordinate phosphine complexes of M(I) (M = Cu, Ag, Au) have been previously studied [18] and bear out our results; the P–M–P angle and the M–Cl distance increase from Cu to Au and reflect the different nature of the metal–chlorine bond.

3.4. Solution studies: ^{31}P and ^{13}C NMR

In the ^{13}C NMR spectra, the aromatic carbon atoms bonded to the phosphorus and the nitrogen atoms exhibit markedly different behavior. Compared to free NPm the shift of the carbons bonded to nitrogen is practically unchanged upon complexation (147.2 versus 148.1 ppm in the free ligand). By contrast, the carbons bonded to phosphorus are significantly shielded after complexation (131.4 versus 137.3 ppm). In the ^{13}C spectra the $^1J(CH_2–P)$ coupling constant is markedly different in the complex and the free ligand (22.9 versus 14.9 Hz). We do not observe resonances attributable to the free ligand in the ^{13}C spectra of the complexes.

The structural integrity of solid gold(I) phosphine complexes is not necessarily retained in solution, and discrete crystalline compounds were found to give several solution species in rapid exchange equilibrium [38–40]. A variable temperature NMR study may be a convenient mean to elucidate this kind of problem. The ^{31}P NMR spectra of the complex have been studied from 213 to 323 K. In the range 300–323 K, the $^{31}P\{^1H\}$ spectrum of $(NPm)_2AuCl$ exhibits a single peak at +21.5 ppm. On cooling the solution, the spectra broaden and the resonance moves progressively to higher frequency, to finally give a sharp signal at 233 K. Below 233 K the spectrum shows no change with only a single resonance at +31.5 ppm. Thus between 300 and 233 K the observed signal indicates that a rapid equilibrium exchange occurs between the two species. Since as previously noted we do not observe resonances attributable to the free ligand, the signal at +31.5 ppm may correspond to $(NPm)_2AuCl$, while the signal at +21.5 ppm may correspond to $[(NPm)_2Au]^+$. Previous works have shown that the ^{31}P chemical shift of a covalent complex appears at higher frequency compared to its ionic homologue [25].

Inconsistences between the species present in solution and those obtained by crystallization are reported for various gold–phosphine complexes [40]. Schmidbaur and Franke [28] studying the interaction of $P(OMe)_3$ with $[Au\{P(OMe)_3\}_2]^+$ concluded that two- and four-coordinated species are present in solution. Mays and Vergnano [39] indicated that the addition of PEt_3 to $[Au(PEt_3)_2]^+$ resulted in the successive formation of $[Au(PEt_3)_3]^+$ and $[Au(PEt_3)_4]^+$. The ^{31}P spectra of the complex $(NPm)_2AuCl$ were recorded in the presence of various amounts of added ligand, with a view to examining if other species were present in solution. At room temperature addition of free ligand results only in a broadening and a progressive shift of the signal from +21.5 ppm towards the position of the free ligand as increasing amounts are added. Addition of 0.5 mol equiv. of ligand causes the appearance of a second sharp peak at +23.0 ppm, the initial peak being at +31.5 ppm. Addition of more ligand results in a diminution of intensity of the initial peak which completely disappears when 2 mol equiv. are added while the second peak remains unchanged in its position. When more aliquots are added a new sharp peak appears at -25 ppm which is attributed to the presence of free ligand. This experiment indicates that by addition of more ligand to $(NPm)_2AuCl$ only one species is formed. The fact that this species is formed until the phosphine:gold ratio is greater than 4:1 indicates that the formation of $[AuL_4]^+$ species occurs. This assumption is supported by the conductivity measurements; by addition of ligand to the complex the conductivity increases and when the concentration of ligand is raised to a phosphine:gold ratio of 4:1 a limiting value is obtained (95 Ω^{-1} cm^2 mol^{-1} in acetonitrile).

4. Supplementary material

Tables of atomic coordinates, displacement parameters, bond lengths, bond angles and torsional angles for $(NPm)_2AuCl$ (3 pages) are available from the authors on request.

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