Alternating Right- and Left-Handed Helical Loops in a Self-Assembled Polymer: Direct Observation of Ring-Opening Polymerization of a Macrocyclic Gold Complex

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Abstract: Reaction of the ligand *N,N'*-bis(pyridin-3-yl)-1,3-benzenedicarboxamide (**1**) with the diphosphanedigold(I) complex [(μ-PP)(AuO_2CCF_3)$_2$] occurred by displacement of the trifluoroacetate ligands by the pyridyl groups of **1**, and crystallization gave the macrocyclic complex [Au_2(μ-PP)(μ-**1**)](CF_3CO_2)$_2$ (**2b**), when PP = *trans*-[Ph_2PCH=$CHPPh_2$] but the polymer [{Au_2(μ-PP)(μ-**1**)}$_x$](CF_3CO_2)$_{2x}$ (**3**), when PP = $Ph_2PCH_2CH_2PPh_2$. The polymer **3** contains a series of helical turns connected by linear chain sections, and the helices have alternating right- and left-handed conformations. The polymer **3** dissolves to give an equilibrium mixture of the macrocyclic ring complex [Au_2(μ-PP)(μ-**1**)](CF_3CO_2)$_2$ (**2a**), and ring-opened oligomers, thus giving insight into the mechanism of the ring-opening polymerization reaction.

Keywords: aurophilicity · crystal engineering · gold · helical structures · ring-opening polymerization

Introduction

The use of coordination chemistry in association with weak secondary binding effects of several kinds can give self-assembly of diverse functional macromolecules.[1] If a molecular building block has a tendency to twist, then helical structures are commonly formed in the self-assembly, in a process that is akin to chain-end control in polymerization but which is conformationally based and usually selective.[2] Unless the building block is a single enantiomer, the oligomer or polymer formed by such self-assembly will be racemic, and if individual coils are described as *R* or *S*, the material will normally contain equal amounts of *RRR* and *SSS* chains. Examples are found in many areas of chemistry from simple elemental structures like tellurium and vinyl polymers,[2] to more complex organic structures such as peptide nucleic acids[3] or, more directly relevant to the present work, the oligo(isophthalamide)s and similar derivatives.[4] The helicity is most commonly induced and maintained through hydrogen bonding, though several other secondary bonding forces can also be effective.[2–5] Herein we report the easy self-assembly of a polymer containing individual coils that are arranged in the sequence *RSRS..*, that is with alternating left- and right-handed helical coil units. We are not aware of any other crystalline polymer having such a structure, but there are some with more restricted helicity.[6, 7] An interesting example is present in the infinite loop structure found in a polymeric silver(I) bipyrazine complex, which contains alternating half-coils with opposite chirality,[6] and there are a few other relevant examples.[7] By analogy with the isotactic and syndiotactic nomenclature in polymer chemistry, the *RRRR/SSSS* and *RSRS* arrangements in conformationally asymmetric oligomers or polymers might be termed isohelic and syndiohelic, but syndiohelic polymers are rare,[6, 7] and the nomenclature will be needed only if the field undergoes further growth. The polymer reported below is formed by self-assembly using linear gold(I) connectors[8] and it is shown that in solution, oligomers are formed easily and reversibly by ring-opening of a digold(I) macrocycle and that the formation of aurophilic attractions[9] is a driving force for the ring-opening.

Results and Discussion

Reaction of the ligand *N,N'*-bis(pyridin-3-yl)-1,3-benzenedicarboxamide (**1**; Scheme 1) with the diphosphaedigold(I) complex [Au_2(μ-PP)(O_2CCF_3)$_2$] proceeds by displacement of the trifluoroacetate ligands by the pyridyl groups of **1**, and crystallization gave the macrocyclic complex **2b** when PP = *trans*-[Ph_2PCH=$CHPPh_2$] but the unusual polymer **3** when PP = $Ph_2PCH_2CH_2PPh_2$.

The structure of **2b** is shown in Figure 1 and bond lengths and angles are listed in Table 1. In the 19-membered ring structure, the core atoms of **1** are only slightly distorted from planarity, as apparently required to accommodate the

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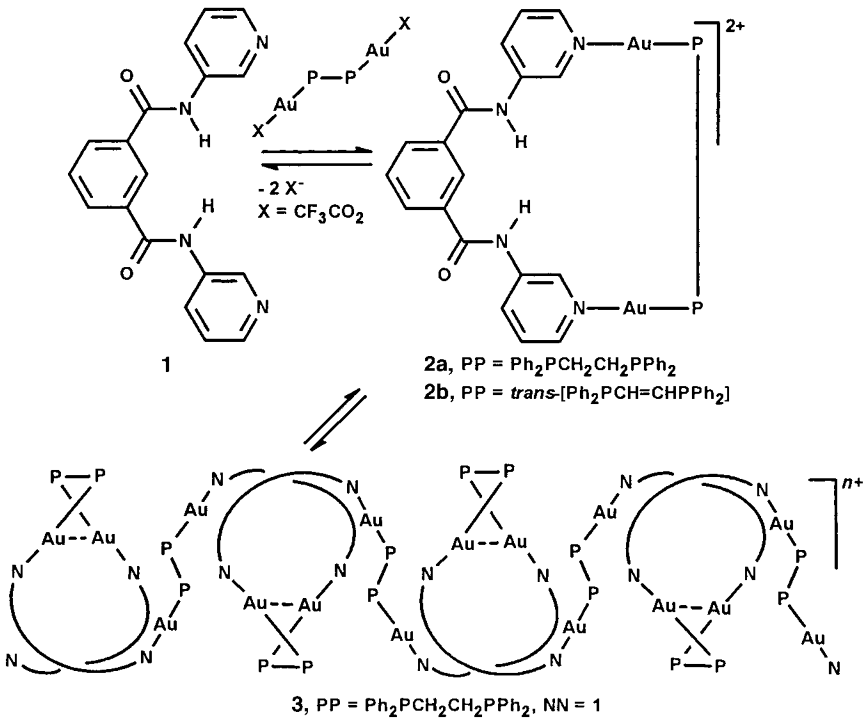

Scheme 1. Synthesis of the macrocycles **2** and polymer **3**.

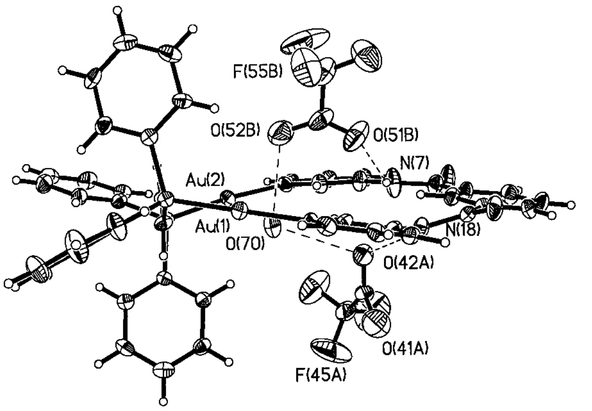

Figure 1. A side view of the structure of macrocyclic complex **2b**, illustrating the near planarity of the ligand **1**, and threading of the $[CF_3CO_2\cdots HOH\cdots O_2CCF_3]^{2-}$ units.

Table 1. Selected bond lengths [Å] and angles [°] for complex **2b**.

Au(1)–N(1)	2.064(6)	Au(2)–N(21)	2.069(5)
Au(1)–P(1)	2.226(2)	Au(2)–P(2)	2.232(2)
N(1)-Au(1)-P(1)	173.8(2)	N(21)-Au(2)-P(2)	177.9(1)

Au-(μ-PP)-Au unit. The bite distance N(1)–N(21) 7.8 Å is shorter than the corresponding distances of 8.3–10.4 Å found in various stable conformations of the free ligand **1**, in which distortions from planarity are more pronounced than in **2b**. Thus, dihedral angles O=C–C–C^2 in the free ligand **1** are typically about 40°, as calculated by molecular mechanics and determined experimentally in related compounds,[4] to minimise HNC(O)CC^{2}H H···H interactions. The transannular Au···Au distance of 6.26 Å in **2b** is much too long for any bonding interaction.[8, 9] There is a water molecule, O(70), close to the ring plane that is strongly H-bonded to a trifluoroacetate ion on either side (O(70)–O(52A) 2.72, O(70)–O(42B) 2.86 Å), thus forming an unusual pseudorotaxane structure. Each trifluoroacetate forms hydrogen bonds more weakly to an NH proton of the ligand **1** (O(42B)–N(18) 2.93, O(51A)–N(7) 3.10 Å).

The remarkable structure of **3** is shown in Figure 2, with bond parameters in Table 2. Figure 2a shows a short section of the polymer chain. There are two very different conformations of the more flexible diphosphane ligand, one (P(3)P(4), phenyl groups omitted for clarity) having the *anti* conformation leads to a "linear" section of chain with long separation Au(3)–Au(4) = 6.97 Å, while the other (P(1)P(2)) has a distorted *syn* conformation that allows a short contact Au(1)···Au(2) 2.99 Å and promotes curvature of the chain. Each ligand **1** is bowed from planarity and a single trifluoroacetate forms hydrogen bonds to both NH groups as shown in Figure 2a (N···O distances in the

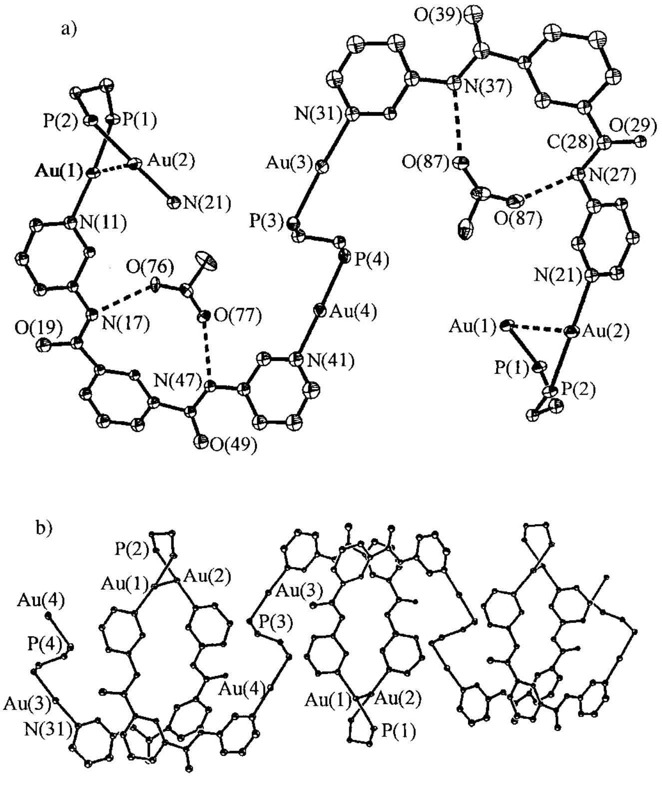

Figure 2. The structure of polymeric complex **3**: a) A short section of the chain illustrating the conformations of the diphosphane ligands, bowing of the ligands **1**, and H-bonding of trifluoroacetate ions (F atoms and phenyl groups omitted for clarity). b) A longer section of the cationic chain, illustrating the alternating left- and right-handed coils separated by linear sections.

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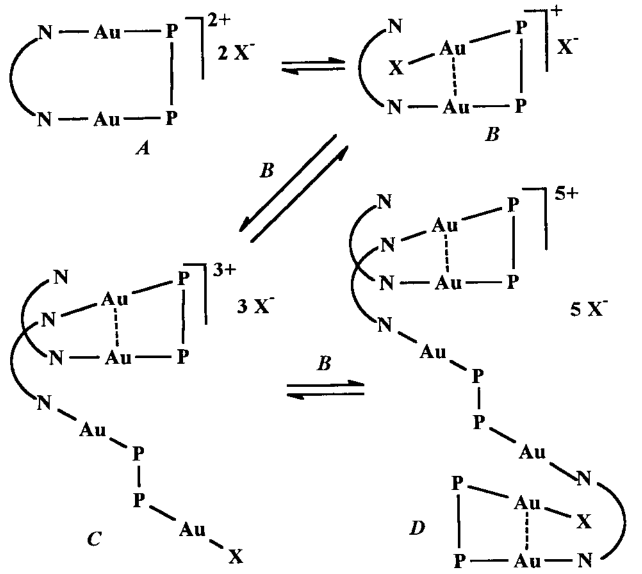
Table 2. Selected bond lengths [Å] and angles [°] for complex **3**.

Au(1)–Au(2)	2.994(1)	Au(1)–N(11)#1	2.10(1)
Au(2)–N(21)	2.07(1)	Au(3)–N(31)	2.08(2)
Au(4)–N(41)	2.09(2)	Au(1)–P(1)	2.236(5)
Au(2)–P(2)	2.242(5)	Au(3)–P(3)	2.233(5)
Au(4)–P(4)	2.242(6)		
N(11)#1-Au(1)-P(1)	175.5(4)	N(21)-Au(2)-P(2)	178.7(5)
N(31)-Au(3)-P(3)	175.8(4)	N(41)-Au(4)-P(4)	178.8(6)
N(11)#1-Au(1)-Au(2)	94.6(4)	P(1)-Au(1)-Au(2)	87.4(1)
N(21)-Au(2)-Au(1)	92.6(4)	P(2)-Au(2)-Au(1)	88.3(2)

range 2.67–2.75 Å). The bite distances for the bridging ligands **1** (N(11)–N(41) 9.79, N(21)–N(31) 9.90 Å) are longer than in **2b** but in the range expected for the unstrained ligand. Figure 2b shows part of the infinite chain structure of the cation, illustrating the alternating left- and right-handed coils. Each coil has favorable Au ··· Au aurophilic bonds, π stacking of pairs of ligands **1**, and π stacking involving phenyl groups (not shown). A regular helical structure would lead to unfavorable phenyl–phenyl and anion–anion repulsions between substituents on adjacent coils and so the observed structure with alternating coil and linear chain sections is preferred.

The structures of the complexes in solution were investigated by variable-temperature NMR spectroscopy. The structure **2b**, with the rigid backbone diphosphane PP = *trans*-[$Ph_2PCH{=}CHPPh_2$], is maintained over the temperature range 293–193 K as shown, for example, by the presence of a single ^{31}P NMR resonance at $\delta = 25.5$. However, the case is more complex when PP = $Ph_2PCH_2CH_2PPh_2$, and the spectra are both temperature and concentration dependent. At 293 K, the ^{1}H and ^{31}P NMR spectra are well defined and similar to those of **2b**, suggesting a similar ring structure **2a**. However, at lower temperatures, the ^{31}P NMR resonance, observed at $\delta = 26.5$ at room temperature and at a concentration of 7.5×10^{-3} M in CD_2Cl_2 solution, moves to higher δ and broadens down to 233 K ($\delta = 26.8$), then splits to give a singlet at $\delta = 26.0$ assigned to **2a** and two broad equal intensity envelopes at $\delta = 28.5$ and 30.3 assigned to ring-opened forms (Scheme 2). Complications arise due to additional equilibria between H-bonded, ion-paired and free anions. In addition, low-temperature spectra can only be obtained for dilute solutions since the polymer **3** precipitates at concentrations above 10^{-2} M (concentrations are based on a digold(I) unit as in **2**). For these reasons, the system is too complex for quantitative study, but the following conclusions are possible. At the concentration of 7.5×10^{-3} M, more than 80% of the complex is present as form **2a** at 293 K and interconversion with ring-opened forms is rapid so that only an average chemical shift is observed. At low temperature, exchange is slow and separate resonances are observed for ring and ring-opened forms. At 213 K, integration indicates that less than 40% is present as **2a**. At higher concentrations, the equilibrium favors ring-opened forms. For a saturated solution at 213 K (ca. 10^{-2} M), less than 20% is present as **2a** and the concentration of **2a** is too low to detect at 193 K. The spectra are readily interpreted in terms of Scheme 2, in which increasing concentration and lower temperature both favor ring-opened products and higher average molecular weights. At 193 K, the spectra are consistent with structure **3** in which the two phosphorus chemical shifts are assigned to phosphane ligands coordinated to gold atoms involved or not-involved in aurophilic bonding, but average chain length is only two to four units. The role of the anion is also important (Scheme 2); with noncoordinating anions such as triflate the polymers are formed irreversibly and are insoluble in noncoordinating solvents. In solution, only low molecular weight ring-opened fragments can be observed and so physical properties expected for a true polymer solution, such as greatly increased viscosity, are not observed.



Scheme 2. Proposed mechanism of ring-opening polymerization.

Conclusion

The system described above gives a clear picture of how ring-opening polymerization of **2a** to **3** occurs, and gives insight into the kinetic and thermodynamic factors involved. Clearly, in solution, enthalpy effects strongly favor ring-opened oligomers, whereas entropy effects strongly favor the ring **2a**, such that the equilibrium is very strongly temperature dependent. The favorable aurophilic and π-stacking effects in the coil sections of **3**, together with relief of ring strain present in **2a**, will give important enthalpic contributions to ring opening. Similar equilibration between cyclic and chain structures has been analyzed similarly for organic systems involving hydrogen bonding.[5] Since the ring-opened form of **2b** could not give similar coils as found in **3**, as a result of the rigidity of the diphosphane backbone, the enthalpy of ring opening is less favorable and the ring structure is preferred even at low temperature. The difference of two hydrogen atoms between **2a** and **2b** makes a big difference to the chemistry!

Experimental Section

NMR spectra were recorded using a Varian Mercury 400 and an Inova 400 spectrometer. ^{1}H chemical shifts are reported relative to tetramethylsilane, while ^{31}P and ^{19}F chemical shifts are reported relative to 85 % H_3PO_4 and to $CFCl_3$, as external references, respectively. IR spectra were recorded as Nujol mulls. Conformations of the ligand **1** were calculated by molecular mechanics, using PCMODEL (Serena Software, 1999).

[μ-(*trans*-[$Ph_2PCH{=}CHPPh_2$])Au_2(μ-NC_5H_4-3-NHC(O)-1-C_6H_4-3-C(O)NH-3-C_5H_4N)]$(CF_3COO)_2$ (2b): To a solution of 1,3-C_6H_4(CONH-3-C_5H_4N)$_2$ (0.050 mmol) in CH_2Cl_2 (5 mL) was added a filtered solution of [μ-(*trans*-[$Ph_2PCH{=}CHPPh_2$])$Au_2(O_2CCF_3)_2$] (0.050 mmol), prepared from [μ-(*trans*-[$Ph_2PCH{=}CHPPh_2$])Au_2Cl_2] (0.050 mmol) and AgO_2CCF_3 (0.10 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred for 0.5 h, the volume was reduced to 4 mL, and pentane (10 mL) was added to give a white precipitate of the product, which was collected by filtration, washed with diethyl ether and pentane, and dried under vacuum. Yield: 71 %: m.p.: 152 °C (decomp); ^1H NMR (CD_2Cl_2): $\delta = 11.31$ (s, 2H; CONH), 9.36 (s, 2H; H^2 py), 8.83 (s, 1H; H^2 ph), 8.65 (d, 2H; H^6 py), 8.34 (d, 2H; H^4 py), 8.15 (d, 2H; H^4, 6 ph), 7.51 – 7.80 (m, 20H; C_6H_5), 7.48 (m, 3H; H^5 py + H^5 ph), 3.05 (br s, 4H; PCH_2); ^{31}P NMR: $\delta = 26.58$ (s); ^{19}F NMR: $\delta = -75.33$; elemental analysis calcd (%) for $Au_2C_{48}H_{36}N_4F_6O_6P_2$: C 43.20, H 2.72, N 4.20: found: C 42.61, H 2.40, N 4.22. Single crystals were grown by slow evaporation from a solution in dichloromethane.

[{(μ-$Ph_2PCH_2CH_2PPh_2$)Au_2(NC_5H_4-3-NHC(O)-1-C_6H_4-3-C(O)NH-3-C_5H_4N)}$_x$]$(CF_3COO)_{2x}$ (3): This was prepared similarly by using the analogous complex with the ligand $Ph_2PCH_2CH_2PPh_2$. Yield: 79 %; m.p.: 152 °C (decomp); ^1H NMR (CD_2Cl_2): $\delta = 11.23$ (s, 2H; CONH), 9.32 (d, 2H; H^2 py), 8.87 (s, 1H; H^2 ph), 8.79 (d, 2H; H^6 py), 8.30 (d, 2H; H^4 py), 8.19 (m, 2H; H^4, 6 ph), 7.56 – 7.75 (m, 21H; H^5 ph + C_6H_5), 7.54 (m, 2H; H^5 py), 7.29 (m, 2H;=CH); ^{31}P NMR: $\delta = 25.50$ (s); ^{19}F NMR: $\delta = -75.37$ (s); IR (Nujol): $\tilde{\nu} = 3059, 3178, 3243$ (ν(NH)); 1681 (ν(CO)) cm^{-1}: elemental analysis calcd(%) for $Au_2C_{48}H_{38}N_4F_6O_6P_2$: C 43.13, H 2.87, N 4.19: found: C 43.32, H 2.65, N 4.07. Single crystals were grown by slow diffusion of hexane into a solution of the complex in acetone.

X-ray structure determinations: Crystals were mounted on glass fibers. Data were collected by using a Nonius Kappa-CCD diffractometer with COLLECT (Nonius, 1998) software. The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using the Nonius DENZO package. The data were scaled by using SCALEPACK (Nonius, 1998). The SHELXTL 5.1 (Sheldrick, G.M., Madison, WI) program package was used to solve and refine the structure by direct methods. A summary of crystallographic data can be found in Table 3. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-168450 and CCDC-168451. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.uk).

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Table 3. Crystal and refinement data of complexes **2b** and **3**.

	3 · Me_2CO · hexane · H_2O	**2b** · CH_2Cl_2 · H_2O
formula	$C_{105}H_{96}Au_4F_{12}N_8O_{14}P_4$	$C_{49}H_{38}Au_2Cl_2F_6N_4O_7P_2$
fw	2833.64	1435.61
T [K]	200(2)	200(2)
λ [Å]	0.71073	0.71073
space group	$P2(1)/c$	$P\bar{1}$
a [Å]	11.3587(9)	9.7445(4)
b [Å]	33.551(3)	14.5183(7)
c [Å]	28.731(2)	19.6781(7)
α [°]	90	107.024(3)
β [°]	92.277(4)	99.854(3)
γ [°]	90	98.263(2)
V [Å^3]	10940(1)	2566.6(2)
Z, ρ_{calcd} [g cm^{-3}]	4, 1.720	2, 1.858
μ [mm^{-1}]	5.489	5.952
F(000)	5512	1384
reflections	41 936	26 007
unique reflections	14 639	11 703
$R1$, w$R2$	0.0777, 0.1729	0.0492, 0.0843

[1] J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, **1995**.

[2] a) H. V. Boenig, *Structure and Properties of Polymers*, Wiley, New York, **1973**; b) C. E. Carraher, *Polymer Chemistry*, Dekker, New York, **2000**.

[3] P. E. Nielsen, *Acc. Chem. Res.* **1999**, *32*, 624.

[4] a) V. Berl, M. J. Krische, I. Huc, J.-M. Lehn, M. Schmutz, *Chem. Eur. J.* **2000**, *6*, 1938; b) V. Berl, I. Huc, R. J. Khoury, J.-M. Lehn, *Chem. Eur. J.* **2001**, *7*, 2798.

[5] a) D. S. Lawrence, T. Jiang, M. Levett, *Chem. Rev.* **1995**, *95*, 2229; b) M. Gallant, M. T. P. Viet, J. D. Wuest, *J. Org. Chem.* **1991**, *56*, 2284; c) M. M. Conn, J. Rebek Jr., *Chem. Rev.* **1997**, *97*, 1647; d) D. C. Sherrington, K. A. Taskinen, *Chem. Soc. Rev.* **2001**, *30*, 83; e) T. Ezuhara, K. Endo, Y. Aoyama, *J. Am. Chem. Soc.* **1999**, *121*, 3279.

[6] R.-D. Schnebeck, E. Freisinger, B. Lippert, *Eur. J. Inorg. Chem.* **2000**, 1193.

[7] a) W. W. Ellis, M. Schmitz, A. A. Arif, P. J. Stang, *Inorg. Chem.* **2000**, *39*, 2547; b) H. Iwamura, K. Inoue, N. Koga, *New J. Chem.* **1998**, 201; c) Y. Shii, Y. Motoda, T. Matsuo, F. Kai, T. Nakashima, J.-P. Tuchagues, M. Matsumoto, *Inorg. Chem.* **1999**, *38*, 3513.

[8] R. J. Puddephatt, *Coord. Chem. Rev.* **2001**, *216 – 217*, 313.

[9] H. Schmidbaur, *Gold: Progress in Chemistry, Biochemistry and Technology*, Wiley, New York, **1999**.

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0947-6539/02/0803-0738 $ 17.50+.50/0