Multidonor Ligands, 1

Synthesis and Structural Characterization of Gold(I) and Silver(I) Complexes of the Multidonor Ligand 2-(Phenacylthio)pyridine − Crystal Structures of $[(AuPPh_3)\{py\{SCH_2C(O)Ph\}\text{-}2\}](ClO_4)$ and $[(AgPPh_3)(OClO_3)\text{-}\{py\{SCH_2C(O)Ph\}\text{-}2\}]$

José Vicente*[a], Maria-Teresa Chicote*[a], Sonia Huertas, M. Carmen Ramírez de Arellano[b], and Peter G. Jones*[b]

Grupo de Química Organometálica, Departamento de Química Inorgánica, Facultad de Química[a], Universidad de Murcia, Aptdo. 4021, E-30071 Murcia, Spain

Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig[b], Postfach 3329, D-38023 Braunschweig, Germany

Received October 20, 1997

Keywords: Gold(I) / Silver(I) / S-donor and N-donor ligand

The ligand properties of 2-(phenacylthio)pyridine towards gold(I) and silver(I) have been investigated. From the reactions of the ligand with acetone solutions of $[M(PPh_3)(acetone)]ClO_4$ (M = Ag, Au) under various experimental conditions, complexes $[(AuPPh_3)_n\{py\{SCH_2C(O)Ph\}\text{-}2\}](ClO_4)_n$ and $[(AgPPh_3)_n(OClO_3)_n\{py\{SCH_2C(O)Ph\}\text{-}2\}]$ ($n = 1-3$) have been obtained. The crystal structures of the complexes $[(AuPPh_3)\{py\{SCH_2C(O)Ph\}\text{-}2\}]ClO_4$ and $[(AgPPh_3)(OClO_3)\text{-}\{py\{SCH_2C(O)Ph\}\text{-}2\}]$ have been determined by X-ray diffraction. In the cationic gold complex the metal is linearly coordinated to nitrogen and phosphorus, whereas the corresponding silver complex displays a trigonal planar geometry with pyridine, phosphane and perchlorato ligands.

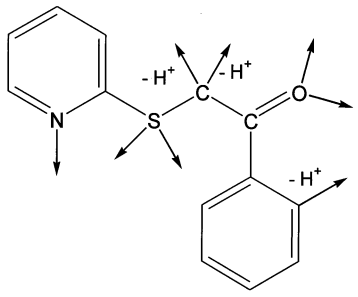
Introduction

The use of functionalized ligands, such as 2-(methylthio)pyridine, pyridine-2(1*H*)-thione, benzoxazole-2(3*H*)-thione,[1] or ylides derived from 2-pyridylmethylene(triaryl)-phosphonium salts,[2][3] has allowed us to synthesize a variety of mono- and polynuclear silver(I) and gold(I) derivatives including a new class of $[Au_3]^{3+}$, $[Au_2Ag]^{3+}$, and $[Au_2Cu]^{3+}$ clusters. Such polynuclear complexes offer the possibility of studying metal−metal interactions in d^{10} systems, which are the subject of considerable interest.[3][4][5][6][7][8][9][10][11][12]

The objective of the present work is to study the ligand properties of 2-(phenacylthio)pyridine [py{$SCH_2C(O)Ph$}-2], of which, as far as we are aware, there is no previously known complex. According to Scheme 1, this ligand could coordinate through the nitrogen, sulfur, or oxygen atoms while the anionic ligands resulting from deprotonation of the methylene group or the *ortho* position of the phenyl ring offer two additional coordination sites, together resulting in the possibility of coordinating up to eight metal centers. In this paper we explore the chemistry of gold(I) and silver(I) complexes with this ligand.

Gold(I) has a limited tendency to coordinate to neutral N or S donor ligands (L_N or L_S). In fact, only a few complexes of the type $[Au(L_N)(PR_3)]^+$ have been described with full experimental and spectroscopic details.[13][14][15][16][17][18][19][20][21] In this family, most complexes contain primary, secondary or tertiary amines while the only reported complexes with pyridinic ligands (L_{py}) are those with L_{py} = py,[22] or 2,2′-bipyridine,[23][24][25] and the dinuclear complex $[Au_2\{\mu_2\text{-}py(PPh_2)\text{-}2\}]^{2+}$.[19]

Scheme 1



Gold(I) complexes with neutral sulfur donor ligands are less frequent and also less stable than those with thiolate and other anionic sulfur ligands.[22][25][24][26][27][28][29][30][31] Such low stability is attributable to the weakness of the Au^I-SR_2 bond. In fact, [AuCl(tht)] (tht = tetrahydrothiophene)[32] is the most widely used starting gold(I) complex because of the facile replacement of the sulfur ligand.[33] From [AuCl(tht)] other synthetic intermediates, such as $[Au(C_6F_5)_n(tht)]$ (n = 1, 3)[32][33][34] have been prepared and used as starting materials for many (pentafluorophenyl)gold(I) and -gold(III) complexes after replacement of tht.[35]

The similarly low tendency of gold(I) to coordinate to both N or S neutral donor ligands prompted us to study

  1434−1948/98/0404−0511 $ 17.50+.50/0

the coordinative preferences of the mixed N-S ligand py{$SCH_2C(O)Ph$}-2 towards the $Au(PPh_3)^+$ moiety. In the absence of X-ray diffraction data, we have previously suggested that in complexes $[Au\{py(SMe)\text{-}2\}(L)]^+$ (L = tht, PPh_3) and $[Au\{py(SMe)\text{-}2\}_2]^+$ the mixed ligand would act as an S- rather than an N-donor ligand according to the preference of the soft gold(I) acid for the softer sulfur base. In fact, gold(I) complexes with pyridine-2-thiol or its conjugate base are always *S*-coordinated.[36][37] Similarly, in the complex $[Au\{py\{CS(=NC_6H_4OMe\text{-}2)\}\text{-}2\}(PPh_3)]$ the $AuPPh_3^+$ group is bonded to sulfur and interacts only weakly with the pyridine N atom.[38] Here we show for the first time the opposite preference of gold(I) for the N- rather than the S-donor atoms in the ligand py{$SCH_2C(O)Ph$}-2.

Synthesis of the Ligand

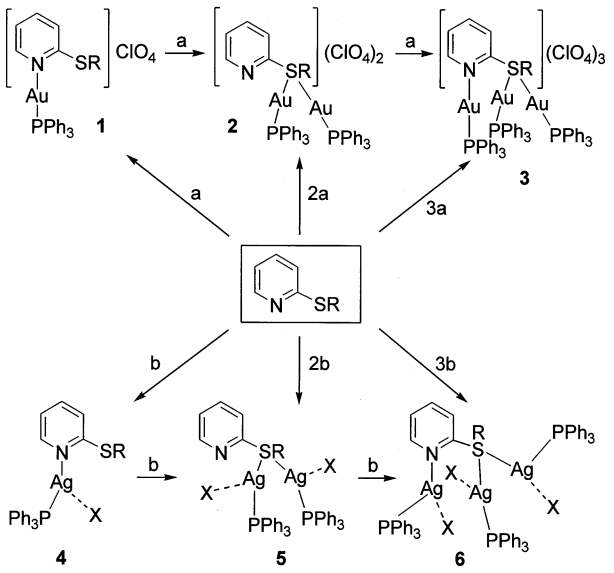
2-(Phenacylthio)pyridinium bromide was first obtained[39] by allowing 2-bromoacetophenone to react with 2-mercaptopyridine in refluxing ethanol for several hours. This and other sulfides resulting from the reaction of α-halo ketones or α-halo acetals with mercaptopyridine can be cyclized in good yield to form thiazolopyridinium salts.[39][40] We have found that equimolar amounts of 2-bromoacetophenone and 2-mercaptopyridine produce, after stirring in diethyl ether at room temperature for only 30 min, a quantitative yield of [Hpy{$SCH_2C(O)Ph$}-2]Br, which in turn reacts with aqueous NaOH to give 2-(phenacylthio)pyridine [py{$SCH_2C(O)Ph$}-2]. As far as we are aware the ligand properties of py{$SCH_2C(O)Ph$}-2 have not previously been explored.

Gold(I) and Silver(I) Complexes

When py{$SCH_2C(O)Ph$}-2 is treated with acetone solutions of $[M(PPh_3)(acetone)]ClO_4$ (M = Au, Ag) in 1:1, 1:2 or 1:3 molar ratios, complexes $[(AuPPh_3)_n\{py\text{-}\{SCH_2C(O)Ph\}\text{-}2\}](ClO_4)_n$ [*n* = 1 (**1**), 2 (**2**), 3 (**3**)] or $[(AgPPh_3)_n(OClO_3)_n\{py\{SCH_2C(O)Ph\}\text{-}2\}]$ [*n* = 1 (**4**), 2 (**5**), 3 (**6**)] are, respectively, obtained (Scheme 2). The reactions leading to polynuclear derivatives can be performed stepwise and thus **2** or **5** can be obtained from **1** or **4** and one equivalent of $[M(PPh_3)(acetone)]ClO_4$ while **3** or **6** can be prepared from **2** or **5** or from **1** or **4** upon addition of one or two equivalents, respectively, of the corresponding $[M(PPh_3)(acetone)]ClO_4$ complex. In the case of the gold complexes the purest products are obtained by the stepwise procedure.

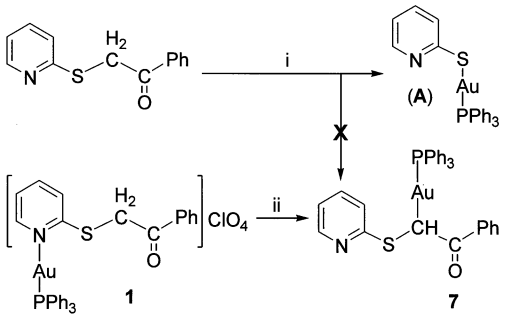
We have shown that (acetylacetonato)gold(I) complexes react with a variety of organic substrates containing moderately acidic protons to give gold(I) complexes, including alkyl, alkynyl, ylide, diphenylphosphide, (diphenylphosphanyl)methanide, hydrosulfide and thiolato derivatives.[1][2][3][17][42][42a] However, the reaction of $[Au(acac)PPh_3]$ with 2-(phenacylthio)pyridine, meant to produce the organometallic complex **7** (Scheme 3), gave instead the known complex **A,** the structure of which we determined by X-ray diffraction methods; it had been previously reported.[36]

Scheme 2[a]



[a] R = $CH_2C(O)Ph$; X = $OClO_3$; a: + $[Au(PPh_3)(acetone)]ClO_4$; b: + $[Ag(PPh_3)(acetone)]ClO_4$.

Scheme 3[a]



[a] i: + $[Au(acac)PPh_3]$ − Hacac; ii: + NaH − H_2 − $NaClO_4$.

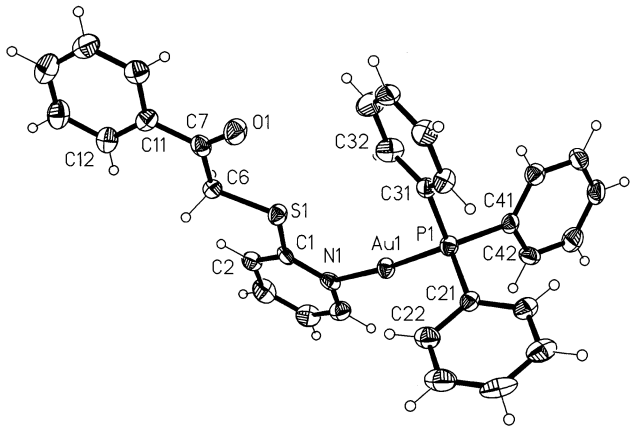
The reaction of **1** with NaH (1:2.3, in dichloromethane, 2.5 h) gave the desired complex **7** resulting from deprotonation of the methylene group and the rearrangement of the $AuPPh_3^+$ group from N to C. The preference of gold for C rather than N donor ligands is well known. Although the elemental analyses of **7** were correct, it is difficult to separate it from traces of the starting material and some decomposition products (see below).

Crystal Structure of Complexes 1 and 4

Complex **1** crystallizes in the triclinic system with 3 molecules of acetone and two independent molecules in the asymetric unit. The crystal structure (Figure 1) shows cations in which the gold atoms are in almost linear environments, with N−Au−P angles of 175.46(12) and 173.91(12)° and tetrahedral ClO_4 anions. The Au−N distances [2.082(4) and 2.092(4) Å] are similar to the 2.086(16) Å found in $[Au_2\{\mu_2\text{-}py(PPh_2)\text{-}2\}]^{2+}$.[19] In $[Au(bipy)(PPh_3)]^+$ a distorted trigonal planar coordination leads as expected to Au−N bond lengths [2.166(2) and 2.406(2) Å] longer than those in **1**.[25]

The Au−P bond lengths [2.2359(13) and 2.2388(13) Å] in **1** are larger than those in $[Au_2\{\mu_2\text{-py}(PPh_2)\text{-}2\}]^{2+}$ [2.215(6) Å][19] or $[Au(bipy)(PPh_3)]^+$ [2.212(1) Å].

Figure 1. Structure of the cation of complex **1**[a]

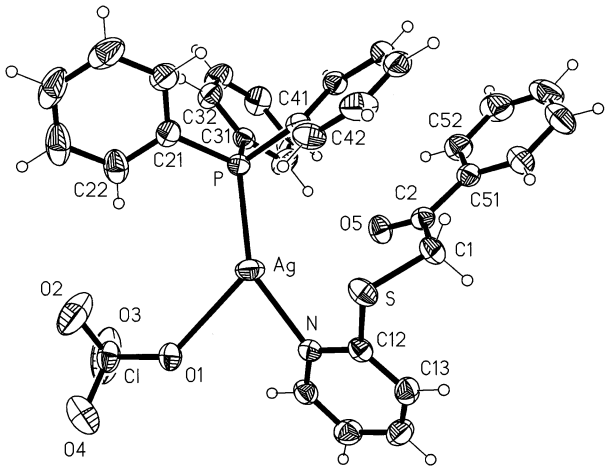


[a] 50% probability ellipsoids; selected bond lengths [Å] and angles [°]: Au(1)−N(1) 0.082(4), Au(2)−N(2) 2.092(4), Au(1)−P(1) 2.2359(13), Au(2)−P(2) 2.2388(13); N(1)−Au(1)−P(1) 175.46(12), N(2)−Au−P(2) 173.91(12).

The coordination of the $AuPPh_3^+$ group to N instead of S [Au···S, 3.071, 3.063(1) Å] is surprising because the soft gold(I) acid should prefer the softer sulfur base; when the ligand is pyridine-2-thiol or its conjugate base, gold(I) is always bonded to sulfur.[36][37] In addition, in the complex $[Au\{py\{C(S)(=NC_6H_4OMe\text{-}2)\}\text{-}2\}(PPh_3)]$ the $AuPPh_3^+$ group is bonded to sulfur (Au−S, 2.317 Å) and only weakly to the pyridine N atom (Au−N, 2.574 Å).[38] Probably the presence of the electron-withdrawing carbonyl group in **1** makes the sulfur atom less soft than usual.

Complex **4** crystallizes in the monoclinic system and its crystal structure (Figure 2) shows the silver atoms in a very distorted trigonal planar environment (the Ag atom lies 0.21 Å out of the plane of the donor atoms. The N−Ag−P [148.5(5)°], P−Ag−O [129.7(6)°], and N−Ag−O [79.0(5)°] bond angles show PPh_3 to be the most sterically demanding ligand. Two of the four Ag−N bond lengths [2.272, 2.268, 2.386, 2.407(4) Å] and the Ag−P [2.380, 2.377(1) Å] bond lengths at the two independent Ag atoms of $[Ag(8\text{-hydroxyquinoline})_2(PPh_3)]^+$ are similar to the Ag−N [2.263(2) Å] and Ag−P [2.3845(7) Å] bond lengths in **4**.[43] In the complex $[Ag(OClO_3)(O_2NO)\{py\{C(AuPPh_3)_2PPh_3\}\text{-}2\}]$[3] the Ag−N [2.178(8) Å] and Ag−$OClO_3$ [2.663(9) Å] bond lengths are shorter and similar, respectively, than the corresponding ones in complex **4** [Ag−O, 2.688(6) Å]. The long Ag−O bond length (compared with Ag−N [2.263(2) Å]) and the wide P−Ag−N [148.5(5)°] bond angle indicate the weak coordination of the anion to Ag^I, as does the wide Cl−O(1)−Ag angle [133.8(1)°]. The sulfur atom forms short intra- [3.097(1) Å] and intermolecular [2.998(1) Å] Ag−S contacts leading to weakly associated, centrosymmetric dimers.

Figure 2. Structure of complex **2**[a]



[a] 50% probability ellipsoids; selected bond lengths [Å] and angles [°]: Ag−N 2.263(2), Ag−P 2.3845(7), Ag−O(1) 2.688(6); N−Ag−P 148.47(6), P−Ag−O 129.7(6), N−Ag−O 79.0(5).

NMR Spectra

Because the resonance from the methylene protons in the ^{1}H-NMR spectrum of complex **1** at −60°C appears as a singlet, we propose that, in solution, the ligand acts as an N donor, as in its solid-state structure. Coordination through the sulfur atom would convert it into a chiral center and the methylene protons would be non-isochronous unless a rapid scrambling of the $AuPPh_3^+$ group between both sp^3 sulfur pairs occurred even at −60°C. In fact, at −60°C the *S*-bonded isomer of the silver complex **4** (**4**-S) is detected because the ^{1}H-NMR spectrum shows an AB system highfield of the CH_2 singlet, and in the ^{31}P-NMR spectrum four doublets corresponding to two different phosphorus nuclei (molar ratio 8:1) resonating at δ = 13.21 [$^1J(P^{109}Ag)$ = 742 Hz, $^1J(P^{107}Ag)$ = 643 Hz; **4**] and 11.69 [$^1J(P^{109}Ag)$ = 555 Hz, $^1J(P^{107}Ag)$ = 481 Hz; **4**-S] are observed. The $^1J(P^{109}Ag)$ and $^1J(P^{107}Ag)$ values are similar to those in complex **6** [$J(P^{109}Ag)$ = 770.6 Hz, $J(P^{107}Ag)$ = 667.6 Hz, *P*AgN; $J(P^{109}Ag)$ = 569 Hz, $J(P^{107}Ag)$ = 493 Hz, 2*P*AgS] where Ag^I is coordinated to both N and S.

The dinuclear complexes **2** and **5** show only one type of phosphorus nucleus at low temperature (−60°C), indicating that both $MPPh_3$ units coordinate to sulfur. This is also a surprising result because, according to the above explanation of the *N*-coordination, the sulfur atom has its donor ability reduced by the vicinity of the electron-withdrawing carbonyl group. However, a reasonable explanation for these facts is based on the marked tendency of gold(I) and silver(I) to establish short M···M contacts, a phenomenon termed aurophilicity,[7][8][9][10][11][12] or numismophilicity (from the Latin numisma = money, coin)[3] when it applies to gold or to the three coinage metals, respectively. Because the numismophilic interactions are weak (of similar energy to hydrogen bonds when the metal is gold)[44] the structure adopted is that in which there is a minimum of repulsion between the phosphane ligands, i.e., the double metalation of the sulfur atom is preferred to the alternative mixed *N*,*S*

metalation. At room temperature, the behavior of these complexes is different. Whereas the silver complex **5** shows a broad resonance, probably because of dissociative processes involving cleavage of S−AgPPh$_3$ and/or Ag−PPh$_3$ bonds, in the gold complex **2** such equilibria do not exist because its spectrum is not significantly different from that at −60°C.

The $^{31}P\{^1H\}$-NMR spectrum of **3** at −60°C consists of two singlets of 2:1 relative intensity, consistent with the structure proposed in Scheme 2, but at room temperature shows only a singlet, indicating that a fluxional process interchanging all three $AuPPh_3^+$ units occurs. Similarly, in the case of **6** the room-temperature $^{31}P\{^1H\}$-NMR spectrum shows a broad resonance, which at −60°C splits into two (2:1 relative intensities) pairs of doublets.

Resonances appearing at δ = 4.75 and 31.02 in the ^{1}H- and ^{31}P-NMR spectra, respectively, of **7** are due to the presence of traces of **1**, while a small amount of $[Au(PPh_3)_2]^+$ could account for the resonance at δ = 44.24. The slight conductivity of **7** (Λ_M = 11 Ω^{-1} cm^2 M^{-1}) is also consistent with the presence of both impurities.

IR Spectra

The bands assignable to the ν̃(CO) mode in the IR spectra of the ligand and the complexes appear in the narrow range of 1672−1680 cm^{-1}. The gold complexes **1**−**3** show the expected two bands for the tetrahedral ClO_4 anion in the ranges 1088−1094 and 621−622 cm^{-1}, respectively. This accords with the marked tendency of gold(I) to give dicoordinate complexes. In complexes **4**, **5** and **6**, a new band around 923 cm^{-1} and two bands in each of the two above-mentioned regions are observed. This is in agreement with the expected splitting when the symmetry of the ClO_4 decreases from T_d to C_{3v}. Therefore, it is reasonable to assume that, in the solid state, each ClO_4 anion is monocoordinated to one metal centre.

These differences among gold(I) and silver(I) complexes in the solid state disappear in acetone solutions, because all complexes show molar conductivities indicating the dissociation of all the perchlorate anions, i.e., complexes **1**−**6** behave as 1:1 electrolytes, **2** and **5** as 2:1 electrolytes, and **3** and **6** as 3:1 electrolytes.[45] Therefore, in acetone solutions of the silver complexes the solvent replaces the anion in the coordination sphere of the metal.

We thank the *DGES* and the *Fonds der Chemischen Industrie* for financial support. M. C. R. A. is grateful for an *Alexander von Humboldt Grant* and to the *Ministerio de Educación y Cultura* for a contract.

Experimental Section

General: The IR spectra, elemental analyses, conductance measurements in acetone and melting-point determinations were carried out as described earlier[42a]. − NMR: Varian Unity-300. Chemical shifts are referred to TMS [^{1}H, $^{13}C\{^1H\}$] or H_3PO_4 [$^{31}P\{^1H\}$]. − If not stated otherwise, the reactions were carried out at room temperature without special precautions against moisture. ***Warning:*** Perchlorate salts with organic cations may be explosive. − 2-Mercaptopyridine (HSpy) was purchased from Fluka and 2-bromoacetophenone [$BrCH_2C(O)Ph$] from Aldrich.

[Hpy{SCH$_2$C(O)Ph}-2]Br: A solution of equimolar amounts of pySH-2 (1.11 g, 10 mmol) and $BrCH_2C(O)Ph$ (1.99, 10 mmol) were stirred in diethyl ether (30 ml) for 0.5 h. The resulting yellow suspension was filtered off, the solid washed with diethyl ether (3 × 15 ml) and air-dried to give 3.07 g (99%) of colorless crystals, m.p. 200°C (ref.[39] 200°C). − IR (Nujol): ν̃ = 1693 cm^{-1} (CO). − $C_{13}H_{12}BrNOS$ (310.2): calcd. C 50.34, H 3.90, N 4.52, S 10.33; found: C 50.18, H 4.07, N 4.62, S 10.44.

py{SCH$_2$C(O)Ph}-2: To a solution of [Hpy{SCH$_2$C(O)Ph}-2]Br (2.48 g, 8 mmol) in water (50 ml) NaOH (0.5 M in water) was added dropwise until pH = 7. The resulting white suspension was extracted with dichloromethane (4 × 20 ml) and the organic layer was dried with anhydrous $MgSO_4$ and then filtered. Removing the volatiles in vacuo gave 514 mg of 2-(phenacylthio)pyridine (28%) as a pale yellow oil. − IR (Nujol): ν̃ = 1668 cm^{-1} (CO). − ^{1}H NMR ([D$_6$]acetone): δ = 4.79 (s, 2 H, C*H*$_2$), 6.93 [m, 1 H, *H4* (py)], 7.22 [m, 1 H, *H3* (py)], 7.3−7.8 [m, 4 H, *H5* (py) + *m-H* (Ph) + *p-H* (Ph)], 8.04 [d, ^3J(HH) = 7 Hz, 2 H, *o-H* (Ph)], 8.34 [m, 1 H, *H6* (py)]. − $C_{13}H_{11}NOS$ (229.3): calcd. C 68.10, H 4.84, N 6.11, S, 13.98; found: C 68.38, H 4.89, N 6.28, S 14.02.

[(AuPPh$_3$)$_n${py{SCH$_2$C(O)Ph}-2}](ClO$_4$)$_n$ [*n* = 1 (**1**), 2 (**2**), 3 (**3**)]. − *Preparation of Solutions of [Au(PPh$_3$)(acetone)]ClO$_4$:* An equimolecular mixture of [AuCl(PPh$_3$)] and $AgClO_4$ (1:1 molar ratio) in degassed acetone (25 ml mmol^{-1}) was stirred for 0.5 h under nitrogen and then the AgCl removed by filtration.

Complex **1**: A solution of [Au(PPh$_3$)(acetone)]ClO_4, from [AuCl(PPh$_3$)] (406 mg, 0.82 mmol) and $AgClO_4$ (107 mg, 0.82 mmol), was added dropwise under nitrogen to a solution containing py{SCH$_2$C(O)Ph}-2 (188 mg, 0.82 mmol) in degassed acetone (15 ml). The resulting suspension was stirred for 0.5 h and then filtered through Celite. The solvent was removed in vacuo and the oily residue was vigorously stirred with diethyl ether (20 ml) for 0.5 h to give 626 mg of **1** (97%), white solid, m.p. 137°C. − IR (Nujol): ν̃ = 1672 cm^{-1} (CO). − Λ_M = 144 Ω^{-1} cm^2 M^{-1}. − ^{1}H NMR (CD_2Cl_2, 20°C): δ = 4.90 (s, 2 H, C*H*$_2$), 7.48−7.67 [m, 20 H, C(O)*Ph* + P*Ph*$_3$], 7.83 [m, 1 H, *H3* (py)], 8.04 [m, 2 H, *H4* (py) + *H5* (py)], 8.50 [m, 1 H, *H6* (py)]. − ^{1}H NMR (CD_2Cl_2, −60°C): δ = 4.95 (s, 2 H, C*H*$_2$), 7.44 − 7.68 [m, 20 H, C(O)*Ph* + P*Ph*$_3$], 7.97 [m, 1 H, *H3* (py)], 8.08 [m, 2 H, *H4* (py) + *H5* (py)], 8.42 [m, 1 H, *H6* (py)]. − $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20°C and −60°C): δ = 29.44. − $C_{31}H_{26}AuClNO_5PS$ (788.0): calcd. C 47.25, H 3.33, N 1.78, S 4.07; found: C 47.42, H 3.79, N 1.73, S 3.71.

Complex **2**: A solution of [Au(PPh$_3$)(acetone)]ClO_4, from [AuCl(PPh$_3$)] (125 mg, 0.25 mmol) and $AgClO_4$ (53 mg, 0.25 mmol), was added dropwise to a solution containing **1** (200 mg, 0.25 mmol) in degassed acetone (15 ml). The resulting suspension was stirred for 1.5 h and then filtered through Celite. The solution was concentrated (2 ml) and diethyl ether added (20 ml) to give a suspension that was filtered, the solid washed with diethyl ether (5 ml), dried in the air and then in an oven at 60°C for 30 min to give 327 mg of **2** (97%), cream solid, m.p. 103°C. − IR (Nujol): ν̃ = 1672 cm^{-1} (CO). − Λ_M = 183 Ω^{-1} cm^2 M^{-1}. − ^{1}H NMR ([D$_6$]acetone, 20°C): δ = 5.28 (s, 2 H, C*H*$_2$), 7.40−8.36 [m, 38 H, *H3* (py) + *H4* (py) + *H5* (py)+ C(O)*Ph* + P*Ph*$_3$], 9.03 [m, 1 H, *H6* (py)]. − $^{31}P\{^1H\}$ NMR ([D$_6$]acetone, 20°C): δ = 29.66 (s). − $^{31}P\{^1H\}$ NMR ([D$_6$]acetone, −60°C): δ = 28.29 (s). − $C_{49}H_{41}Au_2Cl_2NO_9P_2S$ (1346.7): calcd. C 43.70, H 3.07, N 1.04, S 2.38; found: C 43.68, H 3.33, N 1.19, S 2.28.

Complex **3**: A solution of [Au(PPh$_3$)(acetone)]ClO_4, from [AuCl(PPh$_3$)] (92 mg, 0.19 mmol) and $AgClO_4$ (38 mg, 0.19 mmol), was added dropwise to a solution containing **2** (250 mg, 0.19 mmol) in degassed acetone (10 ml). The resulting suspension was stirred

for 2 h and then filtered through $MgSO_4$. The solvent was evaporated to dryness and the resulting solid stirred with diethyl ether (20 ml) to give a suspension that was filtered and dried under nitrogen to give 355 mg of **3** (98%), cream solid, m.p. 107°C. − IR (Nujol): $\tilde{\nu}$ = 1673 cm^{-1} (CO). − Λ_M = 285 Ω^{-1} cm^2 M^{-1}. − ^1H NMR ([D$_6$]acetone, 20°C): δ = 5.38 (s, 2 H, C*H*$_2$), 7.38−7.64 [m, 51 H, *H3* (py) + C(O)*Ph* + P*Ph*$_3$], 8.07 [m, 2 H, *H4* (py) + *H5* (py)], 8.78 [m, 1 H, *H6* (py)]. − $^{31}P\{^1H\}$ NMR([D$_6$]acetone, 20°C): δ = 29.12 (s). − $^{31}P\{^1H\}$ NMR([D$_6$]acetone, −60°C): δ = 28.21 (s, Ph$_3$*P*AuN), 29.68 (s, Ph$_3$*P*AuS). − $C_{67}H_{56}Au_3Cl_3NO_{13}P_3S$ (1905.4): calcd. C 42.23, H 2.96, N 0.74, S 1.68; found: C 42.14, H 3.27, N 0.62, S 1.70.

[(AgPPh$_3$)$_n$(OClO$_3$)$_n${py{SCH$_2$C(O)Ph}-2}] [*n* = 1 (**4**), (**5**), 3 (**6**)]. − *Preparation of Solutions of [Ag(PPh$_3$)*(acetone)]ClO_4: PPh_3 is added to an equimolecular amount of $AgClO_4$ in degassed acetone (15 ml $mmol^{-1}$).

Complex **4**: A solution of [Ag(PPh$_3$)(acetone)]ClO_4, from $AgClO_4$ (203 mg, 0.98 mmol) and PPh_3 (257 mg, 0.98 mmol), was added dropwise to a solution containing py{SCH$_2$C(O)Ph}-2 (225 mg, 0.98 mmol) in degassed acetone (5 ml) under nitrogen. The resulting suspension was stirred for 75 min and then concentrated to dryness. The residue was washed with diethyl ether (20 ml) and recrystallized from dichloromethane/diethyl ether to give 589 mg of **4** (86%), white solid, m.p. 137°C. − IR (Nujol): $\tilde{\nu}$ = 1677 cm^{-1} (CO). − Λ_M = 101 Ω^{-1} cm^2 M^{-1}. − ^1H NMR (CD_2Cl_2, 20°C): δ = 4.74 (s, 2 H, C*H*$_2$), 7.30−7.67 [m, 20 H, C(O)*Ph* + P*Ph*$_3$], 7.82 [m, 1 H, *H3* (py)], 7.97 [m, 2 H, *H4* (py) + *H5* (py)], 8.57 [m, 1 H, *H6* (py)]. − ^1H NMR (CD_2Cl_2, −60°C): δ = 3.93, 4.22 (AB system, $^2J_{HH}$ = 13 Hz, **4**-S, see Discussion), 4.55 (s, br., 2 H, C*H*$_2$), 7.03−7.77 [m, 21 H, *H3* (py) + C(O)*Ph* + P*Ph*$_3$], 8.05 [m, 2 H, *H4* (py) + *H5* (py)], 8.23 [m, 1 H, *H6* (py)]. − $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20°C): δ = 15.00 (s, br.). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −60°C): δ = 13.21 [2 d, 88% P, $^1J(P^{109}Ag)$ = 742 Hz, $^1J(P^{107}Ag)$ = 643 Hz; **4**, see Discussion], 11.69 [2 d, 12% P, $^1J(P^{109}Ag)$ = 555 Hz, $^1J(P^{107}Ag)$ = 481 Hz; **4**-S, see Discussion]. − $C_{31}H_{26}AgClNO_5PS$ (698.9): calcd. C 53.28, H 3.75, N 2.00, S 4.59; found: C 53.31, H 3.76, N 1.96, S 4.48.

Complex **5**: A solution of [Ag(PPh$_3$)(acetone)]ClO_4, from $AgClO_4$ (612 mg, 2.96 mmol) and PPh_3 (775 mg, 2.96 mmol), was added dropwise to a solution containing py{SCH$_2$C(O)Ph}-2 (339 mg, 1.48 mmol) in degassed acetone (5 ml) under nitrogen. The resulting suspension was stirred for 2.5 min and then concentrated to dryness. The resulting solid was washed with *n*-hexane (20 ml) and the suspension filtered to give 1.61 g of **5** (99%), white solid, m.p. 150°C. − IR (Nujol): $\tilde{\nu}$ = 1680 cm^{-1} (CO). − Λ_M = 186 Ω^{-1} cm^2 M^{-1}. − ^1H NMR ([D$_6$]acetone, 20°C): δ = 5.01 (s, 2 H, C*H*$_2$), 7.40−7.80 [m, 35 H, C(O)*Ph* + P*Ph*$_3$], 7.93 [m, 1 H, *H3* (py)], 8.10 [m, 2 H, *H4* (py) + *H5* (py)], 8.61 [m, 1 H, *H6* (py)]. − $^{31}P\{^1H\}$ NMR ([D$_6$]acetone, 20°C): δ = 10−16 (br.). − $^{31}P\{^1H\}$ NMR ([D$_6$]acetone, −60°C): δ = 12.68 [2 d, $J(P^{109}Ag)$ = 759 Hz, $J(P^{107}Ag)$ = 658 Hz]. − $C_{49}H_{41}Ag_2Cl_2NO_9P_2S$ (1168.5): calcd. C 50.37, H 3.54, N 1.20, S 2.74; found: C 50.59, H 3.64, N 1.25, S 2.49.

Complex **6**: A solution of [Ag(PPh$_3$)(acetone)]ClO_4, from $AgClO_4$ (896 mg, 2.96 mmol) and PPh_3 (1.134 g, 2.96 mmol), was added dropwise to a solution containing of py{SCH$_2$C(O)Ph}-2 (330 mg, 1.48 mmol) in degassed acetone (5 ml) under nitrogen. The resulting suspension was stirred for 2.5 min and then concentrated to dryness. The resulting oil was washed with *n*-hexane (20 ml) and the resulting suspension filtered to give 2.33 g of **6** (99%), m.p. 138°C. − IR (Nujol): $\tilde{\nu}$ = 1681 cm^{-1} (CO). − Λ_M = 269 Ω^{-1} cm^2 M^{-1}. − ^1H NMR ([D$_6$]acetone, 20°C]: δ = 5.02 (s, 2 H, C*H*$_2$), 7.30−7.82 [m, 51 H, *H3* (py) + CO*Ph* + P*Ph*$_3$], 7.85−8.20 [m, 2 H, *H4* (py) + *H5* (py)], 8.61 [m, 1 H, *H6* (py)]. − $^{31}P\{^1H\}$ NMR ([D$_6$]acetone, 20°C): δ = 10−14 (br.). − $^{31}P\{^1H\}$ NMR ([D$_6$]acetone, −60°C): δ = 11.77 [2 d, $J(P^{109}Ag)$ = 569 Hz, $J(P^{107}Ag)$ = 493 Hz, 2 *P*AgS], 12.77 [2 d, $J(P^{109}Ag)$ = 770.6 Hz, $J(P^{107}Ag)$ = 667.6 Hz, *P*AgN]. − $C_{67}H_{56}Ag_3Cl_3NO_{13}P_3S$ (1638.1): calcd. C 49.13, H 3.45, N 0.86, S 1.96; found: C 50.21, H 3.62, N 0.90, S 2.05.

[Au{CH(Spy-2){C(O)Ph}}(PPh$_3$)] (**7**): To a solution of **1** (600.8 mg mg, 0.76 mmol) in dichloromethane (15 ml), NaH (Fluka, 50% in mineral oil, 86 mg, 1.79 mmol) was added. After 2.5 h of stirring, the resulting suspension was filtered through Celite. The solution was concentrated to dryness, the residue stirred with diethyl ether (2 × 15 ml) and the suspension filtered to give 290 mg of **7** (55%), pale cream solid, m.p. 106°C (dec.). − IR (Nujol): $\tilde{\nu}$ = 1638 (CO). − Λ_M = 11 Ω^{-1} cm^2 M^{-1}. − ^1H NMR ($CDCl_3$, 20°C): δ = 4.75 (s, traces, complex **1**, see Discussion), 5.42 [d, 1 H, C*H*, ^3J(PH) = 9.9 Hz], 6.42−7.56 (m, 19 H, PPh_3 + py). − $^{31}P\{^1H\}$ NMR: δ = 31.02 (s, traces, complex **1**, see Discussion), 39.24 (s), 44.24 (s, traces, $[Au(PPh_3)_2]^+$). − $C_{31}H_{25}AuNOPS$ (687.5): calcd. C 54.16, H 3.67, N 2.04, S 4.66; found: C 53.95, H 3.79, N 2.03S 4.55.

X-ray Crystallographic Studies: Crystal data are given in Table 1. Crystals of **1**·1.5 Me_2CO and **2** were mounted in inert oil on a glass fiber and transferred to the diffractometer (Siemens P4 with LT2 low-temperature attachment). Measurements were performed at −100°C using monochromated Mo-K_α radiation (λ = 0.71073 Å).

Table 1. Crystal Data for complexes **1**·1.5 Me_2CO and **2**

	1·1.5 Me_2CO	**2**
empirical formula	$C_{35.50}H_{35}AuClNO_{6.50}PS$	$C_{31}H_{26}AgClNO_5PS$
M	875.09	698.88
a [Å]	14.079(2)	13.5113(8)
b [Å]	14.663(2)	21.2262(14)
c [Å]	16.989(2)	11.1835(10)
α[°]	94.926(10)	90
β[°]	97.627(10)	113.332(6)
γ[°]	94.509(12)	90
Z	4	4
D_x [Mg/m^3]	1.685	1.576
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
crystal size [mm]	0.76 × 0.36 × 0.22	0.40 × 0.40 × 0.20
θrange [°]	3.01−25.00	3.18−27.50
reciprocal lattice segment	$-h, \pm k, \pm l$	$\pm h, +k, -l$
reflections measured	12737	8559
independent reflections	12092	6727
μ [mm^{-1}]	4.498	0.942
max/min transmission	0.767/0.915	0.925/0.821
parameters	853	370
F(000)	1736	1416
max Δρ [e Å^{-3}]	1.45	1.15
*R*1[a]	0.0313	0.0333
*wR*2[b]	0.0640	0.0819

[a] $R1 = \sigma||F_o| - |F_c||/\sigma|F_o|$ for reflections with $I > 2\sigma(I)$. − [b] $wR2 = \{\sigma[w(F_o^2 - F_c^2)^2]/\sigma[w(F_o^2)^2]\}^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_o^2)/3$ and *a* and *b* are constants set by the program.

Unit cell parameters were determined from a least-squares fit of ca. 80 accurately centered reflections (10° < 2θ < 27°). Intensities were registered using ω scans. Absorption corrections were based on ψ scans. The structures were solved by the heavy-atom method and refined anisotropically on F^2 (program SHELXL-93).[46] Hy-

drogen atoms were included using a riding model or as rigid methyl groups.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre under the number CCDC-100752. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code + (1223)336−033, e-mail: deposit@ccdc.cam.ac.uk).

[1] J. Vicente, M. T. Chicote, C. Rubio, *Chem. Ber.* **1996**, *129*, 327.
[2] J. Vicente, M. T. Chicote, M. C. Lagunas, P. G. Jones, *J. Chem. Soc., Chem. Commun.* **1991**, 1730.
[3] J. Vicente, M. T. Chicote, M. C. Lagunas, *Inorg. Chem.* **1993**, *32*, 3748.
[4] J. Vicente, M.-T. Chicote, M.-D. Abrisqueta, R. Guerrero, P. G. Jones, *Angew. Chem.* **1997**, *109*, 1252; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1203.
[5] I. G. Dance, M. L. Scudder, L. J. Fitspatrick, *Inorg. Chem.* **1985**, *24*, 2547.
[6] O. Steigelmann, P. Bissinger, H. Schmidbaur, *Angew. Chem.* **1990**, *102*, 1473; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1399.
[7] H. Schmidbaur, *Chem. Soc. Rev.* **1995**, 391.
[8] P. G. Jones, *Gold Bull.* **1981**, *14*, 102.
[9] P. G. Jones, *Gold Bull.* **1981**, *14*, 159.
[10] P. G. Jones, *Gold Bull.* **1983**, *16*, 114.
[11] P. G. Jones, *Gold Bull.* **1986**, *19*, 46.
[12] H. Schmidbaur, *Gold Bull.* **1990**, *23*, 11.
[13] A. Grohmann, J. Riede, H. Schmidbaur, *Z. Naturforsch., B* **1992**, *47*, 1255.
[14] E. G. Perevalova, K. I. Grandberg, V. P. Dyadchenko, T. V. Baukova, *J. Organomet. Chem.* **1981**, *217*, 403.
[15] J. F. Vollano, D. H. Picker, J. A. Statler, *Inorg. Chem. Acta*, **1989**, *155*, 31.
[16] E. M. Kinsch, D. W. Stephan, *Inorg. Chem. Acta*, **1984**, *91*, 263.
[17] J. Vicente, M. T. Chicote, R. Guerrero, P. G. Jones, *J. Chem. Soc., Dalton Trans.* **1995**, 1251.
[18] A. Burini, R. Galassi, B. R. Pietroni, G. Rafaiani, *J. Organomet. Chem.* **1996**, *519*, 161.
[19] Y. Inoguchi, B. Milewski-Mahrla, H. Schmidbaur, *Chem. Ber.* **1982**, *115*, 3085.
[20] J. M. Lopez de Luzuriaga, M. Soldner, A. Schier, H. Schmidbaur, *Z. Naturforsch., B* **1997**, *52*, 209.
[21] K. Angermaier, H. Schmidbaur, *J. Chem. Soc., Dalton Trans.* **1995**, 559.
[22] P. G. Jones, A. G. Maddock, M. J. Mays, M. M. Muir, A. F. Williams, *J. Chem. Soc., Dalton Trans.* **1977**, 1434.
[23] G. C. H. Jones, P. G. Jones, A. G. Maddock, M. J. Mays, P. A. Vergnano, A. F. Williams, *J. Chem. Soc., Dalton Trans.* **1977**, 1440.
[24] R. Usón, A. Laguna, A. Navarro, R. V. Parish, L. S. Moore, *Inorg. Chim. Acta* **1986**, *112*, 205.
[25] W. Clegg, *Acta Crystallogr.* **1976**, *B32*, 2712.
[26] M. G. B. Drew, M. J. Riedl, *J. Chem. Soc., Dalton Trans.* **1973**, 52.
[27] P. W. R. Corfield, H. M. M. Shearer, *Acta Crystallogr.* **1967**, *C23*, 156.
[28] S. Fuchs, J. M. Lopez de Luzuriaga, M. E. Olmos, A. Sladek, H. Schmidbaur, *Z. Naturforsch., B* **1997**, *52*, 217.
[29] A. J. Blake, R. O. Gould, J. A. Greig, A. J. Holder, T. I. Hyde, M. Schröder, *J. Chem. Soc., Chem. Commun.* **1989**, 876.
[30] A. Sladek, H. Schmidbaur, *Z. Naturforsch., B* **1996**, *51*, 1207.
[31] C. A. McAuliffe, R. V. Parish, P. D. Randall, *J. Chem. Soc., Dalton Trans.* **1979**, 1730.
[32] R. Usón, J. Laguna, J. Vicente, *J. Organomet. Chem.* **1977**, *131*, 471.
[33] For some selected and recent examples, see: V. G. Albano, L. Busetto, M. C. Cassani, P. Sabatino, A. Schmitz, V. Zanotti, *J. Chem. Soc., Dalton Trans.* **1995**, 2087. − Z. Assefa, B. G. McBurnett, R. J. Staples, J. P. Fackler, Jr., *Inorg. Chem.* **1995**, *34*, 4965. − P. J. Bonasia, D. E. Gindelberger, J. Arnold, *Inorg. Chem.* **1993**, *32*, 5126. − A. F. Chiffey, J. Evans, W. Levason, M. Webster, *Polyhedron* **1996**, *15*, 591. − S. Coco, P. Espinet, S. Falagan, J. M. Martín-Alvarez, *New J. Chem.* **1995**, *19*, 959. − J. Forniés, R. Navarro, E. P. Urriolabeitia, *J. Organomet. Chem.* **1993**, *452*, 241. − A. M. Gibson, G. Reid, *J. Chem. Soc., Dalton Trans.* **1996**, 1267. − M. C. Gimeno, E. Jambrina, A. Laguna, M. Laguna, H. H. Murray, R. Terroba, *Inorg. Chim. Acta* **1996**, *249*, 69. − S. Alvarez, O. Rossell, M. Seco, J. Valls, M. A. Pellinghelli, A. Tiripicchio, *Organometallics* **1991**, *10*, 2309. − C. G. Arena, D. Drommi, F. Faraone, M. Lanfranchi, F. Nicolo, A. Tiripicchio, *Organometallics* **1996**, *15*, 3170. − J. C. Jeffery, P. A. Jelliss, F. G. A. Stone, *Organometallics* **1994**, *13*, 2651. − L. K. Liu, L. S. Luh, Y. S. Wen, U. B. Eke, M. A. Mesubi, *Organometallics* **1995**, *14*, 4474. − I. Neda, A. Fischer, T. Kaukorat, P. G. Jones, R. Schmutzler, *Chem. Ber.* **1994**, *127*, 1579. − H. G. Raubenheimer, L. Lindeque, S. Cronje, *J. Organomet. Chem.* **1996**, *511*, 177. − V. Riera, M. A. Ruiz, A. Tiripicchio, M. Tiripicchio-Camellini, *Organometallics* **1993**, *12*, 2962. − I. D. Salter, V. Sik, S. A. Williams, T. Adatia, *J. Chem. Soc., Dalton Trans.* **1996**, 643. − M. Slany, M. Bardaji, M. J. Casanove, A. M. Caminade, J. P. Majoral, B. Chaudret, *J. Am. Chem. Soc.* **1995**, *117*, 9764. − A. M. Z. Slawin, M. B. Smith, J. D. Woollins, *J. Chem. Soc., Dalton Trans.* **1996**, 1283. − E. Zeller, A. Schier, H. Schmidbaur, *Z. Naturforsch., B* **1994**, *49*, 1243. − S. Ahrland, K. Dreisch, B. Noren, A. Oskarsson, *Mater. Chem. Phys.* **1993**, *35*, 281. − M. T. Bautista, P. S. White, C. K. Schauer, *J. Am. Chem. Soc.* **1994**, *116*, 2143. − M. Viotte, B. Gautheron, M. M. Kubicki, I. E. Nifant′ev, S. P. Fricker, *Met.-Based Drugs* **1995**, *2*, 311. − P. G. Jones, B. Ahrens, *Chem. Ber.* **1997**, *130*, 1813.
[34] R. Usón, A. Laguna, M. Laguna, E. J. Fernández, P. G. Jones, G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.* **1982**, 1971.
[35] E. J. Fernandez, M. C. Gimeno, P. G. Jones, A. Laguna, M. Laguna, E. Olmos, *J. Chem. Soc., Dalton Trans.* **1996**, 3603.
[36] P. D. Cookson, E. R. T. Tiekink, *J. Chem. Soc., Dalton Trans.* **1993**, 259.
[37] R. Usón, A. Laguna, M. Laguna, J. Jimenez, M. P. Gómez, A. Sainz, P. G. Jones, *J. Chem. Soc., Dalton Trans.* **1990**, 3457.
[38] L. G. Kuzmina, K. I. Grandberg, L. G. Ilina, *Zh. Neorg. Khim.* **1995**, *40*, 1827 (*Chem. Abstr.* **1995**, *123*, 184068n).
[39] F. S. Babichev, V. N. Bubnowskaya, *Ukr. Khim. Zh.* **1964**, *30*, 848 (*Chem. Abstr.* **1965**, *62*, 1766c).
[40] C. K. Bradsher, D. F. J. Lohr, *J. Heterocycl. Chem.* **1966**, *3*, 27.
[41] A. A. Martynowskii, A. A. Brazhko, V. G. Bulakh, T. V. Panasenko, B. A. Samura, E. A. Krasnykh, *Khim.-Farm. Zh.* **1991**, *25*, 20 (*Chem. Abstr.* **1991**, *115*, 49360z).
[42] J. Vicente, M. T. Chicote, J. A. Cayuelas, J. Fernandez-Baeza, P. G. Jones, G. M. Sheldrick, P. Espinet, *J. Chem. Soc., Dalton Trans.* **1985**, 1163. − J. Vicente, M. T. Chicote, I. Saura-Llamas, J. Turpin, J. Fernandez-Baeza, *J. Organomet. Chem.* **1987**, *333*, 129. − J. Vicente, M. T. Chicote, I. Saura-Llamas, P. G. Jones, K. Meyer-Bäse, C. F. Erdbrügger, *Organometallics* **1988**, *7*, 997. − J. Vicente, M. T. Chicote, I. Saura-Llamas, *J. Chem. Soc., Dalton Trans.* **1990**, 1941. − J. Vicente, M. T. Chicote, I. Saura-Llamas, M. C. Lagunas, *J. Chem. Soc., Chem. Commun.* **1992**, 915. − J. Vicente, M. T. Chicote, P. G. Jones, *Inorg. Chem.* **1993**, *32*, 4960. − J. Vicente, M. T. Chicote, P. González-Herrero, P. G. Jones, B. Ahrens, *Angew. Chem.* **1994**, *106*, 1966; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1852. − J. Vicente, M. T. Chicote, P. González-Herrero, P. G. Jones, *J. Chem. Soc., Dalton Trans.* **1994**, 3183. − J. Vicente, M. T. Chicote, M. D. Abrisqueta, *J. Chem. Soc., Dalton Trans.* **1995**, 497. − J. Vicente, M. T. Chicote, P. González-Herrero, P. G. Jones, *J. Chem. Soc., Chem. Commun.* **1995**, 745. − J. Vicente, M. T. Chicote, R. Guerrero, P. G. Jones, *J. Am. Chem. Soc.* **1996**, *118*, 699. − J. Vicente, M. T. Chicote, R. Guerrero, P. G. Jones, M. C. Ramírez de Arellano, *Inorg. Chem.* **1997**, *36*, 4438. J. Vicente, M. T. Chicote, M. C. Lagunas, P. G. Jones, B. Ahrens, *Inorg. Chem.* **1997**, *36*, 4938. − [42a] J. Vicente, M. T. Chicote, M. C. Lagunas, P. G. Jones, *J. Chem. Soc., Dalton Trans.* **1991**, 2579.
[43] A. H. Othman, S.-C. Coh, H.-K. Fun, K. Sivakumar, *Acta Crystallogr.* **1996**, *C52*, 2760.
[44] H. Schmidbaur, W. Graf, G. Müller, *Angew. Chem.* **1988**, *100*, 439; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 417.
[45] W. J. Geary, *Coord. Chem. Rev.* **1971**, *7*, 81.
[46] G. M. Sheldrick, University of Göttingen, **1993**.

[97239]