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Mono- and bimetallic gold(I) and silver(I) pentafluoropropionates and related compounds

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Abstract

A series of eight new carboxylate complexes of the general type $(L)_nMOC(O)R$ ($L = PMe_3$; $n = 1$; M = Ag, Au; $R = C_2F_5$. $L = PPh_3$; $n = 1$–3; M = Ag; $R = C_2F_5$, *t*-Bu) have been prepared in high yields. Crystal and molecular structures have been determined for three representative examples. The crystal structure of $(Ph_3P)AgOC(O)C_2F_5$ contains dimers in which the silver atoms are bridged by the carboxylate oxygen atoms. This bridging resembles the structural motif found in silver carboxylates without ligand support. Usage of the smaller phosphine PMe_3 leads to the formation of a polymeric chain structure in $(Me_3P)AgOC(O)C_2F_5$ with bridging carboxylate anions and short Ag–Ag contacts holding the monomers together. The reaction of $(4\text{-}Me_2N\text{-}C_6H_4)Ph_2PAuCl$ with two equivalents of $C_2F_5CO_2Ag$ leads to the formation of a mixed metal product containing both gold and silver. The crystal structure analysis of this compound revealed a tetranuclear complex containing a central dimeric silver pentafluoropropionate unit which is chelated by the (triarylphosphine)gold(I) pentafluoropropionate molecules via Ag–Au metallophilic contacts and Ag–O donor/acceptor interactions.

Keywords: Gold complexes; Silver complexes; Argentophilicity; Mixed metal metallophilicity; Carboxylate complexes

1. Introduction

The concept of “metallophilic bonding” has added a new range of intermolecular interactions to the spectrum of chemical bonding in supramolecular aggregates [1]. A small number of scattered observations in the early structural chemistry of gold(I) complexes [2] has grown into a wealth of reports on related phenomena in the last two decades, which finally provided a clear pattern of the conditions under which direct interactions between closed-shell gold(I) centers can contribute significantly to the stability of molecular and multidimensional structures [3]. The underlying “aurophilic” bonding [4] has been analyzed in theoretical studies which have confirmed the experimental results and gave an explanation for the finding that the “metallophilic” bonding is strongest and therefore most obvious for heavy metals in general, and for gold complexes in particular [5]. Notwithstanding, there has also been growing evidence for weak metallophilic bonding between low-coordinate silver atoms [6] and – as a logical consequence – for gold–silver metallophilicity [7]. In the present report we present new and noteworthy examples taken from the important class of silver and gold perfluorocarboxylates. These compounds have interesting photophysical properties [6c] and are relevant to homogeneous gold catalysis [8] and to gold/silver thin film technology [9].

Previous structural studies of (phosphine)*gold*(I) perfluorocarboxylates have shown that these compounds are isolated monomers of the type **A** or Au–Au bonded dimers of the type **A₂** depending on the steric effect of the tertiary phosphine employed [8a,8b]. In both forms the gold atoms are linearly two-coordinate with monohapto carboxylate groups. By contrast, in the

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corresponding (phosphine)*silver*(I) perfluorocarboxylates the coordination number of the metal atoms can be expanded with the carboxylate groups becoming *O*,*O*′-dihapto bridges between the metal atoms (**B**) [6c]. Donor-free silver(I) perfluorocarboxylates are known to be cyclic dimers of type **C** in the solid state (Scheme 1) [10].

2. Preparative results

Tri*aryl* phosphine complexes of *gold*(I) pentafluoropropionate were synthesized and structurally characterized in a previous study in this laboratory. Owing to the steric bulk of the phosphines, the compounds are monomers with a molecular structure of type **A** [8a]. (Tri*methyl* phosphine)*gold*(I) pentafluoropropionate has now been prepared from the chloride complex and silver pentafluoropropionate in dichloromethane at −70 °C in good yield (70.8%) [Eq. (1)], but the product proved unstable in solution where it decomposed slowly at temperatures above −30 °C. It could therefore not be crystallized and its structure – most probably an oligomer with short aurophilic contacts as already demonstrated [8b] for the trifluoroacetate – could not be determined. The compound was identified by elemental analysis, NMR spectroscopy and mass spectrometry.

$$(Me_3P)AuCl + C_2F_5CO_2Ag \xrightarrow[-AgCl]{} (Me_3P)AuOC(O)C_2F_5 \qquad (1)$$

$$[(4\text{-}Me_2N\text{–}C_6H_4)Ph_2P]AuCl \xrightarrow[-AgCl]{+C_2F_5CO_2Ag} [(4\text{-}Me_2N\text{–}C_6H_4)Ph_2P]AuOC(O)C_2F_5 \qquad (2)$$

$$2[(4\text{-}Me_2N\text{–}C_6H_4)Ph_2P]AuCl \xrightarrow[-2AgCl]{+4C_2F_5CO_2Ag} Au_2Ag_2[(4\text{-}Me_2N\text{–}C_6H_4)Ph_2P]_2[OC(O)C_2F_5]_4 \qquad (3a)$$

$$2(R_3P)AuOC(O)C_2F_5 \xrightarrow{+2C_2F_5CO_2Ag} Au_2Ag_2(R_3P)_2[OC(O)C_2F_5]_4 \qquad (3b)$$

$R_3P = (4\text{-}Me_2N\text{–}C_6H_4)Ph_2P$

Pure products of type **A** are only obtained if the stoichiometric ratio of the components $(R_3P)AuCl$ and $AgOC(O)C_2F_5$ is strictly 1:1. Under these stringent conditions, the 1:1 complex with $(4\text{-}Me_2N\text{–}C_6H_4)Ph_2P$ has been prepared previously without any difficulties [Eq. (2)] [8a]. However, if an excess of $AgOC(O)C_2F_5$ is employed, mixed-metal products containing both gold and silver are formed which can only be crystallized as the molar ratio 1:2 is reached. The compound with diphenyl(4-dimethylamino-phenyl)phosphine as a ligand could be obtained as single crystals [Eq. (3a)] and was amenable to a diffraction study (below). This product is obtained in even higher yield from an addition of LAuX to AgX in the molar ratio 1:1 [Eq. (3b)].

$$C_2F_5CO_2Ag + Me_3P \rightarrow (Me_3P)AgOC(O)C_2F_5 \qquad (4)$$

$$C_2F_5CO_2Ag + Ph_3P \rightarrow (Ph_3P)AgOC(O)C_2F_5 \qquad (5)$$

$$C_2F_5CO_2Ag + 2\ Ph_3P \rightarrow (Ph_3P)_2AgOC(O)C_2F_5 \qquad (6)$$

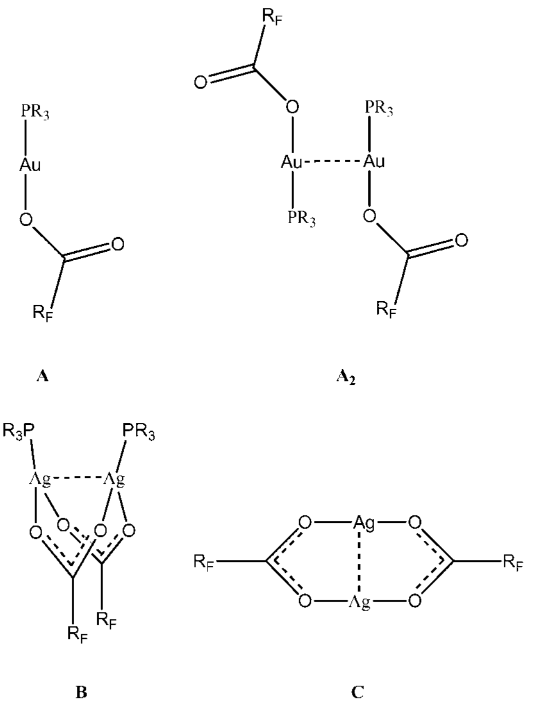
$$C_2F_5CO_2Ag + 3\ Ph_3P \rightarrow (Ph_3P)_3AgOC(O)C_2F_5 \qquad (7)$$

Silver pentafluoropropionate is readily dissolved in a mixture of ethanol and dichloromethane (1:2 by volume) upon addition of a solution of one equivalent of trimethylphosphine in toluene. Colorless crystals, m.p. 151 °C, can be grown from dichloromethane/pentane at −70 °C (85.7% yield) [Eq. (4)]. A colorless, crystalline triphenylphosphine complex (m.p. 208 °C) was obtained similarly (from dichloromethane, 91% yield) [Eq. (5)]. With two or three equivalents of Ph_3P the corresponding 2:1 and 3:1 complexes could be isolated [Eqs. (6), (7)]. The latter was obtained as single crystals and its structure has been determined (below).

In order to be able to compare the properties of the perfluorinated silver carboxylates and alkylated counterparts, the three related mono-, bis- and tris(triphenylphosphine)silver(I) pivalates were also prepared. The compounds were all obtained in high yields and found to be stable colorless solids which dissolve readily in polar solvents. The solutions are light-sensitive and decompose slowly upon standing at room temperature. The stoichiometry and general properties thus showed no anomalies.

3. Structural studies

(Trimethylphosphine)silver(I) pentafluoropropionate crystallizes in the monoclinic space group $C2/c$ with $Z = 16$ formula units in the unit cell. The asymmetric unit contains two independent molecules with similar geometrical parameters. These monomers are aggregated into chains with the two independent units (containing the silver atoms Ag1 and Ag2) alternating along the chain as shown in Fig. 1. Neighbouring silver atoms are bridged by pentafluoropropionate groups and



Scheme 1.

maintain short argentophilic contacts [Ag1–Ag2 2.8914(5), Ag1–Ag2′ 2.8652(5) Å].

Each silver atom is three-coordinate with a phosphorus atom and two oxygen atoms in a common plane, but the P–Ag–O and O–Ag–O angles show that the geometry is closer to T-shaped than to trigonal planar. The sums of angles at Ag1 and Ag2 are 359.6(1)° and 359.4(1)°, respectively. Of the two sets of three angles, P1–Ag1–O3 and P2–Ag2–O2 are the largest at 155.6(1) and 160.5(1)°, representing the distorted molecular axis of the individual unit. The Ag–Ag contacts extend above and below the P–Ag–O2 planes in an almost linear geometry with angles Ag1–Ag2–Ag1′ 163.57(1)° and Ag2–Ag1–Ag2′ 162.39(1)°.

Double-bridging by carboxylate groups of a pair of metal atoms entertaining argentophilic contacts was also encountered in the crystals of $(Ph_3P)Ag–OC(O)C_2F_5$ (monoclinic, space group $P2_1/c$, $Z = 8$, two independent formula units in the asymmetric unit). However, the association for this complex is limited to dimers (Fig. 2) instead of linear polymers. The bulk of the larger Ph_3P ligand requires more space than the small Me_3P ligand, and this requirement is better fulfilled at the small oligomer. Ag2 has a planar T-shaped geometry, while Ag1 has a planar distorted Y-shaped coordination pattern. The Ag1–Ag2 distance of 3.553(1) Å is longer than in the Me_3P complex, probably owing to the steric effect of the two Ph_3P groups.

The crystal structures of $(R_3P)Ag–OC(O)C_2F_5$ compounds (R = Me, Ph) with three-coordinate metal atoms bridged – at approximately right angles (Fig. 1) – by carboxylate groups, and short argentophilic contacts, is entirely different from that of the analogous gold(I) complexes which were found to be associated solely via aurophilic contacts between strictly linearly two-coordinate metal atoms [8a,8b].

The association of (phosphine)silver(I) pentafluoropropionates is absent in the complexes with more than one phosphine ligand per metal atom. An example in

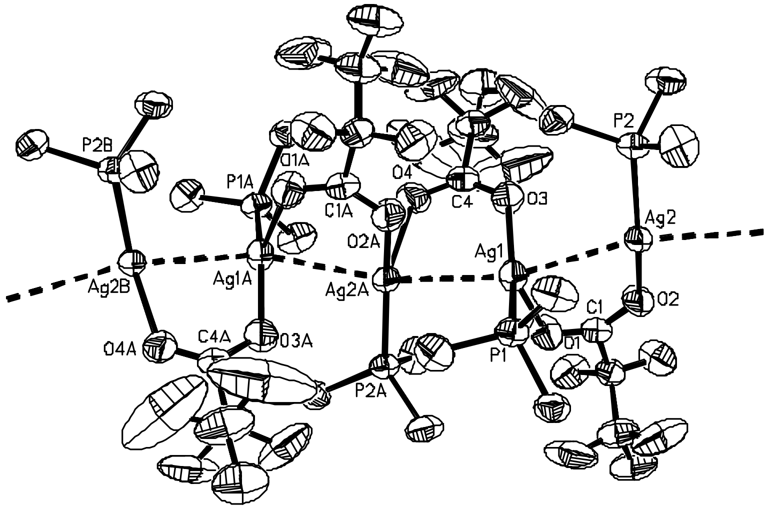


Fig. 1. Chain structure of $AgOCOC_2F_5 \cdot PMe_3$ (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Ag1–O1 2.400(3), Ag1–P1 2.347(1), Ag1–O3 2.197(3), Ag2A–O2A 2.194(3), Ag2A–P2A 2.343(1), Ag2A–O4 2.438(4), Ag1 ··· Ag2 2.8914(5), Ag1 ··· Ag2A 2.8652(5); O3–Ag1–P1 155.6(1), O3–Ag1–O1 90.6(1), P1–Ag1–O1 113.3(1), O3–Ag1 ··· Ag2A 84.1(1), P1–Ag1 ··· Ag2A 94.75(3), O1–Ag1 ··· Ag2A 102.1(1), O3–Ag1 ··· Ag2 78.3(1), P1–Ag1 ··· Ag2 100.86(3), O1–Ag1 ··· Ag2 79.2(1), Ag2A ··· Ag1 ··· Ag2 162.39(1), O2A–Ag2A–P2A 160.5(1), O2A–Ag2A–O4 87.0(1), P2A–Ag2A–O4 111.8(1), O2A–Ag2A ··· Ag1 79.6(1), P2A–Ag2A ··· Ag1 97.79(3), O4–Ag2A ··· Ag1 80.1(1), O2A–Ag2A ··· Ag1A 84.2(1), P2A–Ag2A ··· Ag1A 98.45(3), O4–Ag2A ··· Ag1A 96.1(1), Ag1A ··· Ag2A ··· Ag1 163.57(1).

case is the structure of $(Ph_3P)_3Ag–OC(O)C_2F_5$ which crystallizes as the tetrahydrofuran solvate (triclinic, space group $P\bar{1}$, $Z = 2$). The tetrahydrofuran molecule in this phase is disordered near a center of inversion. The asymmetric unit contains one chiral formula unit (Fig. 3) which is related with its enantiomer by a center of inversion. The silver atom is tetracoordinate with a quasi-tetrahedral coordination geometry. The pentafluoropropionate group is η^1-bonded to the metal with an Ag–O1 distance of 2.433(2) Å.

The most interesting structural aspect in this report is the arrangement of the components of the mixed-metal tetranuclear compound $L_2Au_2Ag_2X_2$ or $(AgX)_2(LAuX)_2$ $[X = C_2F_5CO_2;\ L = (4\text{-}Me_2N–C_6H_4)Ph_2P]$. This adduct crystallizes in the triclinic space group $P\bar{1}$ with $Z = 1$ formula unit in the unit cell. The asymmetric unit contains half of the tetranuclear complex, the other half being related by a center of inversion (Fig. 4). The aggregate has a neutral dimer $[C_2F_5CO_2Ag]_2$ as a core unit with a planar eight-membered ring already familiar from previous studies of silver carboxylates [10]. It should be noted that this dimer has a short argentophilic transannular contact Ag–Ag [2.9939(6) Å].

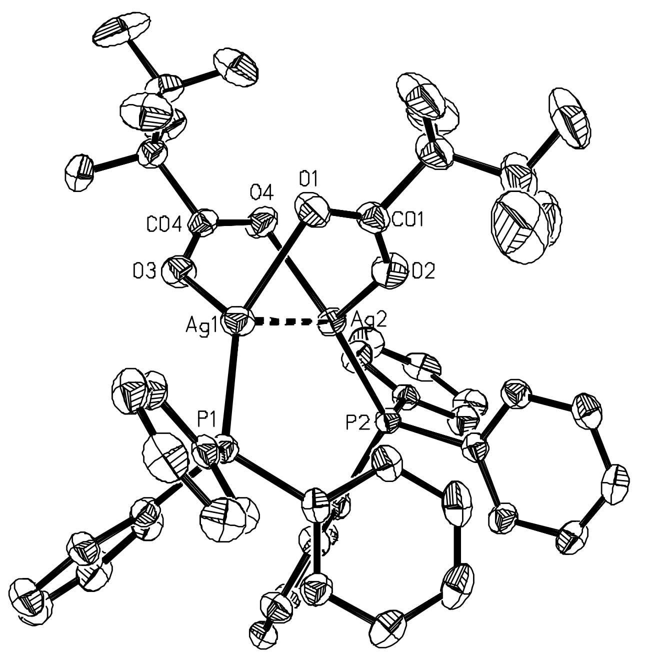


Fig. 2. Dimeric structure of $AgOCOC_2F_5 \cdot PPh_3$ (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Ag1–O1 2.73(2), Ag1–O3 2.310(2), Ag1–P1 2.351(1), Ag2–O2 2.362(2), Ag2–O4 2.212(2), Ag2–P2 2.347(1), Ag1···Ag2 3.553(1); O1–Ag1–O3 92.76(8), O1–Ag1–P1 136.87(6), O3–Ag1–P1 130.34(5), O4–Ag2–P2 150.02(6), O4–Ag2–O2 89.14(8), P2–Ag2–O2 117.83(5).

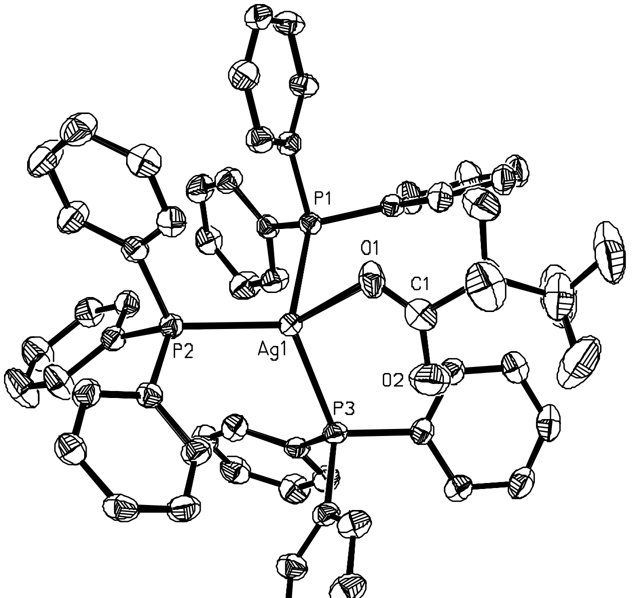


Fig. 3. Molecular structure of $AgOCOC_2F_5 \cdot 3\ PPh_3 \cdot 0.5thf$ (ORTEP drawing with 50% probability ellipsoids, H-atoms and disordered solvent molecule omitted for clarity). Selected bond lengths [Å] and angles [°]: Ag1–O1 2.433(2), Ag1–P1 2.6026(8), Ag1–P2 2.5441(7), Ag1–P3 2.5432(7); O1–Ag1–P1 91.09(7), O1–Ag1–P2 107.50(6), O1–Ag1–P3 108.67(6), P1–Ag1–P2 112.96(2), P1–Ag1–P3 115.59(2), P2–Ag1–P3 117.34(3).

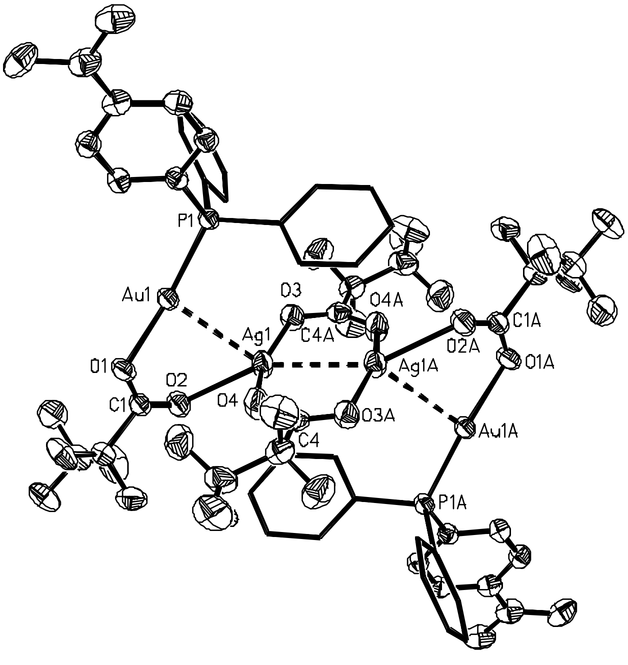


Fig. 4. Structure of tetranuclear $[(AgOCOC_2F_5)_2((4\text{-}Me_2NC_6H_4)Ph_2PAuOCOC_2F_5)_2]$ (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Au1–O1 2.080(2), Au1–P1 2.2240(8), Au1···Ag1 3.0253(3), Ag1–O2 2.245(3), Ag1–O3 2.195(3), Ag1–O4 2.204(3), Ag1···Ag1A 2.9439(6); O1–Au1–P1 173.56, O1–Au1···Ag1 86.69(7), P1–Au1···Ag1 99.08(2), O2–Ag1–O3 110.1(1), O2–Ag1–O4 90.3(1), O3–Ag1–O4 159.6(1), O2–Ag1···Ag1A 155.72(7), O3–Ag1···Ag1A 82.68(7), O4–Ag1···Ag1A 78.49(8), O2–Ag1···Au1 68.87(6), O3–Ag1···Au1 103.36(7), O4–Ag1···Au1 83.07(8), Ag1A···Ag1···Au1 129.76(2).

The two L–Au–OC(O)C_2F_5 molecules are attached to this core unit via two external metallophilic contacts Ag–Au [3.0253(2) Å] and two silver–oxygen contacts Ag1–O2 [2.456(3) Å]. Each (phosphine)gold perfluoropropionate unit is thus chelating a silver atom employing its metal atom and one carboxylate oxygen atom for the bite. Consequently, the resulting metal atom chain Au–Ag–Ag–Au is not linear but has two Au–Ag–Ag angles of 129.78(2)°.

The coordination of each silver atom by its oxygen donor atoms is planar T-shaped not unlike the situation in the oligomeric or dimeric homometallic (phosphine)silver(I) pentafluoropropionates described above. By contrast, the gold atoms remain linearly two-coordinate [P1–Au1–O1 173.56(7)°] with the Au–Ag contacts perpendicular to the molecular axis [O1–Au1–Ag1 86.69(7)°].

An array of this type was recently also found in a 1:2 adduct of dimeric silver trifluoroacetate and [diphenyl (phenylthiomethyl)phosphine]pentafluorophenylgold (I) [7k]. In this case the LAuX units are attached to the $(CF_3CO_2Ag)_2$ core unit via Ag–S and Au–Ag contacts. The Au–Ag and Ag–Ag distances are similar in both structures. However, in the reference compound the Au–Ag–Ag–Au chain is not extended but highly bent, with Au–Ag–Ag angles as small as 71.69(2)° giving it a “lightning” shape. The details of the two structures thus are consistent in showing the affinity (metallophilicity) of linearly two-coordinate silver atoms for linearly two-coordinate gold atoms, but they also demonstrate that this affinity has no directional element and can occur anywhere in a belt around each metal.

4. Experimental

All experiments were carried out in an atmosphere of dry nitrogen. Glassware was oven-dried and filled with nitrogen. Solvents were dried, distilled and stored under nitrogen. Standard equipment was used throughout. The glass apparatus was protected against light by an aluminium foil wrapper. The silver pentafluoropropionate and all tertiary phosphines are commercially available. (Phosphine)gold(I) chlorides were prepared following literature procedures [11].

*4.1. (Trimethylphosphine)gold(I) pentafluoropropionate (**1**)*

A suspension of $C_2F_5CO_2Ag$ (220 mg, 0.81 mmol) in dichloromethane (5 ml) is cooled to −70 °C and treated with a solution of $(Me_3P)AuCl$ (250 mg, 0.81 mmol) in 10 ml of CH_2Cl_2 with stirring. After 2 h the precipitation of AgCl is complete. The reaction mixture is filtered and the filtrate concentrated in a vacuum to a volume of ca. 5 ml. The product is precipitated by addition of *n*-pentane (5 ml) at −70 °C, collected and recrystallized from tetrahydrofuran/pentane to give 250 mg (70.8% yield) of a colorless solid which decomposes at room temperature. Solutions in dichloromethane or tetrahydrofuran decompose already above −30 °C. NMR (CD_2Cl_2) ^1H: 2.74 ppm, d, *J* 11.4 Hz; $^{31}P\{^1H\}$: −16.2 ppm, s. MS (FAB): *m/e* 436 (6.3%) $[M]^+$; 349 (4.3) $[L_2Au]^+$; 289 (100) $[LAuO]^+$; 273 (8.5) $[LAu]^+$. Elemental analysis found C 16.2, H 1.9; calcd. for $C_6H_9AuO_2PF_5$ (436.05) C 16.5, H 2.1%.

*4.2. (Trimethylphosphine)silver(I) pentafluoropropionate (**2**)*

A suspension of $C_2F_5CO_2Ag$ (300 mg, 1.11 mmol) in a mixture of ethanol (5 ml) and dichloromethane (10 ml) is treated with a solution of Me_3P in toluene (1.11 ml, 1.11 mmol) with stirring at room temperature. After 3 h a clear solution is obtained, which is concentrated in a vacuum to a volume of ca. 5 ml and cooled to −70 °C. Addition of cold pentane leads to the precipitation of the product, which is recrystallized from dichloromethane/pentane to give colorless crystals (330 mg, 85.7% yield), m.p. 151 °C. NMR (CD_2Cl_2), ^1H: 1.44, d, *J* 9.8 Hz. $^{31}P\{^1H\}$: −34.8, s. MS (FAB): *m/e* 531 (15.8%) $[L_2AgX]^+$; 259 (100) $[L_2Ag]^+$; 183 (41.9) $[LAg]^+$.

*4.3. (Triphenylphosphine)silver(I) pentafluoropropionate (**3**)*

A suspension of $C_2F_5CO_2Ag$ (250 mg, 0.93 mmol) in 10 ml of dichloromethane is treated with a solution of Ph_3P (240 mg, 0.93 mmol) in the same volume of the same solvent at room temperature. A clear solution is obtained, the volume of which is reduced to ca. 5 ml in a vacuum. Addition of cold pentane (−70 °C) gives a colorless precipitate which is recrystallized from dichloromethane/pentane (450 mg, 91% yield), m.p. 208 °C. NMR ($CDCl_3$), ^1H: 7.38–7.56, m, Ph; $^{13}C\{^1H\}$: 163.2, t, *J* 25.5 Hz, CO_2; CF_2 and CF_3 were not detected; 128.9, d, *J* 37.4 Hz; 129.3, d, *J* 10.1 Hz; 131.5, s; 133.9, d, *J* 17.0 Hz (for C-ipso, *-meta*, *-para*, and *-ortho*, resp.); $^{31}P\{^1H\}$: 15.4, s. IR (KBr): 1653 cm^{-1}, $\nu(CO)$. MS (FAB): *m/e* 631 (31.1%) $[L_2Ag]^+$; 385 (3.0) $[LAgO]^+$; 369 (100) $[LAg]^+$; 262 (47.5) $[L]^+$. Elemental analysis, found C 47.3, H 2.7, P 6.2; calcd. for $C_{21}H_{15}AgO_2PF_5$ (533.17) C 47.3, H 2.8, P 5.8%.

*4.4. Bis(triphenylphosphine)silver(I) pentafluoropropionate (**4**)*

$C_2F_5CO_2Ag$ (200 mg, 0.74 mmol) is suspended in 10 ml of dichloromethane and a solution of Ph_3P (387 mg, 1.48 mmol) in the same volume of the same solvent is slowly added with stirring. After 2 h the solvent is evaporated to leave the product, which is recrystallized from tetrahydrofuran/pentane; colorless solid (540 mg, 92% yield), m.p. 164 °C with decomposition. NMR (CD_2Cl_2), ^1H: 7.33–7.51, m, Ph. $^{13}C\{^1H\}$: 162.1, t, *J* 23.7 Hz, $\mathit{C}O_2$; $\mathit{C}F_2$ and $\mathit{C}F_3$ not detected; 129.9, d, *J* 8.3 Hz; 130.6, s; 133.4, d, *J* 31.1 Hz, 133.8, d, *J* 15.6 Hz (for C-*meta*, -*para*, -ipso, and -*ortho*). $^{31}P\{^1H\}$: 8.7, s. MS (FAB): *m/e* 631 (82%) $[L_2Ag]^+$; 385 (4.0) $[LAgO]^+$; 369 (100) $[LAg]^+$; 262 (54.4) $[L]^+$. Elemental analysis, found C 58.9, H 3.8, P 7.7; calcd. for $C_{39}H_{30}AgO_2P_2F_5$ (795.43) C 58.8, H 3.8, P 7.7%.

*4.5. Tris(triphenylphosphine)silver(I) pentafluoropropionate (**5**)*

The compound is prepared from $C_2F_5CO_2Ag$ (200 mg, 0.74 mmol) and Ph_3P (580 mg, 2.22 mmol) in a total of 30 ml of dichloromethane at 40 °C. After 2 h of stirring the reaction mixture is concentrated to a small volume (ca. 8 ml) and cold pentane (−70 °C) is added to precipitate the colorless product, which is crystallized from tetrahydrofuran/pentane; 770 mg (98.7% yield), m.p. 169 °C with decomposition. NMR (CD_2Cl_2), ^1H: 7.29–7.69, m, Ph; $^{13}C\{^1H\}$: 160.9, t, *J* 22.4 Hz, $\mathit{C}O_2$; $\mathit{C}F_2$ and $\mathit{C}F_3$ not detected; 128.7, d, *J* 9.6; 130.2, s; 133.4, d, *J* 28.2 Hz; 133.8, d, *J* 14.7 Hz (C-*meta*, -*para*, -ipso, and -*ortho*, resp.); $^{31}P\{^1H\}$: 5.2, s.MS (FAB): *m/e* 631 (100) $[L_2Ag]^+$; 385 (2.9) $[LAgO]^+$; 369 (89.8) $[LAg]^+$; 262 (28.2 $[L]^+$). Elemental analysis, found C 58.5, H 3.9, F 11.7; calcd. for $C_{57}H_{45}AgO_2P_3F_5$ (1057.7) C 58.9, H 3.8, F 11.9%.

*4.6. [(4-Dimethylamino-phenyl)diphenylphosphine]gold (I) pentafluoropropionate (**6**)*

$[(4\text{-}Me_2N\text{–}C_6H_4)Ph_2P]AuCl$ (250 mg, 0.46 mmol) is dissolved in dichloromethane (10 ml) and added to a suspension of $C_2F_5CO_2Ag$ (130 mg, 0.46 mmol) in 5 ml of the same solvent with stirring at −70 °C. After 2 h the AgCl precipitate is filtered off and the filtrate is concentrated in a vacuum to a volume of ca. 5 ml. The colorless product is precipitated by the addition of cold pentane (−70 °C); 270 mg (88% yield), m.p. 132 °C with decomposition. NMR (CD_2Cl_2), ^1H: 3.0, s, 6H, Me; 6.74 and 7.36, d, 2H each, C_6H_4; 7.38–7.42, m, 10H, Ph. $^{31}P\{^1H\}$: 24.84, s. IR (KBr): 1658 cm^{-1}, $\nu(C=O)$. MS (FAB): *m/e* 1167 (5.0%) $[L_2Au_2X]^+$; 807 (25) $[L_2Au+H]^+$; 806 (1.6) $[L_2Au]^+$; 665 (7.6) $[M]^+$; 502 (100) $[LAu]^+$; 304 (48.9) $[L]^+$. Elemental analysis found C 39.8, H 3.0, N 2.0; calcd. for $C_{23}H_{20}AuNO_2PF_5$ (665.3) C 41.5, H 3.0, N 2.1%.

*4.7. Bis[(4-dimethylamino-phenyl)diphenylphosphine]digold(I)-disilver(I) tetrakis(pentafluoropropionate) (**7**)*

$C_2F_5CO_2Ag$ (65 mg, 0.225 mmol) is suspended in dichloromethane (5 ml), cooled to −70 °C and treated with a solution of $[(4\text{-}Me_2N\text{–}C_6H_4)Ph_2P]AuOC(O)C_2F_5$ (150 mg, 0.225 mmol) in 10 ml of the same solvent. After 2 h of stirring a clear solution is obtained, which is concentrated in a vacuum to a volume of ca. 5 ml. Addition of 10 ml of cold pentane (−70 °C) leads to precipitation of the product, which is recrystallized from dichloromethane/pentane (180 mg, 84% yield); colorless, air-stable crystals (m.p. 86 °C), which decompose slowly in solution in daylight at 20 °C. NMR (CD_2Cl_2), ^1H: 3.0, s, 6H, Me; 6.74 and 7.36, d, 2H each, C_6H_4; 7.38–7.42, m, 10H, Ph. $^{31}P\{^1H\}$: 25.4, s. IR (KBr): 1675 and 1645 cm^{-1}, $\nu(C=O)$. MS (FAB): *m/e* 807 (32%) $[L_2Au+H]^+$; 806 (2.0) $[L_2Au]^+$; 518 (1.9) $[L_2Ag]^+$; 502 (100) $[LAu]^+$; 412 (11.5) $[LAg]^+$; 304 (88.7) $[L]^+$. Elemental analysis found C 33.0, H 2.3, N 1.4; calcd. for $C_{26}H_{20}NPAgAuO_4F_{10}$ (936.2) C 33.3, H 2.1, N 1.5%.

*4.8. (Triphenylphosphine)silver(I) pivalate (2,2-dimethylpropionate) (**8**)*

Me_3CCO_2Ag (150 mg, 0.72 mmol) is dissolved in 15 ml of dichloromethane containing Ph_3P (190 mg, 0.72 mmol). After 3 h a clear solution is obtained. The solvent is evaporated and the residue washed with diethyl ether and crystallized from dichloromethane/pentane (270 mg, 79.6% yield), colorless solid, m.p. 105 °C with decomposition. NMR (CD_2Cl_2), ^1H: 1.20, s, 9H, Me; 7.31–7.64, m, 15H, Ph; $^{31}P\{^1H\}$: 14.3, s. MS (FAB): *m/e* 841 (8.1%) $[L_2Ag_2X]^+$; 631 (53.6) $[L_2Ag]^+$; 369 (100) $[LAg]^+$; 262 (10.9) $[L]^+$. Elemental analysis found C 60.5, H 5.2, P 6.6; calcd. for $C_{23}H_{24}AgO_2P$ (471.26) C 58.6, H 5.1, P 6.6%.

*4.9. Bis(triphenylphosphine)silver(I) pivalate (**9**)*

As described above for the 1:1 complex, the compound is prepared using Me_3CCO_2Ag (150 mg, 0.72 mmol) and Ph_3P (375 mg, 1.44 mmol) in the molar ratio 1:2; 480 mg (91% yield), m.p. 158 °C with decomposition. NMR (CD_2Cl_2), ^1H: 1.22, s, 9H, Me; 7.28–7.62, m, 30H, Ph. $^{13}C\{^1H\}$: 28.7, s, Me; 39.0, s, $\mathit{C}(Me)_3$; 171.1, s, $\mathit{C}O_2$; 128.9, d, *J* 9.3 Hz; 130.3, d, *J* 1.6 Hz; 132.5, d, *J* 26.6 Hz; 134.0, d, *J* 16.6 Hz (for C-*meta*, -*para*, -ipso, and -*ortho*). $^{31}P\{^1H\}$: 9.7, s. MS (FAB): *m/e* 840 (2.7%) $[L_2Ag_2X]^+$; 631 (29.2) $[L_2Ag]^+$; 369 (100) $[LAg]^+$; 262 (29.8) $[L]^+$. Elemental analysis found C 66.7, H 5.2, P 8.5; calcd. for $C_{41}H_{39}AgO_2P$ (733.54) C 67.1, H 5.4, P 8.4%.

*4.10. Tris(triphenylphosphine)silver(I) pivalate (**10**)*

As described above for the 1:1 and 1:2 complexes, the compound is obtained from Me_3CCO_2Ag (200 mg, 0.96 mmol) and Ph_3P (760 mg, 2.87 mmol) at 35 °C; 780 mg (81.8% yield), m.p. 165 °C with decomposition. NMR (CD_2Cl_2), ^1H: 1.44, s, 9H, Me; 7.33–7.82, m, 45H, Ph.

Table 1
Crystal data, data collection, and structure refinement

	$AgOCOC_2F_5 \cdot PMe_3$	$AgOCOC_2F_5 \cdot PPh_3$	$AgOCOC_2F_5 \cdot 3PPh_3 \cdot 0.5thf$	$[(AgOCOC_2F_5)_2((4\text{-}Me_2NC_6H_4)Ph_2PAuOCOC_2F_5)_2]$
Crystal data				
Formula	$C_6H_9AgF_5O_2P$	$C_{21}H_{15}AuF_5O_2P$	$C_{59}H_{49}AgF_5O_{2.5}P_3$	$C_{52}H_{40}Ag_2Au_2F_{20}N_2O_8P_2$
M_r	346.97	533.17	1093.76	1872.42
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	$C2/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	19.763(1)	11.1020(2)	13.2283(2)	9.8412(2)
b (Å)	11.258(1)	15.7720(3)	13.9276(2)	12.1484(2)
c (Å)	20.960(1)	23.4850(3)	14.0641(3)	13.3469(2)
α (°)	90	90	85.394(1)	79.694(1)
β (°)	101.099(3)	100.355(1)	75.115(1)	88.845(1)
γ (°)	90	90	89.420(1)	69.417(1)
V (Å^3)	4576.2(5)	4045.3(1)	2496.0(1)	1468.1(1)
ρ_{calc} (g cm^{-3})	2.014	1.751	1.455	2.118
Z	16	8	2	1
$F(000)$	2688	2112	1120	892
μ(Mo Kα) (cm^{-1})	19.46	73.24	5.64	58.10
Data collection				
T (°C)	−130	−130	−130	−130
Measured reflections	42,002	142,495	72,545	42,408
Unique reflections	4887 [$R_{int} = 0.041$]	8333 [$R_{int} = 0.033$]	10,354 [$R_{int} = 0.035$]	6089 [$R_{int} = 0.034$]
Absorption correction	DELABS	none	DELABS	DELABS
T_{min}/T_{max}	0.282/0.729	–	0.478/0.831	0.506/0.843
Refinement				
Refined parameters	271	541	613	397
Final R values [$I \geqslant 2\sigma(I)$]				
$R1$	0.0425	0.0350	0.0455	0.0263
$wR2$[a]	0.0980	0.0896	0.1187	0.0660
ρ_{fin}(max/min) (e Å^{-3})	0.876/−0.580	0.876/−0.833	1.101/−3.605	1.004/−1.388

[a] $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0349$ ($AgOCOC_2F_5 \cdot PMe_3$), 0.0537 ($AgOCOC_2F_5 \cdot PPh_3$), 0.0631 ($AgOCOC_2F_5 \cdot 3PPh_3 \cdot 0.5thf$), 0.0384 ($[(AgOCOC_2F_5)_2((4\text{-}Me_2NC_6H_4)Ph_2PAuOCOC_2F_5)_2]$); $b = 13.97$ ($AgOCOC_2F_5 \cdot PMe_3$), 4.47 ($AgOCOC_2F_5 \cdot PPh_3$), 4.55 ($AgOCOC_2F_5 \cdot 3PPh_3 \cdot 0.5thf$), 0.90 ($[(AgOCOC_2F_5)_2((4\text{-}Me_2NC_6H_4)Ph_2PAuOCOC_2F_5)_2]$).

$^{31}P\{^1H\}$: 8.1, s. MS (FAB): m/e 840 (2.2%) $[L_2Ag_2X]^+$; 631 (100) $[L_2Ag]^+$; 369 (91.6) $[LAg]^+$; 262 (13.9) $[L]^+$. Elemental analysis found C 70.4, H 5.3, P 8.9; calcd. for $C_{59}H_{54}AgO_2P_3$ (955.8) C 71.1, H 5.5, P 9.3%.

4.11. X-ray crystallography

Specimens of suitable quality and size were mounted on the ends of quartz fibers in F06206R oil and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite-monochromated Mo Kα radiation. The structures were solved by a combination of direct methods (SHELXS-97) and difference-Fourier syntheses and refined by full matrix least-squares calculations on F^2 (SHELXL-97). The thermal motion was treated anisotropically for all non-hydrogen atoms, except for the disordered solvent molecule in the lattice of $AgOCOC_2F_5 \cdot 3PPh_3 \cdot 0.5thf$ which was included with fixed positions and fixed isotropic contributions. All hydrogen atoms were calculated and allowed to ride on their parent atoms with fixed isotropic contributions. Further information on crystal data, data collection and structure refinement are summarized in Table 1. Important interatomic distances and angles are shown in the corresponding figure captions.

5. Supplementary material

Crystallographic data for the structural analyses with thermal parameters and complete tables of interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). The data are available on request on quoting CCDC-213207-213210.

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References

[1] D. Braga, F. Grepioni, G.R. Desiraju, Chem. Rev. 98 (1998) 1375.

[2] P.G. Jones, Gold Bull. 14 (1981) 102.

[3] (a) H. Schmidbaur, Gold Bull. 23 (1990) 11;
(b) H. Schmidbaur, Gold Bull. 33 (2000) 3;
(c) H. Schmidbaur, Chem. Soc. Rev. 24 (1995) 443.

[4] (a) F. Scherbaum, A. Grohmann, B. Huber, C. Krüger, H. Schmidbaur, Angew. Chem. Int. Ed. Engl. 27 (1988) 1544;
(b) H. Schmidbaur, W. Graf, G. Müller, Angew. Chem. Int. Ed. Engl. 27 (1988) 417.

[5] P. Pyykkö, Chem. Rev. 97 (1997) 597, and references therein.

[6] (a) M. Jansen, Angew. Chem. Int. Ed. Engl. 26 (1987) 1098;
(b) G.W. Eastland, M.A. Mazid, D.R. Russell, M.C.R. Symons, J. Chem. Soc., Dalton Trans. (1980) 1682;
(c) C. Kappenstein, A. Ouali, M. Guerin, J. Cernak, J. Chomic, Inorg. Chim. Acta 147 (1988) 189;
(d) F.A. Cotton, X. Feng, M. Matusz, R. Poli, J. Am. Chem. Soc. 110 (1988) 7077;
(e) X.-M. Chen, T.C.W. Mak, J. Chem. Soc., Dalton Trans. (1991) 1219;
(f) J. Vicente, M.T. Chicote, M.C. Laguna, Inorg. Chem. 32 (1993) 3748;
(g) M. Quiros, Acta Crystallogr. C 50 (1994) 1236;
(h) K. Singh, J.R. Long, P. Stavropoulos, J. Am. Chem. Soc. 119 (1997) 2942;
(i) J. El-Bahraoui, J. Molina, D. Portal, J. Phys. Chem. 102A (1998) 2443;
(j) E.J. Fernandez, J.M. Lopez-de-Luzuriaga, M. Monge, M. Rodriguez, O. Crespo, M.C. Gimeno, A. Laguna, P.G. Jones, Inorg. Chem. 37 (1998) 6002;
(k) L.S. Ahmed, J.R. Dilworth, J.R. Miller, N. Wheatley, Inorg. Chim. Acta 278 (1998) 229;
(l) M.A. Omary, T.R. Webb, Z. Assefa, G. Shankle, H.H. Patterson, Inorg. Chem. 37 (1998) 1380;
(m) C.-M. Che, M.-C. Tse, M.C.W. Chan, K.-K. Cheung, D.L. Phillips, K.-H. Leung, J. Am. Chem. Soc. 122 (2000) 2464;
(n) E.J. Fernandez, M.C. Gimeno, A. Laguna, J.M. Lopez-de-Luzuriaga, M. Monge, P. Pyykkö, D. Sundholm, J. Am. Chem. Soc. 122 (2000) 7287;
(o) P. Römbke, A. Schier, H. Schmidbaur, Z. Naturforsch. 58B (2003) 168.

[7] (a) O.M. Ak-Salah, C.B. Knobler, J. Organomet. Chem. 302 (1986) C10;
(b) R. Uson, A. Laguna, M. Laguna, A. Uson, P.G. Jones, C.F. Erdbrügger, Organometallics 6 (1987) 1778;
(c) M.E. Olmos, A. Schier, H. Schmidbaur, Z. Naturforsch. 52B (1997) 203;
(d) A. Sladek, H. Schmidbaur, Z. Naturforsch. 52B (1997) 301;
(e) J. Vicente, M.-T. Chicote, I. Saura-Llamas, M.-C. Lagunas, M.C. Ramirez de Arellano, P. Gonzalez-Herrero, M.-D. Abrisqueta, R. Guerrero, in: P. Braunstein, L.A. Oro, P.R. Raithby (Eds.), Metal Clusters in Chemistry, Wiley-VCH, Weinheim, 1999, p. 493;
(f) J. Vicente, M.-T. Chicote, M.-C. Lagunas, P.G. Jones, B. Ahrens, Inorg. Chem. 36 (1997) 4938;
(g) M.-A. Rawashdeh-Omary, M.A. Omary, J.P. Fackler, Inorg. Chim. Acta 334 (2002) 376;
(h) M.C. Blanco, E.J. Fernandez, M.E. Olmos, O. Crespo, A. Laguna, P.G. Jones, Organometallics 21 (2002) 2426;
(i) O. Crespo, E.J. Fernandez, M. Gil, G.M. Conception, P.G. Jones, A. Laguna, J.M. Lopez-de-Luzuriaga, M.E. Olmos, J. Chem. Soc., Dalton Trans. (2002) 1319;
(j) H.-J. Haupt, O. Seewald, U. Floerke, V. Buss, T. Weyhermueller, J. Chem. Soc., Dalton Trans. (2001) 3329;
(k) E.J. Fernandez, J.M. Lopez-de-Luzuriaga, M. Monge, M.A. Rodriguez, O. Crespo, M.C. Gimeno, A. Laguna, P.G. Jones, Chem. Eur. J. 6 (2000) 636;
(l) M. Contel, J. Garrido, M.C. Gimeno, M. Laguna, J. Chem. Soc., Dalton Trans. (1998) 1083;
(m) M. Contel, J. Garrido, M.C. Gimeno, P.G. Jones, A. Laguna, M. Laguna, Organometallics 15 (1996) 4939;
(n) R. Uson, A. Laguna, M. Laguna, P.G. Jones, G.M. Sheldrick, Chem. Commun. (1981) 1097;
(o) M. Contel, J. Garrido, M.C. Gimeno, J. Jimenez, P.G. Jones, A. Laguna, M. Laguna, Inorg. Chim. Acta 254 (1997) 157.

[8] (a) P. Römbke, A. Schier, H. Schmidbaur, Z. Naturforsch. 57B (2002) 605;
(b) M. Preisenberger, A. Schier, H. Schmidbaur, J. Chem. Soc., Dalton Trans. (1999) 1645;
(c) G.C. Bond, D.T. Thompson, Gold Bull. 33 (2000) 41.

[9] R.J. Puddephatt, in: H. Schmidbaur (Ed.), Gold: Progress in the Chemistry, Biochemistry and Technology, J. Wiley & Sons, Chichester, 1999, p. 237.

[10] (a) R.G. Griffin, J.D. Ellett Jr., M. Mehring, J.G. Bullitt, J.S. Waugh, J. Chem. Phys. 57 (1972) 2147;
(b) A.E. Blakeslee, J.L. Hoard, J. Am. Chem. Soc. 78 (1956) 3029.

[11] (a) N.C. Baenziger, W.E. Bennet, D.M. Soboroff, Acta Crystallogr. B 32 (1976) 962;
(b) K. Angermaier, E. Zeller, H. Schmidbaur, J. Organomet. Chem. 472 (1994) 371;
(c) A.K. Al-Sa'ady, C.A. McAuliffe, R.V. Parish, J.A. Sandbank, Inorg. Synth. 23 (1985) 191;
(d) H. Schmidbaur, B. Brachthäuser, S. Gamper, A. Schier, O. Steigelmann, Z. Naturforsch. 47b (1992) 1725.