Gold(I) and Silver(I) Complexes with Methanide Ligands $[C\{PPh_2(X)\}_3]^-$ (X = O, S). Crystal Structures of $[M\{C(PPh_2(X))_3\}(PPh_3)]$ (M = Au, X = O; M = Ag, X = S)

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Metal complexes $[M(acac)(PPh_3)]$ act as deprotonating agents in the reaction with equimolar amounts of $[CH\{PPh_2(X)\}_3]$ to give the neutral complexes $[M\{C(PPh_2(X))_3\}(PPh_3)]$ [M = Ag, X = O (**1**) or S (**2**); M = Au; X = O (**3**) or S (**4**)]. The crystal structures of **2** and **3** have been established by X-ray crystallography. In the structure of **2** (two independent molecules) the silver(I) atoms display a distorted tetrahedral coordination by phosphorus (of PPh_3) and three sulfur atoms. In complex **3** the gold(I) atom exhibits linear coordination by phosphorus of PPh_3 and the carbon atom of $[C\{PPh_2(O)\}_3]^-$. The reaction of $[CH\{PPh_2(X)\}_3]$ with $[Ag(CF_3SO_3)]$ or $[Ag(CF_3SO_3)(PPh_3)]$ (molar ratio 1:1) leads to $[Ag(CF_3SO_3)\{CH(PPh_2(X))_3\}]$ [X = O (**5**), S (**6**)] or $[Ag\{CH(PPh_2(S))_3\}(PPh_3)](CF_3SO_3)$ (**7**), respectively.

Tris(diphenylthiophosphanoyl)methanide, $[C\{PPh_2(S)\}_3]^-$, has proved to be a versatile ligand in coordination chemistry[1-7]. Usually, it acts as a bi-[1-3] or tridentate[4-7] chelating ligand, bonding to one metal atom through two or three sulfur atoms. Very few examples of gold or silver complexes with this ligand have been reported; these were $[Au\{C(PPh_2(S))_3\}(PPh_2Bu)]$[3] and $[Ag\{C(PPh_2(S))_3\}(PBu_3)]$[6] where the trithiophosphane acted as a bi- or tridentate ligand, respectively. However the anion tris(diphenylphosphanoyl)methanide, $[C\{PPh_2(O)\}_3]^-$, has been studied far less[8-10] and no gold or silver derivatives have been described.

Here we describe the preparation of gold(I) and silver(I) complexes with these ligands. The structures of $[Ag\{C(PPh_2(S))_3\}(PPh_3)]$ and $[Au\{C(PPh_2(O))_3\}(PPh_3)]$ have been established by single-crystal X-ray analysis; the methanide ligand in the silver derivative is bonded through the three sulfur atoms, but in the gold derivative through the methanide carbon, an unprecedented coordination type for tris(phosphanoyl)methanide or its derivatives.

Synthesis and Properties of the Complexes

The use of acetylacetonato (acac) complexes, such as $[M(acac)(PPh_3)]$ (M = Au, Ag), has been previously reported in the synthesis of ylide or methanide complexes of gold[11,12] or silver[13]. They are excellent precursors for abstracting protons from CH or CH_2 groups and forming new C–M(PPh_3) bonds. Thus, $[CH\{PPh_2(X)\}_3]$ (X = O, S) reacts with one equivalent of $[M(acac)(PPh_3)]$ with deprotonation of the CH group of the triphosphane and formation of the neutral complexes $[M\{C(PPh_2(X))_3\}(PPh_3)]$ (equation 1).

$$[CH\{PPh_2(X)\}_3] + [M(acac)(PPh_3)] \rightarrow [M\{C(PPh_2(X))_3\}(PPh_3)] + acacH \quad (1)$$

M = Ag; X = O (**1**), S (**2**)
M = Au; X = O (**3**), S (**4**)

Complexes **1**–**4** are colourless, air-stable solids. Their acetone solutions are non-conducting. In the IR spectra, the methanide group gives rise to a strong absorption at $\tilde{\nu} = 920\ cm^{-1}$, assignable to the CP_3 system when not coordinated through the carbon atom[9,14]. This band appears at $\tilde{\nu} = 951$ or $911\ cm^{-1}$ for complexes **1** or **2**, respectively, and as a double band at $\tilde{\nu} = 922$ and $910\ cm^{-1}$ for complex **4**, but is absent in **3**. This indicates bonding through the chalcogen atoms of the anionic ligand in complexes **1**, **2**, and **4**, but through the carbon atom in **3**. We propose a tetra-coordinated structure for **1** and **2** (Scheme 1, a) and a linear coordination for **3** (Scheme 1, c). This was confirmed by X-ray analysis for complexes **2** and **3** (see below). In complex **4** tetra-coordination is possible but tri-coordination (Scheme 1, b) more probable, as was found in $[Au\{C(PPh_2(S))_3\}(PPh_2Bu)]$[3]. The ν(P=O) band appears at $\tilde{\nu} = 1170\ cm^{-1}$ (s, br) in **3**, near to the neutral free ligand frequency $[CH\{PPh_2(O)\}_3]$ ($\tilde{\nu} = 1183, 1189\ cm^{-1}$)[9], but it shifts to lower energies in the silver derivative (**1**) [$\tilde{\nu} = 1127$ (s, br) and 1096 (s, br) cm^{-1}]. It is more difficult to assign the ν(P=S) vibrations because they are weaker than ν(P=O) and appear in the same region as other phosphane or phenyl bands ($\tilde{\nu} = 500-600\ cm^{-1}$). The positive-ion fast-atom bombardment (FAB) mass spectra show the molecular cation/ion peak (M^+) at *m/z* (%): 985 (75) (**1**) 1123 (9) (**4**) or $[M + H]^+$ at *m/z*: 1035 (22) (**2**) and 1075 (50) (**3**). Other peaks appear at *m/z* (%): 725 (72) (**1**) and 771 (17) (**2**) $[Ag\{C(PPh_2(X))_3\}]^+$, 861 (10) (**4**) $[Au\{C(PPh_2(X))_3\}]^+$,

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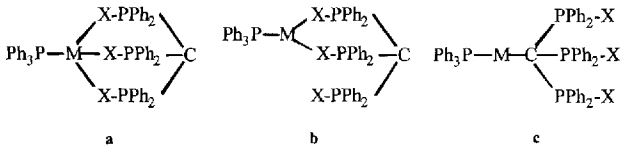
632 (48) (**1**); (100) (**2**) $[Ag(PPh_3)_2]^+$ and 459 (100) (**3**) (100) (**4**) $[Au(PPh_3)]^+$.

Scheme 1



The $^{31}P-\{^1H\}$ NMR spectra (Table 1) show a singlet for the phosphorus atom of the triphosphane, except for complex **3**, which shows a doublet because of coupling with triphenylphosphane. The signal of the phosphorus atom of PPh_3 appear as two doublets in the silver complexes **1** and **2** because of coupling with both ^{107}Ag and ^{109}Ag nuclei, as a quadruplet in complex **3** and as a singlet in **4**.

Table 1. $^{31}P\{^1H\}$- and ^1H-NMR data for the complexes[a]

Complexes	δ(P-X) [J(PP)]	δ(PPh3) [J(PAg)]	δ(C-H) [J(PH)]
1 [Ag{C(PPh2(O))3}(PPh3)]	36.4 (s)	15.2 (dd) [797.2, 691.6]	
2 [Ag{C(PPh2(S))3}(PPh3)][b]	43.8 (s)	9.1 (dd) [519.2, 451.2]	
3 [Au{C(PPh2(O))3}(PPh3)]	34.5 (d) [13.7]	35.3 (q)	
4 [Au{C(PPh2(S))3}(PPh3)]	43.6 (s)	37.5 (s)	
5 [Ag(CF3SO3){CH(PPh2(O))3}]	32.7 (s)		5.5 (q) [8.8]
6 [Ag(CF3SO3){CH(PPh2(S))3}]	44.9 (s)		5.9 (q) [11.4]
7 [Ag{CH(PPh2S)3}(PPh3)](CF3SO3)[b]	43.2 (d) [8.2]	13.6 (ddq) [587.7, 509.0]	6.0 (q) [11.2]

[a] In $CDCl_3$; s = singlet, d = doublet, dd = two doublets, ddq = two doublets of quadruplets, q = quadruplet; coupling constants (Hz) are shown in brackets. – [b] In $[D_6]$acetone.

The neutral ligand $[CH\{PPh_2(X)\}_3]$ reacts with $[Ag(CF_3SO_3)]$ in dichloromethane to give the complexes $[Ag(CF_3SO_3)\{CH(PPh_2(X))_3\}]$ (Equation 2). In a similar way, the reaction of $[CH\{PPh_2(S)\}_3]$ with $[Ag(CF_3SO_3)(PPh_3)]$ leads to the displacement of the triflate anion and formation of the cationic complex $[Ag\{CH(PPh_2(S))_3\}(PPh_3)](CF_3SO_3)$ (**7**). However, the reaction of $[CH\{PPh_2(O)\}_3]$ with $[Ag(CF_3SO_3)(PPh_3)]$ gives a complex mixture of complex **5** and other unidentified products.

$$[CH\{PPh_2(X)\}_3] + [Ag(CF_3SO_3)] \rightarrow [Ag(CF_3SO_3)\{CH(PPh_2(X))_3\}] \quad (2)$$

X = O (**5**), S (**6**)

Complexes **5**–**7** were obtained as air- and moisture-stable white solids at room temperature. Their acetone solutions behave as 1:1 electrolytes. The IR spectra show strong bands from the triflate group at $\tilde{\nu}$ = 1280, 1260, 1160, 1030 and 637 cm^{-1}[15]. The ν(P=O) band appears at $\tilde{\nu}$ = 1115 cm^{-1} (s) in complex **5**. No band is observed in the region $\tilde{\nu}$ = 960–910 cm^{-1} for the complexes **5**–**7**, which confirms the presence of the neutral ligand, $[CH\{PPh_2(X)\}_3]$, and not the methanide. The positive-ion fast-atom bombardment (FAB) mass spectra show the peaks corresponding to $[M - CF_3SO_3]^+$ at *m/z* (%): 723 (87) (**5**), 773 (68) (**6**) and 1035 (36) (**7**).

The $^{31}P-\{^1H\}$ NMR spectra (Table 1) show a singlet for the phosphorus atom of the triphosphane in complexes **5** and **6**. This signal is a doublet in **7**, because of coupling with triphenylphosphane, and the latter gives rise to two doublets of quadruplets, because of the coupling with both ^{107}Ag and ^{109}Ag nuclei. The ^1H-NMR signal of the CH group appears as a quadruplet.

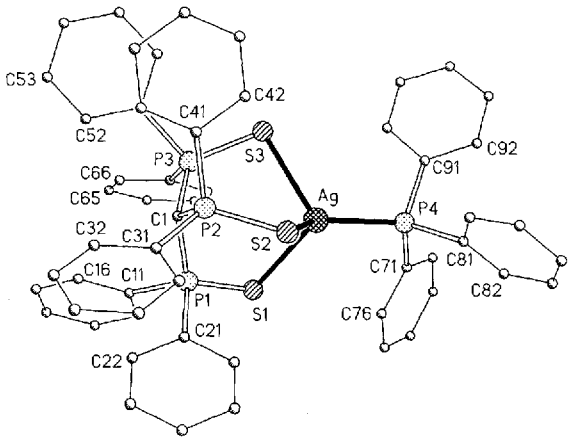
Crystal Structure Determinations

The asymmetric unit of complex **2** contains two independent molecules (**A** and **B**) and one molecule of dichloromethane. The molecular structure of **A** is shown in Figure 1. In both molecules the silver(I) atoms display a distorted tetrahedral geometry, being bonded to three sulfur and one phosphorus (of PPh_3) atoms. The angles S(2)–Ag–S(3) 99.11(4)° and P(4)–Ag–S(2) 127.00(4)° in **A** and S(3′)–Ag′–S(2′) 99.73(4)° and P(4′)–Ag′–S(3′) 128.07(4)° in **B** represent the major deviations from ideal geometry. The distances S–Ag lie in the range 2.5867(14)–2.6679(14) Å and are similar to those found in related tetracoordinated compounds such as $[Ag\{C(PPh_2(S))_3\}(PBu_3)]$[7] [2.639(3), 2.585(2), and 2.670(2) Å] and $[Ag\{(PPh_2)_2C_2B_{10}H_{10}\}\{(SPPh_2)_2CH_2\}]ClO_4$[16] [2.504(2) and 2.588(2) Å]. The P–S distances [1.991(2)–2.008(2) Å] are similar to those found in $[Ag\{C(PPh_2(S))_3\}(PBu_3)]$[7] [1.990(3), 1.999(3), and 1.991(3) Å] and $[Au\{C(PPh_2(S))_3\}(PPh_2Bu)]$[3] [2.051(6), 1.982(5), and 1.993(5) Å] and are longer than in uncoordinated $CH\{PPh_2(S)\}_3$ (P–S ca. 1.94 Å)[17]; lengthening of the P–S bond is expected upon coordination and, additionally, any residual negative charge may be delocalised into this bond. The P–C bond lengths [1.761(4)–1.789(4) Å] are shorter than in the free ligand[17] because of the change of hybridisation of the methanide carbon atom from sp^3 to sp^2. The distances P–Ag [2.4253(13) (**A**) and 2.4027(13) Å (**B**)] are shorter than those found in other silver complexes such as $[Ag(PPh_3)_4]ClO_4$[18] [1 × 2.650(2), 3 × 2.668(5) Å] but are similar to those in the related complex $[Ag\{C(PPh_2(S))_3\}(PBu_3)]$[7] [2.404(3) Å] with four-coordinate silver(I) or $[Ag(dppf)(PPh_3)]ClO_4$[19] [dppf = 1,1′-bis(diphenylphosphano)ferrocene] [2.4386(13)–2.4870(12) Å] where the silver(I) atoms are three-coordinated. The angles around the methanide carbon atom, 114.4(2)–117.3(2)°, are slightly narrower than the ideal value for sp^2 hybridisation.

The structure of complex **3** is shown in Figure 2. The gold atom exhibits linear geometry, C(1)–Au–P(4) 177.64(2)°, with a normal distance Au–P(4) [2.2567(14) Å]; the distance Au–C(1), 2.169(5) Å, is slightly longer than in other methanide complexes, e.g. $[(acac)Au\{CH(Ph_2PAuPPh_2)_2CH\}Au(acac)]$[20] [2.12(2) Å] and $[(Ph_3PAu)_2C(Ph_2PAuPPh_2)_2C(AuPPh_3)_2](ClO_4)_2$[21] [2.104(10), 2.112(10) Å], although the difference may not be significant. The P–C(1) bond lengths lie in the range 1.807(5)–1.838(5) Å. The angles around the central methanide carbon atom, 101.1(2)–115.9(2)°, are distorted from

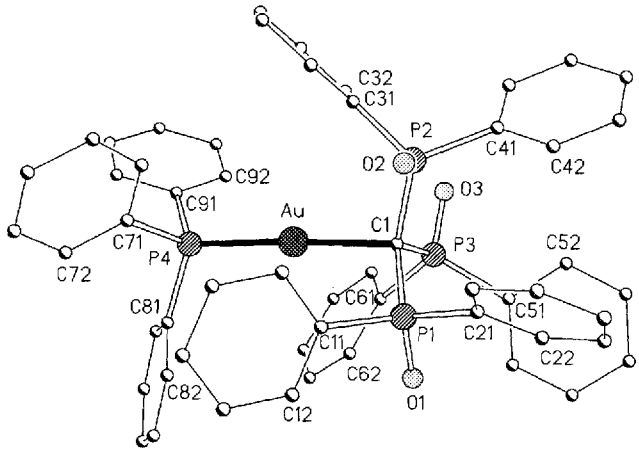
the ideal sp^3 value, probably because of steric effects in the ligand. The bond lengths P–O [1.492(3)–1.497(4) Å] correspond to normal double bonds[22].

Figure 1. Structure of one of the two independent molecules (molecule **A**) of complex **2** in the crystal; radii are arbitrary; H atoms are omitted for clarity[a]



[a] Selected bond lengths [Å] and angles [°]: Ag–S(1) 2.6679(14), Ag–S(2) 2.5943(13), Ag–S(3) 2.6453(13), Ag–P(4) 2.4253(13), S(1)–P(1) 1.993(2), S(2)–P(2) 2.008(2), S(3)–P(3) 1.996(2), P(1)–C(1) 1.789(4), P(2)–C(1) 1.761(4), P(3)–C(1) 1.777(4); P(4)–Ag–S(1) 111.66(4), P(4)–Ag–S(2) 127.00(4), P(4)–Ag–S(3) 114.18(4), S(1)–Ag–S(2) 101.04(4), S(1)–Ag–S(3) 99.89(4), S(2)–Ag–S(3) 99.11(4).

Figure 2. Molecule of complex **3** in the crystal; radii are arbitrary; H atoms are omitted for clarity[a]



[a] Selected bond lengths [Å] and angles [°]: Au–P(4) 2.2567(14), Au–C(1) 2.169(5), C(1)–P(1) 1.807(5), C(1)–P(2) 1.836(5), C(1)–P(3) 1.838(5), P(1)–O(1) 1.492(3), P(2)–O(2) 1.494(4), P(3)–O(3) 1.497(4); P(4)–Au–C(1) 177.64(13), Au–C(1)–P(1) 103.5(2), Au–C(1)–P(2) 104.2(2), Au–C(1)–P(3) 101.1(2), P(1)–C(1)–P(2) 115.3(3), P(1)–C(1)–P(3) 115.9(2), P(2)–C(1)–P(3) 114.2(3).

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Experimental

IR: Range $\tilde{\nu}$ = 4000–200 cm^{-1}, Perkin-Elmer 883, Nujol mulls between polyethylene sheets. – Conductivities: ca. $5 \cdot 10^{-4}$ mol dm^{-3} solutions, Jenway 4010 digital conductimeter, Λ in Ω^{-1} cm^2 mol^{-1}. – C, H and N analyses: Perkin-Elmer 240C microanalyzer. – NMR: Bruker ARX-300 and Varian XL300 Unity spectrometers in $CDCl_3$ or [D_6]acctone; chemical shifts are cited relative to $SiMe_4$ (external, ^1H), 85% H_3PO_4 (external, ^{31}P). – All the reactions were carried out at room temperature; solvents were purified by standard methods and distilled under nitrogen prior to use. – [Ag(acac)-(PPh_3)][23], [Au(acac)(PPh_3)][23], [CH{PPh_2(O)}$_3$][9] and [CH{PPh_2-(S)}$_3$][24] were prepared according to published procedures, [Ag(CF_3SO_3)(PPh_3)] in a similar manner to [Ag($OClO_3$)(PPh_3)][25].

[M{C(PPh$_2$(X))$_3$}(PPh$_3$)] [M = Ag, X = O (**1**), S (**2**); M = Au, X = O (**3**), S (**4**)]: To a solution of [CH{PPh_2(X)}$_3$] [0.5 mmol, X = O (0.308 g), S (0.332 g)] in dichloromethane (25 ml) was added [M(acac)(PPh_3)] [0.55 mmol, M = Ag (0.258 g), Au (0.308 g)]. The mixture was stirred in the dark for 1 d and filtered through a 1-cm pad of Celite. Concentration of the solution to ca. 5 ml and addition of hexane (15 ml) gave complexes **1**–**4** as white solids.

1: Yield 0.276 g (56%). – $C_{55}H_{45}AgO_3P_4$ (985.7): calcd. C 67.0, H 4.6; found C 66.8, H 4.5.

2: Yield 0.536 g (94%). – $C_{55}H_{45}AgP_4S_3$ (1033.9): calcd. C 63.8, H 4.4; found C 63.5, H 4.6.

3: Yield 0.425 g (79%). – Λ_M: 2 Ω^{-1} cm^2 mol^{-1}. – $C_{55}H_{45}AuO_3P_4$ (1074.8): calcd. C 61.4, H 4.2; found C 61.0, H 4.2.

4: Yield 0.472 g (84%). – Λ_M: 2 Ω^{-1} cm^2 mol^{-1}. – $C_{55}H_{45}AuP_4S_3$ (1123.0): calcd. C 58.8, H 4.0; found C 58.0, H 4.1.

[Ag(CF$_3$SO$_3$){CH(PPh$_2$(X))$_3$}] [X = O (**5**), S (**6**)]: To a solution of [$AgCF_3SO_3$] (0.128 g, 0.5 mmol) in dichloromethane (25 ml) was added [CH{PPh_2(X)}$_3$] (0.5 mmol, X = O (0.308 g), S (0.332 g)] and the solution stirred in the dark for 1 h. Partial evaporation of the solvent to ca. 5 ml and addition of diethyl ether (15 ml) gave complexes **5** and **6** as white solids.

5: Yield 0.358 g (82%). – Λ_M: 163 Ω^{-1} cm^2 mol^{-1}. – $C_{38}H_{31}AgF_3O_6P_3S$ (873.5): calcd. C 52.2, H 3.6; found C 51.8, H 3.7.

6: Yield 0.415 g (90%). – Λ_M: 146 Ω^{-1} cm^2 mol^{-1}. – $C_{38}H_{31}AgF_3O_3P_3S_4$ (921.7): calcd. C 49.5, H 3.4; found C 49.3, H 3.1.

[Ag{CH(PPh$_2$(S))$_3$}(PPh$_3$)](CF$_3$SO$_3$) (**7**): To a dichloromethane solution (25 ml) of [Ag(CF_3SO_3)(PPh_3)] (0.259 g, 0.5 mmol) was added [CH{PPh_2(S)}$_3$] (0.332 g, 0.5 mmol). The reaction mixture was stirred in the dark for 1 h, concentrated to ca. 5 ml, and addition of diethyl ether (15 ml) led to complex **7** as a white solid. – Yield 0.538 g (91%). – Λ_M: 115 Ω^{-1} cm^2 mol^{-1}. – $C_{56}H_{46}AgF_3O_3P_4S_4$ (1183.9): calcd. 56.8, H 3.9; found C 56.8, H 4.0.

Crystal Structure Determination of Complex **2**: Crystals were grown from dichloromethane/hexane. – Crystal data: **2** · 1/2 CH_2Cl_2, $C_{55.5}H_{46}AgClP_4S_3$, M = 1076.30, triclinic, $P\bar{1}$, a = 14.367(2), b = 18.801(4), c = 19.691(3) Å, α = 76.137(12), β = 75.562(10), γ = 88.386(14)°, V = 4998(2) Å^3, Z = 4, D_c = 1.430 Mg m^{-3}, $F(000)$ = 2204, μ = 0.748 mm^{-1}, T = –100 °C. – Data collection and reduction: A colourless prism ca. 0.60 × 0.25 × 0.20 mm was mounted in inert oil on a glass fibre. A total of 15798 intensities were registered using monochromated Mo-K_α radiation (λ = 0.71073 Å, $2\Theta_{max}$ = 48°) on a Siemens P4 diffractometer; 15425 unique reflections (R_{int} = 0.0375) were used for all calculations. Cell constants were refined from setting angles of 53 reflections in the range 2Θ = 5–23°. An absorption correction based on Ψ scans was applied, with transition factors 0.77–0.90. – Structure solution and refinement: The structure was solved by Patterson analysis and refined anisotropically on F^2 using the program SHELXL-93[26]. H atoms were included using a riding model. The final $wR(F^2)$ was 0.102 for all reflections, with a conventional $R(F)$ of 0.0431, for 1162 parameters and 1014 restraints (light atom displacement parameters and ring planarity). S = 0.88; max. $\Delta\rho$ =

1.68 eÅ^{-3}. All significant residual electron density is in the solvent region.

Crystal Structure Determination of Complex **3**: Crystals of **3** were grown from dichloromethane/hexane. – Crystal data: $C_{55}H_{45}AuO_3P_4$, M = 1074.76, triclinic, $P\bar{1}$, a = 12.010(3), b = 12.330(2), c = 17.084(4) Å, α = 81.32(2), β = 89.67(2), γ = 71.02(2)°, V = 2362.4(9) Å^3, Z = 2, D_c = 1.511 Mg m^{-3}, $F(000)$ = 1076, μ = 3.29 mm^{-1}, T = −100°C. – Data collection and reduction: As above, with following differences. Colourless plate ca. 0.45 × 0.45 × 0.08 mm, 8892 intensities ($2\Theta_{max}$ = 50°), Siemens R3 diffractometer; 8005 reflections unique (R_{int} = 0.039). Cell constants from setting angles of 62 reflections in the range 2Θ = 6.8–25°. Transmission factors 0.46–0.91. – Structure solution and refinement: As above, with following differences. Final $wR(F^2)$ 0.080, conventional $R(F)$ 0.033 for 568 parameters and 522 restraints. S = 0.961; max. $\Delta\rho$ = 1.2 eÅ^{-3}.

Further details of the structure determinations have been deposited at the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany. Any request for this material should quote a full literature citation and the reference numbers CSD-404568 (**2**) and -404569 (**3**).

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