Inorganica Chimica Acta, *190* (1991) 71–77

Silver(I) complexes with aryldithiocarboxylates and triphenylphosphine. Crystal and molecular structure of the dinuclear complex $[\{Ag(S_2C\text{-}p\text{-tolyl})PPh_3\}_2]$ and NMR investigation of the mononuclear compounds $[Ag(S_2CAr)(PPh_3)_2]$ in solution

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(Received May 31, 1991)

Abstract

^{1}H, ^{13}C, ^{31}P NMR spectra are reported for the complexes $[Ag(S_2CAr)(PPh_3)_2]$ (Ar = phenyl, *o*-tolyl, *p*-tolyl). In solution at room temperature these species are partially dissociated and the phosphine undergoes fast exchange. ^{31}P NMR parameters were obtained from low temperature spectra, ^{13}C and ^{1}H data from room temperature spectra. Overall examination of the spectra shows that no stable species with more than two triphenylphosphine molecules coordinated to one silver atom is detectable, that in phenyl and *p*-tolyl derivatives the dithiocarboxylato group prefers to be coplanar with the aromatic ring also in solution and that in the Ag–S_2CAr bonding the covalent character is rather poor. The monophosphine derivatives $[\{Ag(S_2CAr)PPh_3\}_2]$ (Ar = *o*-tolyl, *p*-tolyl) present incongruent solubility. For the complex with Ar = *p*-tolyl X-ray diffraction methods show an unusual molecular structure, consisting of centrosymmetric species $[\{Ag(CS_2\text{-}p\text{-tolyl})PPh_3\}_2]$, in which the dithioarylate ligand is tridentate; while S(1) bridges two metal centres (2.631(2) and 2.692(3) Å), S(2) is only bonded to one silver atom (2.657(2) Å). Phosphorus atoms from triphenylphosphine (Ag–P = 2.392(2) Å) complete the distorted tetrahedral arrangement of the silver atoms. The crystals are triclinic, space group $P\bar{1}$, with $a = 11.744(3)$, $b = 10.862(2)$, $c = 9.831(2)$ Å, $\alpha = 106.90(2)$, $\beta = 96.51(2)$, $\gamma = 74.54(2)°$ and $Z = 1$. A total of 3206 symmetry independent reflections above background was measured at room temperature and the structure, solved by Patterson and Fourier methods, was refined by full matrix least-squares to $R = 0.050$.

Introduction

The great majority of triarylphosphino silver(I) complexes have formulas $[AgX(PAr_3)_n]_m$ ($n = 1$–4, the values depending on X). In solution the Ag–P bond is labile [1, 2] and there are equilibria among species with different n**.

For $X = YCS_2^-$ only complexes with $n \leqslant 2$ have been isolated [5–8]. When $n = 2$ the Ag atom reaches a coordination number of four with the CS_2 moiety acting as chelating ligand. Among non-phosphinated complexes ($n = 0$), apart from two dithiocarboxylates of the $[\{Ag(S_2CPEt_3)(\mu\text{-}S_2CPEt_3)\}_2]^{2+}$ dinuclear species [9], no chelating behaviour has been reported so far and the YCS_2^- groups either bridge two or three silver atoms or behave as tetradentate ligands [10, 11].

In a previous paper [5] we described the preparation of complexes of the type $[\{Ag(S_2CAr)PPh_3\}_2]$ (Ar = *o*-T (*o*-tolyl), *p*-T (*p*-tolyl)) and $[Ag(S_2CAr)(PPh_3)_2]$ (Ar = Ph, *o*-T, *p*-T). Here we report further information on the behaviour of the monomeric bis-triphenylphosphino complexes in solution, obtained through ^{1}H, ^{13}C and ^{31}P NMR spectra, and the X-ray structure of the $[\{Ag(S_2C\text{-}p\text{-}T)PPh_3\}_2]$ compound, where the dithioarylate ligand

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**For $X = ClO_4^-$ the enthalpy of dissociation of the Ag–P bond is about 50 kJ/mol in monophosphinated complexes and decreases to 45 kJ/mol when more than one phosphine is bound to the silver atom [3, 4].

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shows an unusual example of bridging–chelating mode.

Experimental

The compounds were prepared as previously reported [5].

X-ray data collection and refinement

A single crystal of the $[\{Ag(S_2C\text{-}p\text{-tolyl})PPh_3\}_2]$ complex*, of approximate dimensions $0.2 \times 0.3 \times 0.4$ mm, was used for the X-ray measurements. Unit cell parameters were determined by least-squares refinement of the θ values of $30(\theta, \chi, \phi)_{hkl}$ reflections randomly distributed in the reciprocal space in the range $11.3° \leqslant \theta \leqslant 17.2°$.

Crystal data. $Ag_2P_2S_4C_{52}H_{44}$, $M = 1074.84$, triclinic, $a = 11.744(3)$, $b = 10.862(2)$, $c = 9.831(2)$ Å, $\alpha = 106.90(2)$, $\beta = 96.51(2)$, $\gamma = 74.54(2)°$, $V = 1155.6(5)$ Å^3, space group $P\bar{1}$, $Z = 1$, $D_c = 1.545$ g cm^{-3}, $F(000) = 1088$, $\mu = 11.16$ cm^{-1}.

The X-ray measurements were performed at room temperature on a Philips PW1100 diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). The systematic data collection was carried out in the θ–2θ step scanning mode using scan width from $[\theta - 0.65]°$ to $[\theta + 0.65\ \Delta\lambda\ \lambda^{-1}\ \mathrm{tg}\ \theta]°$ where $\Delta\lambda$ was $\lambda_{\alpha_1} - \lambda_{\alpha_2}$. The net intensities were obtained from the profiles analysis according to Lehmann and Larsen [12]. A total of 4355 $\pm h$, $\pm k$, $+l$ reflections was measured in the $2° \leqslant \theta \leqslant 25°$ range, 3405 having $I \geqslant 2\sigma(I)$. A total of 3206 unique reflections (the agreement between symmetry equivalent reflections was 5%) was used in the crystal structure refinement. The intensities were corrected for absorption effects using the program ABSORB [13]: maximum and minimum values for the absorption coefficients in the polar angles ϕ and μ were 1.38 and 0.83, respectively.

The structure was solved by Patterson and Fourier methods and refined by full matrix least-squares method (353 parameters) using the SHELX package of crystallographic computer programs [14]. Parameters refined were: the overall scale factor, the atomic coordinates and the anisotropic temperature factors for all the atoms with the exception of the H atoms for which isotropic temperature factors were assumed. Eighteen hydrogens were found in the Fourier ΔF map and refined, the remaining four hydrogens were taken in their calculated position with the geometrical constraint C–H = 1.08 Å. The structure refinement converged at $R = 0.050$, $R_w = 0.050$ (unit weights). The maximum height of the electron density in the final Fourier ΔF map was 0.7 e Å^{-3}. Atomic scattering factors corrected for the anomalous dispersion of Ag, S and P were taken from ref. 15. Final atomic coordinates for the non-hydrogen atoms are given in Table 1.

The calculations were carried out on the GOULD 6040 Powernode of the Centro di Studio per la Strutturistica diffrattometrica del CNR, Parma.

NMR spectra

NMR spectra were recorded with a Bruker WP 80 spectrometer, equipped with an Aspect 2000 computer. For ^{1}H spectra the samples were either $CDCl_3$ or C_6D_6 solutions of the compounds in 5 mm tubes, TMS was used as internal standard, spectral width was 1000 Hz, digital resolution 0.125 Hz/pt, flip angle 30°; for integration a flip angle of 90° and 15 s interval between pulses were used. For $\{^1H\}^{13}C$ spectra the samples were $CDCl_3$ solutions in 10 mm tubes, TMS was used as internal standard, spectral width was 6000 Hz, digital resolution 0.75 Hz/pt, flip angle 30°; broad band decoupling; assignment of quaternary carbons was confirmed through the

TABLE 1. Fractional atomic coordinates ($\times 10^4$) with e.s.d.s in parentheses

Atom	*x/a*	*y/b*	*z/c*
Ag	3930(1)	133(1)	1336(1)
S1	6201(1)	−974(2)	1010(2)
S2	4367(2)	−2421(2)	−83(2)
P1	2670(1)	1259(2)	3300(2)
C1	5793(5)	−2398(6)	133(6)
C2	6725(5)	−3630(5)	−439(6)
C3	7900(6)	−3589(7)	−451(7)
C4	8726(7)	−4697(8)	−1105(7)
C5	8450(7)	−5897(7)	−1734(7)
C6	7301(7)	−5956(7)	−1668(7)
C7	6452(6)	−4850(6)	−1040(7)
C8	9356(11)	−7088(11)	−2516(12)
C9	1150(5)	1952(6)	2786(6)
C10	413(6)	3033(7)	3658(8)
C11	−719(6)	3565(8)	3200(9)
C12	−1132(7)	3007(9)	1873(10)
C13	−420(7)	1941(9)	1006(9)
C14	715(7)	1412(7)	1459(8)
C15	3094(5)	2668(5)	4570(6)
C16	3314(6)	2786(7)	6014(7)
C17	3686(6)	3863(7)	6884(7)
C18	3810(6)	4852(7)	6354(7)
C19	3577(6)	4753(7)	4928(7)
C20	3231(5)	3671(6)	4044(6)
C21	2597(5)	178(5)	4377(6)
C22	3588(6)	−813(7)	4497(8)
C23	3618(7)	−1586(7)	5386(9)
C24	2661(7)	−1398(7)	6158(8)
C25	1657(7)	−442(8)	6027(8)

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*The m.p. of this complex is 186–188 °C and not 201–202 °C as erroneously reported [5].

Bruker QUATD.AU pulse sequence. For ^{31}P spectra the samples were CD_2Cl_2 solutions in 10 mm tubes, the shifts were referred to the resonance frequency of triphenylphosphine in CD_2Cl_2 at the same temperature, spectral width was 6000 Hz, digital resolution 1.5 Hz/pt, flip angle 30°; broad band ^{1}H decoupling. At low temperatures the quantity of phosphine originating the signals was monitored by comparison with the integrated signal of a known amount of triphenylphosphinoxide.

Results and discussion

[{Ag(S$_2$CAr)PPh$_3$}$_2$] (Ar = o-T, p-T)

These complexes are unstable in $CDCl_3$ and CD_2Cl_2 solutions. Attempts to dissolve these brown-greenish dinuclear substances at room temperature gave also important quantities of bis-phosphino derivatives and of the almost insoluble [{AgS$_2$CAr}$_n$] compounds. Below −70 °C the main species present in the CD_2Cl_2 solutions are the [Ag(S$_2$CAr)(PPh$_3$)$_2$] complexes, although, for the *o*-tolyl derivative the ^{31}P NMR spectra at −90 °C reveal also the signals of other phosphinated silver compounds.

The X-ray structure shows that in the solid state the [{Ag(S$_2$C-*p*-T)PPh$_3$}$_2$] is a centrosymmetric dimeric species, in which two dithio-*p*-toluato groups bridge two silver atoms (Fig. 1); while S(1) is bonded to both silver atoms (Ag–S(1) = 2.631(2), Ag^{i}–S(1) = 2.692(3) Å) to form a planar Ag–S(1)–Ag^{i}–S(1^{i}) four-membered ring, S(2) is bonded to only one metal (Ag–S(2) = 2.657(2) Å). Thus the dithio-*p*-toluate is tridentate, acting in both bridging and chelating modes. Each triphenylphosphine completes the distorted tetrahedral arrangement around the silver atoms (Ag–P = 2.392(2) Å). The Ag–Ag^{i} intramolecular separation is 3.738(2) Å. Selected bond distances and angles are given in Table 2.

The above bonding mode is unusual for dithioarylato ligands in coinage metal derivatives. In the structures of silver(I) [10, 11] and copper(I) dithioarylates [11, 16, 17] triply bridging $ArCS_2^-$ ligands join the metal atoms in tetranuclear complexes or tetradentate dithioarylato anions connect them in polymeric chains, each sulfur atom of the ligand coordinating two metal centres. Bidentate bridging behaviour of the $ArCS_2^-$ group was found in the square-planar anionic Ag(I) complex [Ag$_4${2,4,6-(CH$_3$)$_3$C$_6$H$_2$CS$_2$}$_6$]$^{2-}$ [10] and in the unique structure reported for Au(I) dithioarylates [18]. However examples of bridging–chelating mode are found, for the $ArCS_3$ groups, in perthioarylato complexes of Group 11 elements. In these compounds the terminal perthio sulfur atom of the chelating anions bridges also an adjacent metal atom, giving rise usually to tetrameric units [5, 11, 19] and to dimeric complexes, when, owing to introduction of additional L (L = py) [11, 20] or LL (LL = bipy or phen) [21] ligands, the degree of association of the starting perthiocarboxylates is reduced.

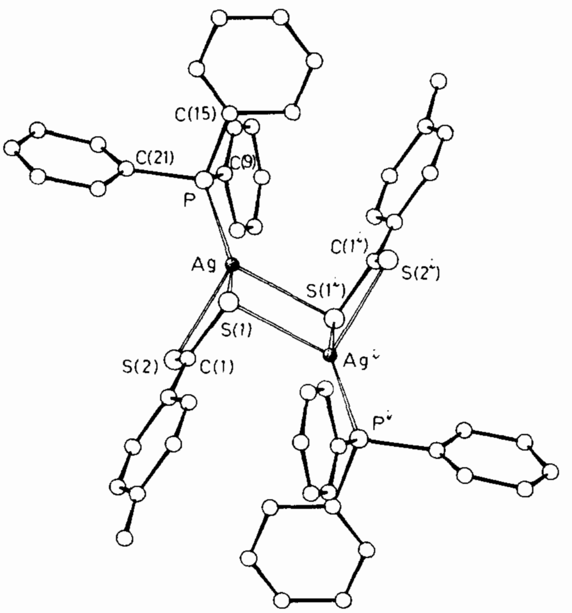

Fig. 1. Perspective view of the complex [{Ag(S$_2$C-*p*-T)PPh$_3$}$_2$], with the atomic numbering scheme.

TABLE 2. Relevant bond distances (Å) and angles (°) in [{Ag(S$_2$C-*p*-tolyl)PPh$_3$}$_2$]

In the coordination polyhedron of Ag			
Ag–S(1)	2.631(2)	Ag–S(1^{i})	2.692(3)
Ag–S(2)	2.657(2)	Ag–P	2.392(2)
S(1)–Ag–S(2)	67.2(1)	S(1)–Ag–S(1^{i})	90.8(1)
S(1)–Ag–P	136.2(1)	S(2)–Ag–S(1^{i})	94.3(1)
S(2)–Ag–P	127.6(1)	P–Ag–S(1^{i})	123.6(1)
In the organic ligands			
C(1)–S(1)	1.700(7)	C(4)–C(5)	1.378(11)
C(1)–S(2)	1.670(7)	C(5)–C(6)	1.378(12)
C(1)–C(2)	1.492(7)	C(6)–C(7)	1.374(9)
C(2)–C(3)	1.394(10)	C(7)–C(2)	1.392(9)
C(3)–C(4)	1.368(9)	C(5)–C(8)	1.507(12)
P–C(9)	1.819(6)	P–C(21)	1.818(7)
P–C(15)	1.818(6)		
S(1)–C(1)–C(2)	119.2(5)	Ag–S(2)–C(1)	86.0(2)
S(2)–C(1)–C(2)	120.3(5)	Ag–S(1)–C(1)	86.3(2)
S(1)–C(1)–S(2)	120.5(4)	Ag–S(1)–Ag^{i}	89.2(1)
Ag–P–C(9)	114.0(2)	C(1)–S(1)–Ag^{i}	94.4(2)
Ag–P–C(15)	115.9(2)	C(15)–P–C(21)	104.0(3)
Ag–P–C(21)	112.3(3)	C(9)–P–C(15)	103.4(3)
C(9)–P–C(21)	106.1(3)		

Symmetry codes: i = 1 − *x*, −*y*, −*z*.

As evidenced by the restricted bite angle of the dithioarylato ligand (S(1)–Ag–S(2) = 67.2(1)°) and by the P–Ag–S bond angles involving the bulky PPh_3 ligand and ranging from 123.6(1)–136.2(1)°, the coordination around the silver atom is far from tetrahedral. The Ag–P distance (2.392(2) Å) is near the lower limit of the range 2.363–2.529 Å found for Ag–PPh_3 bonds [22]. The Ag–S bond lengths in the chelating ring (2.631(2) and 2.657(2) Å) are comparable with those (2.601(4)–2.686(4) Å) found in the monomeric $[Ag(S_2COEt)(PPh_3)_2]$ complex [7]. Asymmetrical chelation of the CS_2 group to the silver atom was already observed in the few $\overline{\text{Ag–S–C–S}}$ structurally characterized chelate rings [7, 9] where also large differences in the Ag–S distances are present (2.668(2)–2.812(2) Å) [9].

The C–S distances in the dithiocarboxylate (1.700(7) and 1.670(7) Å) agree with delocalization of the π-bonding in the CS_2 group. The whole ligand is not far from planarity, the dihedral angle between CS_2 and the *p*-tolyl ring being 9.4(3)°. The C–S–Ag (86.0(2)–94.4(2)°) and Ag–S(1)–Ag^i (89.2(1)°) bond angles as well as the dihedral angle between the dithioarylate ligand and the Ag–S(1)–Ag^i–S(1^i) ring (85.3(1)°) suggest that, in a crude description of the electronic structure, pure *p* sulfur orbitals can be used. This implies also that the Ag^i atom interacts through S(1) with the π-system of the S(1)–C–(Ar)–S(2) ligand.

The centrosymmetric dimeric species contains an $\overline{\text{Ag–S(2)–C(1)–S(1)–Ag}^{i}\text{–S(2}^{i}\text{)–C(1}^{i}\text{)–S(1}^{i}\text{)}}$ chair shaped ring (with strong Ag–S cross-ring interactions) whose formation seems to be unprecedented for dimeric aryldithiocarboxylato complexes of Group 11 elements. To our knowledge the first example, in dimeric silver complexes, of an eight-membered ring containing two CS_2 fragments and two metal centres is present in the $[\{Ag(S_2CPEt_3)(\mu\text{-}S_2CPEt_3)\}_2]^{2+}$ cationic complex [9]; in this, however, both CS_2 moieties of the ring lie on a plane without Ag–S cross-ring interactions. Eight-membered rings similar to that described in the present paper have been observed in coinage metal complexes with dialkyl dithiophosphates [22, 23]. However, in $[\{AgS_2P(OEt)_2PPh_3\}_2]$ [22] the Ag–S distances of the chelate ring (2.821(2) and 2.810(2) Å) are appreciably longer than the cross-ring Ag–S bonds (2.502(2) Å), while in our compound all the Ag–S distances are similar (2.631(2) and 2.657(2) versus 2.692(3) Å).

Looking at the values (Table 2) of the angles subtended at silver by P and S atoms of a chelate $Ag(S_2C\text{-}p\text{-}T)(PPh_3)$ fragment of the dimeric unit (Fig. 1), the present structure can be visualized as arising from two strong intermolecular Ag–S interactions between two such tricoordinated moieties. The bulky PPh_3 ligands accommodate to minimize the steric hindrance with the planar dithio-*p*-tolyl ligands, the dihedral angles formed by the PAgS(1) plane with the $\overline{\text{Ag–S(1)–C(1)–S(2)}}$ and $\overline{\text{Ag–S(1)–Ag}^{i}\text{–S(1}^{i}\text{)}}$ tetraatomic rings being 126.8(2) and 144.5(1)°, respectively.

$[Ag(S_2CAr)(PPh_3)_2]$ (Ar=Ph, o-T, p-T)

These violet monomeric chelate complexes are stable in CD_2Cl_2 at low temperature. Osmometric measurements and NMR data indicate that at room temperature a partial dissociation of the phosphine occurs and in solution $[Ag(S_2CAr)(PPh_3)_2]$ compounds are in equilibrium with free phosphine and other species with PPh_3/Ag ratios <2; owing to the fast exchange of the phosphine, the observed NMR spectra are the average of various situations.

Phosphine ^{31}P NMR spectra

The ^{31}P parameters obtained at −90 °C are reported in Table 3. The spectra consist of the superposition of the two doublets originated by the coupling with ^{107}Ag and with ^{109}Ag, respectively. In silver(I) complexes with aromatic phosphines ^{1}J(Ag, P) depends heavily on the hybridization of silver and on the electronegativity of the other ligands [2, 24]. Our $^{1}J(^{107}Ag, P)$ values are near that of $[\{AgClP(p\text{-}T)_3\}_2]$ (378 Hz) [2, 24], while for $[Ag(S_2PF_2)\{P(p\text{-}T)_3\}_2]$ $^{1}J(^{107}Ag, P)$ is 410 Hz [2] and for $[Ag(NO_3)\{P(p\text{-}T)_3\}_2]$, both in solution [2] and in the solid state [25], 470 Hz. In our compounds the phosphorus atom is noticeably deshielded with respect to free phosphine. Complexation shifts of the same order of magnitude are reported for [AgX{P(*p*-

TABLE 3. Selected NMR parameters for triphenylphosphine in $[Ag(S_2CAr)(PPh_3)_2]$ complexes

Ar	$^{13}C^b$				$^{31}P^c$
	ipso	*ortho*	*meta*	*para*	
Ph^a	133.4(5) (23)	133.9 (17)	128.7 (9)	129.8	15.7 (355)
p-T	133.2 (23)	133.8 (17)	128.6 (9)	129.8	15.6 (352)
o-T	133.2 (23)	133.9 (17)	128.7 (9)	130.0	16.2 (360)
PPh_3	137.4 (−11)	133.8 (19)	128.5 (7)	128.6	0

[a] Not extrapolated. [b] ^{13}C δ values in ppm from TMS, splitting due to carbon–phosphorus coupling in Hz in parentheses, solvent $CDCl_3$, room temperature. [c] For ^{31}P the complexation shifts are reported (ppm from PPh_3), $^{1}J(^{107}Ag, ^{31}P)$ in Hz in parentheses, solvent CD_2Cl_2, −90 °C.

T)$_3$}$_2$] complexes [2]; they increase with decreasing the electron donating properties of X. In the [Ag(S$_2$CAr)(PPh$_3$)$_2$] complexes ^{31}P is remarkably deshielded with respect to the corresponding copper derivatives [26]; the same effect was observed for triphenylphosphino silver and copper nitrates [27]. The ^1J(Ag, P) and δ_P values show a weak dependence on Ar, those of the *o*-T differing significantly from those of the Ph and *p*-T derivatives. At −70 to 60 °C the two doublets due to the coupling with ^{107}Ag and ^{109}Ag become unresolved and the spectra consist of two broadened resonances, which at −30 to 20 °C collapse into a broad signal; further increase of the temperature causes sharpening of this resonance. Such a behaviour, due to the fast intermolecular exchange of the phosphine, is usual for silver complexes with tertiary aromatic phosphines. However, differently from other silver phosphine complexes [2] even small phosphine excess causes dramatic broadening of the resonance at −90 °C.

Phosphine ^{13}C and ^1H NMR spectra

The room temperature {^{1}H}^{13}C spectra of the phosphine consist of doublets (the splitting of the *p*-C resonance is hardly detectable being about 1 Hz).

As [Ag(S$_2$CAr)(PPh$_3$)$_2$] can be the only Ag species in solution provided excess of triphenylphosphine is present, the ^{13}C parameters (Table 3) were obtained by extrapolating to zero PPh$_3$ excess the linear region of the plot, δ_{obs} versus free PPh$_3$ mole fraction. Here only PPh$_3$ and the bis-phospino complex are present in appreciable amounts and δ_{obs} = X(PPh$_3$ complexed) × δ(PPh$_3$ complexed) + X(PPh$_3$ free) × δ(PPh$_3$ free).

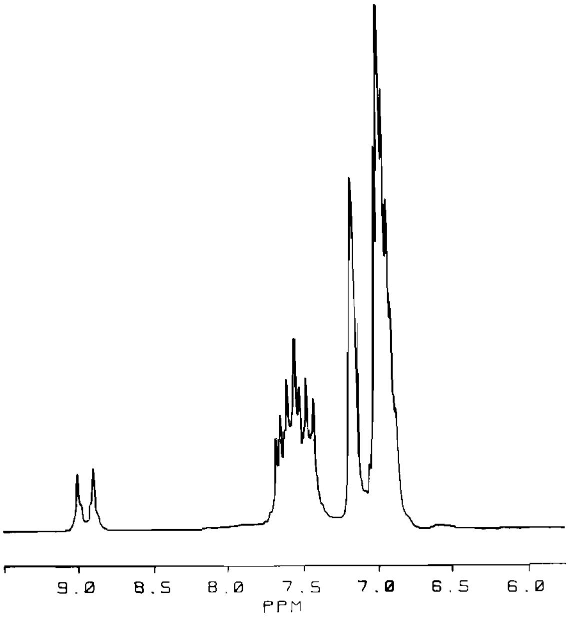

Fig. 2. Spectrum of the aromatic protons of the [Ag(S$_2$C-*p*-T)(PPh$_3$)$_2$] complex in C$_6$D$_6$.

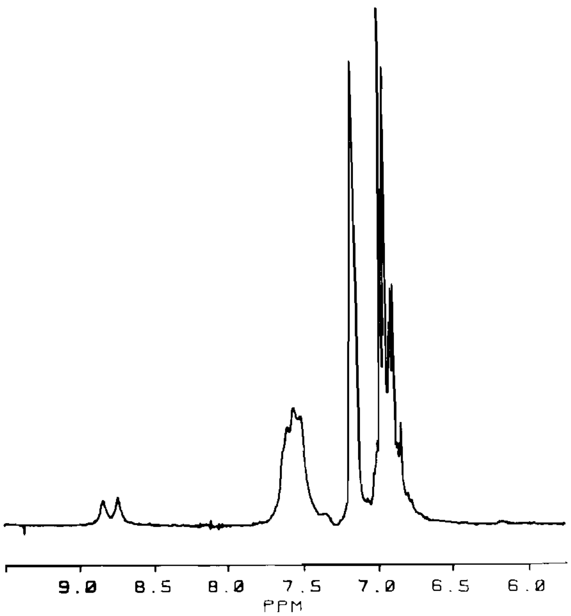

Fig. 3. Spectrum of the aromatic protons of the [Cu(S$_2$C-*p*-T)(PPh$_3$)$_2$] complex in C$_6$D$_6$.

Complexation causes shielding of the *ipso* and deshielding of the *para* carbons and increase of ^1J(P, C); the magnitude of the first two effects indicates that the metal–phosphine interaction is rather moderate. The complexation shift of C *para*, which can be assumed to reflect the electron donation from the phosphine, is close to that observed for the corresponding Cu(I) dppm complexes (dppm = bis(diphenylphosphino)methane) [28].

In CDCl$_3$ the phosphine protons resonate in the 7.05–7.55 ppm range for the [Ag(S$_2$CPh)(PPh$_3$)$_2$] and [Ag(S$_2$C-*p*-T)(PPh$_3$)$_2$] complexes and in the 7.10–7.60 range for the *o*-tolyl derivative (free phosphine 7.25–7.46 ppm). In C$_6$D$_6$ the *ortho* protons resonate in the 7.35–7.70 ppm range for all the three compounds (free phosphine 7.27–7.52 ppm); the *meta* + *para* proton multiplets are in the range 6.80–7.05 ppm for the first two compounds and 6.85–7.10 ppm for the last (free phosphine 6.94–7.10 ppm); i.e. the complexation has a deshielding effect for the *ortho* protons and moves to high fields the *meta* + *para* proton multiplet; homodecoupled spectra confirm that the ^3J(P, H) is larger in complexed (≈10 Hz) than in free phosphine (7.3 Hz). Thus the shift range of the proton spectra show a small but clearly detectable difference between the *o*-tolyl derivative and the other two, the *meta* + *para* proton resonances occurring at lower fields for the former. Apart from this the spectral patterns of the phosphine protons can be considered identical in the three compounds.

Even if the phosphine ^{1}H and ^{13}C parameters of the silver derivatives are close to those of the copper analogues [28, 29], the spectral patterns are different. In the silver complexes the carbon doublets and the well resolved *ortho* proton multiplet (Fig. 2) do not give any evidence for virtual coupling, while in copper complexes the resonances appear as unresolved envelopes (Fig. 3). Only in the former is the exchange fast enough to cancel completely from the room temperature spectrum the effects of the coupling between the nucleus of one phosphine with the phosphorus of the other [30].

Aryldithiocarboxylate ^{13}C and ^{1}H spectra

In the $\{^1H\}^{13}C$ spectra of $[Ag(S_2CAr)(PPh_3)_2]$ complexes only a sharp singlet can be detected for each kind of $ArCS_2$ carbon. Excess PPh_3 does not significantly affect the chemical shifts, reported in Table 4. The deshielding of *para* carbons with respect to the anion (Table 5), which can be assumed to reflect the electron donation from the $ArCS_2^-$ moiety towards the metal, is much lower for our molecules than for the esters, the acids or for the molybdenum(IV) compounds [31], where the CS_2 is involved in strong covalent interaction. Along the series anion, silver, copper, molybdenum derivatives, acids, the shielding of the *ipso* and of the dithiocarboxylato carbons increases (Table 5), the complexation shift of the former with respect to the anion being proportional to that of the *para* carbon. These findings indicate that the covalent character of the $ArCS_2$–metal binding in the silver derivatives is not negligible, even if it is significantly lower than in the copper(I) and much lower than in the molybdenum(IV) derivatives. In our opinion the covalent character, as inferred from the complexation shift of the CS_2 carbon alone [31], is underestimated in the silver complexes, where the contribution of the covalency is small enough to be comparable with those of other factors, likely related to the proximity of the metal.

The aromatic protons in the $[Ag(S_2C\text{-}p\text{-}T)(PPh_3)_2]$ compound approximate an AA'XX' spin system; in $CDCl_3$ both the resonances of the protons *ortho* to CS_2 (δ 8.30 ppm) and of those *meta* to CS_2 ($\delta = 7.07$ ppm) are clearly detectable ($^3J(A,X) + {}^5J(A,X') = 8.2$ Hz), the methyl singlet is at $\delta = 2.34$ ppm; in C_6D_6 the *ortho* and *meta* protons resonances are centered at 8.96 and 6.92 ppm, respectively*, the methyl singlet is at $\delta = 2.01$. In the $[Ag(S_2CPh)(PPh_3)_2]$ molecule the aromatic protons approximate an AA'BXX' spin system (X being the protons *o* to CS_2); in $CDCl_3$ the *o* proton multiplet is centered at 8.32 ppm and the AA'B multiplet is in the range 7.15–7.35 ppm; in C_6D_6 the *ortho* proton multiplet is centered at 8.92 ppm and the AA'B signals are in the range 6.85–7.21 ppm. For the $[Ag(S_2C\text{-}o\text{-}T)(PPh_3)_2]$ derivative in $CDCl_3$ three aromatic protons originate an unresolved multiplet centered at 7.07 ppm, no resonances were detected at δ lower than 7.50 ppm, the methyl singlet is at $\delta = 2.50$ ppm; in C_6D_6 the $ArCS_2$ aromatic protons resonate in the range 6.89–7.20 ppm, being obscured by the *meta* and *para* protons of the phosphine.

Thus, as for the analogous $[\{Cu(S_2CAr)(dppm)\}_2]$ [28] and $[Cu(S_2CAr)(PPh_3)_2]$ [26] complexes a remarkable deshielding of the protons *ortho* to CS_2 is observed in phenyl and *p*-tolyl derivatives, but not in the *o*-tolyl. This indicates that the preferential orientation of the CS_2 group is coplanar with the aromatic ring in the first two compounds, but strongly twisted in the last. In accordance [29] the CS_2 carbon is 7 ppm more deshielded in the *o*-tolyl than in the phenyl and *p*-tolyl derivatives (Table 4). Hence the orientations of the CS_2 groups with respect to the aromatic ring found through X-ray diffraction in other silver(I) and copper(I) aryldithiocarboxylato complexes in the solid state [5, 10, 17, 32, 33] are strongly preferred in solution as well. The conjugation with the aromatic ring differentiates the CS_2 group of phenyl and *p*-tolyl from that of *o*-tolyl derivatives. This perhaps provides the explanation of the small but clearly appreciable differences found in ^{31}P chem-

TABLE 4. Chemical shifts of $ArCS_2$ carbons in $[Ag(S_2CAr)(PPh_3)_2]$ complexes

Ar	Aromatic carbons						CS_2	Me
	C-1	C-2	C-3	C-4	C-5	C-6		
Ph	149.9	126.7	127.1	130.4			251.1	
p-T	146.6	127.7	127.7	140.7			250.6	21.4
o-T	155.0	131.0	126.7^a	130.1^a	125.1^a	125.5^a	258.0	19.8

δ values in ppm from TMS, solvent $CDCl_3$, room temperature. ^{a}Uncertain attribution.

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*The resonances of the *meta* protons are partially obscured by the phosphine and their position was confirmed by decoupling the *ortho* protons.

TABLE 5. ^{13}C complexation shifts (shift of X–shift of $ArCS_2^-$ NEt_4^+)

X	Ar = *p*-T			Ar = Ph			Reference
	CS_2	C-1	C-4	CS_2	C-1	C-4	
$AgS_2CAr(PPh_3)_2$	−1.7	−3.8	2.1	−2.5	−4.1	1.7	this work
$CuS_2CArdppm$	−5.5	−4.9	2.6	−6	−5.6	2.3	28
HS_2CAr	−28	−9.5	5.6	−29	−8.8	3.3	31
$Mo(S_2CAr)_4$	−37	−11.5	5.1	−37	−12.6	4.1	31

Values in ppm, solvent $CDCl_3$, room temperature.

ical shifts, ^1J(Ag, P) values and phosphine proton spectra.

Supplementary material

Anisotropic thermal parameters for the non-hydrogen atoms, fractional atomic coordinates for the hydrogen atoms and observed and calculated structure factors are available from the authors on request.

Acknowledgement

We are grateful to the MURST for financial support of this work.

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