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Neutral and Cationic Complexes Containing η^1 or η^2 $Ph_3P^+CMe_2CS_2^-$ Coordinated to a Palladium, Platinum or Silver Centre

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Abstract

The zwitterionic ligand $Ph_3P^+CMe_2CS_2^-$ forms neutral complexes with Pd(II) or Pt(II) as the metal centre, as well as cationic compounds of stoichiometries MX_2L, $MX_2L(PPh_3)$ (M = Pd, Pt; X = Cl, Br, I, C_6F_5), $[Pd(C_6F_5)L(PEt_3)_2]ClO_4$, $[AgL(PPh_3)]ClO_4$, $[AgL]_x(ClO_4)_x$ and $[AgL_2]ClO_4$. Their structures have been assigned from analytical and spectroscopic (IR and ^1H, ^{19}F and ^{31}P NMR) data.

Introduction

The zwitterionic moieties $R_3P^+CS_2^-$, due to their nucleophilic character have been used as a ligand in the preparation of several types of complexes where the ligand can act as a monodentate or bidentate σ-donor using its sulphur atoms or as a π-donor through a conjugated CS_2-pseudoallylic system [1]. We have recently described the synthesis of several palladium or platinum neutral or cationic perhalophenyl complexes containing $R_3P^+CS_2^-$ moieties, which are acting as monodentate or bidentate chelating ligands [2, 3]. However, although many transition metal complexes containing this type of ligand have been prepared, only a limited number of complexes containing the $R_3P^+CMe_2CS_2^-$ moiety have been described so far [4].

In order to establish the differences in behaviour between the $R_3P^+CS_2^-$ and $R_3P^+CR_2CS_2^-$ ligands we have studied the reactivity of $Ph_3P^+CMe_2CS_2^-$ towards several palladium, platinum or silver compounds.

Experimental

All reactions were routinely carried out at room temperature and under exclusion of light, in solvents purified by standard procedures.

C and H analyses were performed with a Perkin-Elmer 240 B microanalyser. Infrared spectra (4000–200 cm^{-1}) were recorded on a Perkin-Elmer 599 spectrophotometer using Nujol mulls between polyethylene sheets; NMR spectra on a Varian XL 200. Conductivities were measured in 5×10^{-4} mol dm^{-3} acetone solutions with a Philips PW 9509 apparatus.

The complexes $[M(C_6F_5)_2(thf)_2]$ [5] and $[Ag(PPh_3)(ClO_4)]$ [6], and the ligand $S_2CCMe_2PPh_3$ [7] were prepared as described elsewhere.

(a) cis-$[M(C_6F_5)_2(S_2CCMe_2PPh_3)]$ (M = Pd, Pt)

To a yellow solution containing the corresponding complex $[M(C_6F_5)_2(thf)_2]$ (0.25 mmol) in dichloromethane (20 cm^3) was added $S_2CCMe_2PPh_3$ (0.0952 g, 0.25 mmol). After stirring for 2 h, the solvent was evaporated, diethylether (5 cm^3) was added and the orange to red precipitate was filtered off, and washed with Et_2O (2×3 cm^3).

(b) cis-$[M(C_6F_5)_2(SC(S)CMe_2PPh_3)(PPh_3)]$ (M = Pd, Pt)

Triphenylphosphine (0.0525 g, 0.20 mmol) was added to a solution containing *cis*-$[M(C_6F_5)_2(S_2CCMe_2PPh_3)]$ (0.20 mmol) in dichloromethane (25 cm^3). After 15 min stirring, the solution was evaporated to *ca.* 5 cm^3, methanol (10 cm^3) was added and the solution was partially evaporated. The yellow or pink precipitate was filtered off, washed with MeOH (2×3 cm^3) and suction dried. Vacuum drying of compound 4′ gives 4.

(c) $[PdX_2(S_2CCMe_2PPh_3)]_x \cdot xCH_2Cl_2$ (X = Cl, Br)

A solution of $(NR_4)_2[Pd_2X_6]$ (0.30 mmol; X = Cl, R = Et; X = Br, R = Bu) in acetone–dichloromethane (30 cm^3:40 cm^3) was treated with 0.2283 g of $S_2CCMe_2PPh_3$ (0.60 mmol), and an orange precipitate was formed immediately. After 24 h stirring, the solvent mixture was partially evaporated (to *ca.* 10 cm^3) and the solid was filtered off, washed with acetone (2×3 cm^3) and suction dried.

(d) $[PdI_2(S_2CCMe_2PPh_3)]$

To a solution containing 0.2189 g (0.15 mmol) of $(NBu_4)_2[Pd_2I_6]$ in 25 cm^3 of dichloromethane, was

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added 0.1142 g (0.30 mmol) of the ligand S_2CCMe_2-PPh_3. After stirring for 18 h, partial evaporation to *ca.* 5 cm^3 and addition of acetone (10 cm^3) produced a red precipitate which was filtered off, washed with acetone (2 X 2 cm^3) and dried.

(e) [PdX$_2$(SC(S)CMe$_2$PPh$_3$)(PPh$_3$)] (X = Cl, Br)

$[PdX_2(S_2CCMe_2PPh_3)]_x \cdot xCH_2Cl_2$ (0.20 meq) was suspended in 25 cm^3 of dichloromethane and addition of 0.0525 g of PPh_3 (0.20 mmol) gave rise to immediate dissolution. After 4 h stirring, the solvent was partially evaporated (to about 2 cm^3) and, after addition of diethylether (10 cm^3), the orange or, respectively, red precipitate was filtered off and washed with Et_2O (2 X 2 cm^3).

(f) [PdI$_2$(SC(S)CMe$_2$PPh$_3$)(PPh$_3$)]

Triphenylphosphine (0.0262 g, 0.1 mmol) was added to a red solution of $[PdI_2(S_2CCMe_2PPh_3)]_x$ (0.0741 g, 0.1 meq). On stirring, the solution turned orange and, after 4 h, partial evaporation and addition of diethylether gave a solid which was filtered off and washed with 2 X 2 cm^3 of Et_2O.

(g) trans-[Pd(C$_6$F$_5$)(SC(S)CMe$_2$PPh$_3$)(PEt$_3$)$_2$](ClO$_4$)

$AgClO_4$ (0.0518 g, 0.25 mmol) was added to a solution containing 0.1363 g of $[PdCl(C_6F_5)(PEt_3)_2]$ (0.25 mmol). After 30 min stirring, the precipitated AgCl was filtered off and 0.0951 g of $S_2CCMe_2PPh_3$ (0.25 mmol) was added to the filtrate. After 24 h stirring the solvent was evaporated and the yellow solid was washed with 3 X 5 cm^3 of diethylether.

(h) [Ag(SC(S)CMe$_2$PPh$_3$)(PPh$_3$)]ClO$_4$

A solution containing $[Ag(OClO_3)(PPh_3)]$ (0.1174 g, 0.25 mmol) and $S_2CCMe_2PPh_3$ (0.0951 g, 0.25 mmol) in dichloromethane (25 cm^3) was stirred for 4 h. The solvent was evaporated and 5 cm^3 of diethylether added, and the resulting red solid was filtered off and washed with Et_2O (3 X 2 cm^3).

(i) [Ag(S$_2$CCMe$_2$PPh$_3$)](ClO$_4$)$_x$·$\frac{x}{2}$CH$_2$Cl$_2$

$AgClO_4$ (0.1451 g, 0.7 mmol) and $S_2CCMe_2PPh_3$ (0.2664 g, 0.7 mmol) were stirred for 24 h in dichloromethane (25 cm^3). The formed orange solid was filtered off, washed with 2 X 3 cm^3 of benzene and suction dried.

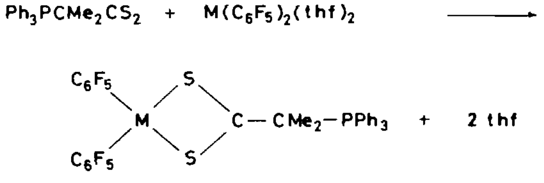
(j) [Ag(S$_2$CCMe$_2$PPh$_3$)$_2$]ClO$_4$

$AgClO_4$ (0.0518 g, 0.25 mmol) and the ligand $S_2CCMe_2PPh_3$ (0.1903 g, 0.5 mmol) were stirred for 6 h in 15 cm^3 of dichloromethane. The solvent was evaporated and the solid was washed with 2 X 5 cm^3 of benzene. The oily residue was treated with ethylether (10 cm^3), filtered off and washed with 2 X 3 cm^3 of Et_2O.

Results and Discussion

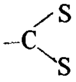
(a) Neutral Palladium or Platinum Derivatives

The reaction between $Ph_3P^+C(Me)_2CS_2^-$ and palladium(II) or platinum(II) complexes containing two substitution-labile groups, $M(C_6F_5)_2(thf)_2$ (thf = tetrahydrofuran), leads immediately (eqn. (1)) to the neutral chelate compounds. Elemental analyses and spectroscopic data for complexes **1** and **2** are listed in Table 1.



(1)

M = Pd (**1**), Pt (**2**)

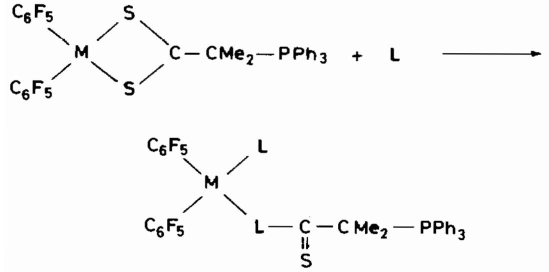
Their IR spectra show two absorptions in the 800–760 cm^{-1} region, assignable to the X-sensitive mode of the pentafluorophenyl ligands, thus confirming [5] the *cis* configuration of the formed complexes. Internal vibrations of the C_6F_5 and PPh_3 groups prevent the assignment of specific absorptions to the  moiety.

The ^{31}P NMR spectrum of complex **1** shows a single peak at 31.9 ppm, while that of compound **2** shows an absorption (δ = 30.9 ppm) along with the corresponding ^{195}Pt satellites (^4J(Pt–P) = 11.6 Hz) in agreement with the presence of only one type of phosphorus nucleus.

The ^{19}F NMR spectra confirm the *cis* geometry for both complexes, showing only one set of *ortho*, *metha* and *para* fluorine atoms; in the case of compound **2**, only the coupling of ^{195}Pt to the *ortho* fluorine nuclei is resolved (^3J(Pt–F) = 460.8 Hz).

The ^{1}H NMR spectra show a complex multiplet centred at 7.7 ppm (arylic protons) and a doublet assignable to the methyl substituents of the betaine, with a chemical shift and a ^3J(P–H) coupling constant at values close to those observed for the free ligand, in agreement with the results of Kunze and Merkel [4].

The reactivity of these complexes towards neutral ligands greatly differs [3] from that of the analogous compounds with the α-betaine $(C_6H_{11})_3P^+CS_2^-$. Although reaction (2) readily takes place when L = PPh_3, no reaction is observed between **1** or **2** and pyridine, even in the presence of a large excess (10:1) of the neutral ligand. Again, the unchanged starting materials are recovered when carbon monoxide is bubbled through dichloromethane solutions of the chelate complexes.



(2)

L = PPh_3; M = Pd (3), Pt (4)

This is a measure of the greater tendency of the β-betaine, as compared with $(C_6H_{11})_3PCS_2$, to act as a chelating ligand, since under the same conditions similar complexes containing the trialkylphosphoniumdithiocarboxylate yield [3] $M(C_6F_5)_2L(\eta^1\text{-}SC(S)PCy_3)$.

Moreover, treatment of solutions containing [5] *cis*-$Pt(C_6F_5)_2(CO)_2$ with an equivalent amount (1:1) of the betaine $Ph_3P^+CMe_2CS_2^-$ leads to the displacement of *both* CO ligands and compound **2** is formed. As has already been reported, monodentate ligands (py, PPh_3) are unable to displace the second carbon monoxide group, while 2,2′-bipyridine or bis(diphenylphosphine)methane do so [5].

On the other hand, addition of 1,2-bis(diphenylphosphino)ethane to solutions of *cis*-$M(C_6F_5)_2(S_2CCMe_2PPh_3)$ (1:2 ratio) does not yield the binuclear compounds containing monodentate $SC(S)CMe_2PPh_3$ and bridging diphosphine; instead, half of the metal complex remains unaltered, while the other half undergoes complete displacement of the betaine, yielding $M(C_6F_5)_2$dppe, as shown by ^{31}P NMR spectroscopy.

The elemental analyses and spectroscopical results are in good agreement with the proposed stoichiometry for compounds **3** and **4** (see Table 1).

The absorptions assignable to the X-sensitive mode of the pentafluorophenyl groups (two for each compound in the 800–760 cm^{-1} region) do not allow us to distinguish *cis* from *trans*, since two absorptions are theoretically expected for both configurations.

The presence of triphenylphosphine, although obscured by the IR absorptions of the phosphonium moiety of the betaine, can be stated from the new bands observed in the 750 and 540–470 cm^{-1} regions.

Compound 4 can also be crystallized with one molecule of dichloromethane (compound **4′**) in which case, noticeable differences in the IR spectrum are observed (see Table 1). Solutions of both solids show, however, identical NMR spectra (but for a peak at 5.3 ppm due to CH_2Cl_2 in the proton spectrum of **4′**) therefore, the differences in colour (**4** pink and **4′** yellow) and in the IR spectra can be ascribed to solid state effects.

The ^1H NMR spectra of compounds **3** and **4** show a complex multiplet around 7.4 ppm (aromatic protons of the triphenylphosphine and betaine ligand) and a doublet at 1.4 ppm assigned to the methyl protons of $Ph_3PCMe_2CS_2$; the chemical shift differs from that of the free or chelate ligand (see above) while the coupling constant ^3J(P–H) barely changes. The spectrum of **3** had to be registered from a freshly prepared sample since changes take place when solutions of this compound are kept for a time. Neither *cis* nor *trans*-$Pd(C_6F_5)_2(PPh_3)_2$ are detected in these solutions (see below) therefore, none of them are the decomposition product.

The ^{19}F NMR spectra of compounds **3** and **4** prove the inequivalency of the pentafluorophenyl ligands and thus, the *cis* geometry of these complexes. An assignment of the observed peaks to the C_6F_5 group *trans* to the phosphine or, respectively, *trans* to the betaine, is only possible in the case of the platinum compound, where the *ortho*-fluorine nuclei *trans* to PPh_3 appear as a false triplet due to an accidental coincidence of ^3J(Fo–Fm) and ^4J(Fo–P). Platinum satellites appear for the *ortho* nuclei as expected.

In the ^{31}P NMR spectra, two types of phosphorus nuclei are observed: that at higher frequencies corresponds to the phosphonium centre, not being coupled either to fluorine or, in the case of compound **4**, to the ^{195}Pt atoms. The other ^{31}P nucleus gives rise to a broad peak at lower frequencies, (along with platinum satellites for compound **4**) due to coupling to fluorine in a *trans* C_6F_5 group [8]

Compounds of stoichiometry $PdX_2(S_2CCMe_2PPh_3)$, (X = Cl (**5**), Br (**6**) or I (**7**)) can be obtained by treating acetone/dichloromethane solutions of the hexahalodipalladates with the equivalent amount (1:2) of the betaine, according to eqn. (3)

$$\tfrac{1}{2}(NBu_4)_2[Pd_2X_6] + S_2CCMe_2PPh_3 \longrightarrow \tfrac{1}{x}[PdX_2(S_2CCMe_2PPh_3)]_x + (NBu_4)X \qquad (3)$$

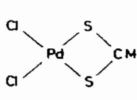
The precipitated orange to dark-red solids analyse correctly for the proposed formulae (see Table 1), but their very low solubility prevents molecular weight determinations and therefore, their nuclearity is uncertain.

The IR spectrum of the chloroderivative (**5**) shows two bands with two shoulders in the 400–250 cm^{-1} region (330sh, 305s, 275s and 250sh cm^{-1}) characteristic of ν(Pd–Cl), in an absorption pattern similar to that exhibited by the analogous compound [3] $[PdCl_2(S_2CPCy_3)]_x$. No distinction is possible between a square-planar geometry (**A**) with two terminal *cis* chlorine atoms (for which two bands are to be expected and a binuclear structure (**B**) with unidentate betaine and a double chloro bridge (for which three absorptions [9] are to be expected) or even other polynuclear structures.

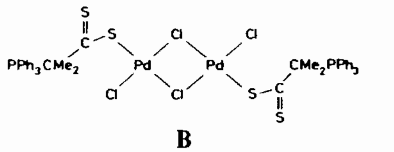
TABLE 1. Analytical and Spectroscopic Data for Complexes **1**–**14** (IR: Nujol mull, NMR: $CDCl_3$ solution)

Compound	Analyses (%)[a]		δ_{Me}	^3J(P–H)	δ_{Fo}	δ_{Fm}	δ_{Fp}	$^3J_{om}$
	C	H						
1 *cis*-$[Pd(C_6F_5)_2(S_2CCMe_2PPh_3)]$	49.3 (49.7)	2.7 (2.6)	1.97	17.3	–114.8	–165.7	–163.7	26
2 *cis*-$[Pt(C_6F_5)_2(S_2CCMe_2PPh_3)]$	45.7 (44.9)	2.7 (2.3)	1.93	17.3	–118.1	–166.7	–165.0	23
3 *cis*-$[Pd(C_6F_5)_2(SC(S)CMe_2PPh_3)(PPh_3)]$	57.0 (57.7)	3.2 (3.3)	1.40	18.6	–114.9br –117.0	b	b	26 23
4 *cis*-$[Pt(C_6F_5)_2(SC(S)CMe_2PPh_3)(PPh_3)]$	53.2 (53.3)	3.4 (3.1)	1.42	18.8	–117.5dd	b	b	19
4' *cis*-$[Pt(C_6F_5)_2(SC(S)CMe_2PPh_3)(PPh_3)]\cdot CH_2Cl_2$	51.3 (50.6)	3.0 (3.0)			–119.0d	b	b	24
5 $[PdCl_2(S_2CCMe_2PPh_3)]_x\cdot xCH_2Cl_2$	42.9 (43.0)	3.5 (3.6)	d	d				
6 $[PdBr_2(S_2CCMe_2PPh_3)]_x\cdot xCH_2Cl_2$	37.4 (37.8)	3.5 (3.2)						
7 $[PdI_2(S_2CCMe_2PPh_3)]_x$	36.3 (35.7)	3.0 (2.9)						
8 $[PdCl_2(SC(S)CMe_2PPh_3)(PPh_3)]\cdot CH_2Cl_2$	53.4 (54.4)	4.0 (4.2)						
9 $[PdBr_2(SC(S)CMe_2PPh_3)(PPh_3)]\cdot CH_2Cl_2$	49.8 (49.5)	4.0 (3.9)	1.99	16.6				
10 $[PdI_2(SC(S)CMe_2PPh_3)(PPh_3)]$	47.7 (47.9)	3.8 (3.6)	1.96	16.8				
11 $[Pd(C_6F_5)(SC(S)CMe_2PPh_3)(PEt_3)_2]ClO_4$	48.6 (48.5)	5.2 (5.2)	2.10	17.8	–115.1	–162.2	–159.6	26
12 $[Ag(SC(S)CMe_2PPh_3)(PPh_3)]ClO_4$	56.1 (56.5)	4.6 (4.3)	1.98	17.5				
13 $[Ag(S_2CCMe_2PPh_3)]_x(ClO_4)_x\cdot\frac{x}{2}CH_2Cl_2$	42.5 (42.9)	3.4 (3.5)	d	d				
14 $[Ag(S_2CCMe_2PPh_3)_2]ClO_4$	53.9 (54.6)	4.4 (4.4)	1.91	17.6				

[a]Calculated values are given in parentheses. [b]Overlapping of multiplets due to *meta*, *meta'*, *para* and *para'* fluorine nuclei prevents assignment. [c]Overlaps with an absorption of $S_2CCMe_2PPh_3$. [d]Insoluble. [e]In $CH_2Cl_2/CDCl_3$.



A



B

The ^{31}P NMR spectra of compounds **6** and **7** show a single peak (at, respectively, 30.5 and 30.0 ppm) indicating that, at least in solution, there is only one type of phosphorus nucleus.

The reactivity of these complexes differs from that shown by the analogous $[PdX_2(S_2CPCy_3)]_x$: while the former react (eqn. (4)) instantaneously with triphenylphosphine to give soluble compounds of stoichiometry $[PdX_2(SC(S)CMe_2PPh_3)(PPh_3)]$ (X = Cl (**8**), Br (**9**) or I (**10**)), the latter react by losing the CS_2 moiety of the α-betaine, as reported earlier [3]

$$PdX_2(S_2CCMe_2PPh_3) + PPh_3 \longrightarrow [PdX_2(SC(S)CMe_2PPh_3)(PPh_3)] \quad (4)$$

Quantitative C and H, and qualitative S analyses are in agreement with the proposed general formula (see Table 1). The ^{31}P NMR spectra of these compounds show two signals: one at *ca.* 31.5 ppm assignable to the phosphonium centre (by analogy to the compounds containing C_6F_5 instead of halogen, see above) and the second corresponding to the phosphorus in the PPh_3 ligand (δ = 27.7 for **8**, 28.3 for **9**

$^3J_{mp}$	^3J(Pt–Fo)	δ_P	^1J(Pt–P)	IR spectra (cm^{-1})		Yield (%)
				C_6F_5	$S_2CCMe_2PPh_3$ (+PR_3)	
20		31.8		1493vs, 1350s, 1046s^c, 948vs, 775m, 770s	1100vs, 1030s, 1015m, 1010m, 995m, 975m, 969m, 750s, 700s, 680s, 540s, 520s, 500m	84
20	461	30.8		1495vs, 1350vs, 1055vs^c, 950vs, 800s, 788s	1100s, 1030s, 1020s, 996s, 980m, 975m, 745s, 705s, 690s, 547s, 520s, 505m	77
b		24.1br 29.8		1488vs, 1340s, 1048vs, 948vs, 780s, 763s	1139m, 1122m, 1098s, 995s, 750s, 745s, 738s, 690s, 550s, 520vs, 489s	77
b	349	18.4	2544	1495vs, 1351s, 1055s, 958vs, 798s, 780s	1198m, 1189m, 1145m, 1130s, 1100s, 1000s, 758s, 751s, 698s, 558s, 538vs, 530s, 520vs, 510s, 500s, 450m	76
b	424	29.0		1500vs, 1360s, 1055vs, 955vs, 800s, 780s	1190m, 1103s, 1078s, 1000m, 750s, 742s, 695s, 540s, 525m, 515s, 500s	
		d			1430s, 1090vs, 1040s, 995s, 968s, 746s, 700s, 690s, 540s, 524s, 503s, 482m	70
		30.5^e			1440s, 1430s, 1260m, 1189m, 1143m, 1100vs, 1090s, 1040s, 1025m, 995s, 970s, 752s, 748s, 700s, 688s, 590m, 542vs, 528s, 510s, 412s	66
		30.0^e			1438s, 1099s, 1028s, 1000s, 972s, 968s, 750m, 698m, 550s, 530s, 510s, 405m	77
		31.6 27.7			1440vs, 1095s, 1035m, 1000m, 985m, 753s, 745vs, 690s, 545m, 520vs, 505vs	60
		31.6 28.3			1445vs, 1095vs, 1030s, 998s, 970s, 745s, 690s, 550s, 528vs, 510s, 485s	70
		31.5 30.1			1440vs, 1095s, 1025s, 995s, 970s, 770s, 755s, 690s, 560s, 530s, 510s, 500s	80
20		33.8 11.1		1500vs, 1350s, 1050vs^c, 950vs, 785s	1435vs, 1315m, 1255m, 1190m, 1100vs, 1030vs, 1000vs, 768vs, 755vs, 698vs, 625vs, 555s, 520vs, 488vs, 430m	84
		33.7 11.7br			1435vs, 1310m, 955m, 745s, 690s, 550s, 520s, 505s, 495s	79
		34.0^e			1435vs, 1038vs, 1000s, 958m, 938m, 752s, 690s, 550s, 525s, 512s	70
		33.0			1440vs, 1043s, 1028s, 995s, 753s, 746s, 688s, 553m, 525s, 515s, 508sh	77

and 30.1 for **10**). Compound **8** slowly decomposes in solution giving *trans*-$PdCl_2(PPh_3)_2$ (as identified by its ^{31}P NMR signal) and some other species (δ = 30.3).

(b) Cationic Palladium or Silver Derivatives

We have tested the reaction between benzene solutions of neutral perchlorato complexes *trans*-$[Pd(C_6F_5)(OClO_3)(PR_3)_2]$ and the β-betaine, in order to obtain compounds similar to those described earlier [2] containing $S_2C{\cdot}PR'_3$. When $PR_3 = PPh_3$, mixtures are formed which might contain $[Pd(C_6F_5)(S_2CCMe_2PPh_3)(PPh_3)]ClO_4$ and $[Pd(C_6F_5)(SC(S)CMe_2PPh_3)(PPh_3)_2]ClO_4$ but not $[Pd(C_6F_5)(PPh_3)_3]ClO_4$, as shown by ^{31}P NMR spectroscopy.

If the phosphine ligand is a more basic one ($PR_3 = PEt_3$) only the monodentate complex **11** is formed (eqn. (5)) as confirmed by quantitative C and H analyses (Table 1). The molar conductivity of acetone solutions of this compound is in good agreement with its formulation as a 1:1 electrolyte.

$$trans\text{-}[Pd(C_6F_5)(OClO_3)(PEt_3)_2] + S_2CCMe_2PPh_3 \longrightarrow$$

$$trans\text{-}[Pd(C_6F_5)(SC(S)CMe_2PPh_3)(PEt_3)_2]ClO_4 \quad (5)$$

The IR spectrum of compound **11** shows the absorptions expected [10] for an uncoordinated perchlorate anion (1100vs,br and 625s cm^{-1}), that at higher energy precluding any assignment of bands to the ν(C–S) vibrations.

The ^{31}P NMR spectrum shows two peaks at 32.3 and 15.5 ppm; in view of the relative integration of these signals, the first can be assigned to the equivalent PEt_3 ligands (which implies a *trans* configuration) while the second one must correspond to the phosphorus atom of the betaine.

Addition of the stoichiometric amount of $S_2CCMe_2PPh_3$ to a dichloromethane solution of $[Ag(OClO_3)(PPh_3)]$ leads to complex **12** (eqn. (6)) whose elemental analyses and conductivity in solution confirm the formulation.

$$[Ag(OClO_3)(PPh_3)] + S_2CCMe_2PPh_3 \longrightarrow [Ag(SC(S)CMe_2PPh_3)(PPh_3)]ClO_4 \qquad (6)$$

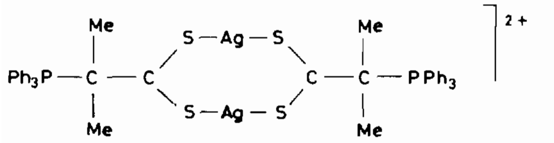
Its IR spectrum shows, as expected for the anionic perchlorate group [10], a broad band at 1085 cm^{-1} and a strong one at 625 cm^{-1}. While the first of them obscures the region assignable to $\nu(C-S)$ vibrations, the rest of the absorptions due to the betaine are mixed with those of the triphenylphosphine ligand.

The ^{31}P NMR spectrum of compound **12** shows two signals: a singlet at 33.7 ppm assisted to the phosphonium centre and a broad multiplet at 11.7 ppm assigned to the phosphorus nuclei directly bound to the silver(I) centre. Owing to the similarity of the magnetogiric ratios (^{107}Ag, $I = \frac{1}{2}$, *n.a.* = 51.83%, $\gamma = 1082.3$ $gauss^{-1}$ s^{-1}; ^{109}Ag, $I = \frac{1}{2}$, *n.a.* = 48.17%, $\gamma = 1244.2$ $gauss^{-1}$ s^{-1}) the coupling is not resolved.

Since silver(I) complexes show mostly a dicoordinate arrangement, it seems sensible that the betaine ligand should be acting as a monodentate one in this compound.

When an equimolecular amount of solid silver perchlorate is added to a dichloromethane solution of the betaine an orange precipitate is formed, which analyses as $Ag(S_2CCMe_2PPh_3)ClO_4 \cdot \frac{1}{2}CH_2Cl_2$.

The low solubility of complex **13** prevents conductivity measurements in solution, and points to a polynuclear structure like



or a higher polymer. The ionic nature of the perchlorate can be inferred [10] from the IR spectrum (1100vs,br and 628s cm^{-1}).

The ^{31}P NMR spectrum shows a single peak at 34.0 ppm, consistent with the presence of only one type of phosphorus nucleus in solution.

Addition of the stoichiometric amount of triphenylphosphine to complex **13** gives compound **12** as identified by IR spectroscopy.

On the other hand, the reaction between the betaine and $AgClO_4$ in a 2:1 molar ratio yields a very soluble ionic compound which analyses according to the stoichiometry proposed in eqn. (7).

$$AgClO_4 + 2(S_2CCMe_2PPh_3) \longrightarrow \frac{1}{2}[Ag(S_2CCMe_2PPh_3)_2]_2(ClO_4)_2 \qquad (7)$$

Its IR spectrum shows two bands at 1095vs,br and 625s cm^{-1}, as expected [10] for a free ClO_4^- anion (T_d symmetry), the first of them partly obscuring the region usually assigned to $\nu(C-S)$ vibrations. Nevertheless, two sharp strong bands at 1045 and 1030 cm^{-1} are observed.

The ^1H NMR spectrum shows a doublet ($\delta = 1.91$ ppm, $^3J(P-H) = 17.6$ Hz) and points to only one kind of ligand in solution. ^{31}P NMR spectroscopy is consistent with this, since only one type of phosphorus nucleus is observed ($\delta = 33.0$ ppm) at room temperature.

However, if the spectrum is recorded at -50 °C, some broadening of the signal is observed and thus, the simplicity of the room temperature spectra can be attributed to stereochemical non-rigidity of the compound.

A study of the conductivity in nitromethane solutions as a function of the equivalent concentration [11] shows the compound to be dinuclear and we believe its structure might be similar to that of $[Ag(S_2CPEt_3)_2]_2(ClO_4)_2$, determined by Bianchini *et al.* [1].

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