

Reactions of Carbonyl Sulphide with Palladium Compounds

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The reactions of carbonyl sulphide (COS) with PdCl_2 (in dimethyl sulphoxide), $\text{Pd}(\text{PPh}_3)_4$, $\text{Pd}(\text{PPh}_3)_2\text{O}_2$ and with PdCl_2 in the presence or absence of PPh_3 and AsPh_3 have been investigated. The reaction products have been characterised and their reactions with PPh_3 , AsPh_3 and SbPh_3 or other small molecules have also been examined. The products have been characterised by elemental analyses, infrared spectra, conductivity measurements, magnetic moments and molecular weight measurements (wherever possible). In most of the cases COS forms molecular complexes. However, in some cases, it forms SPPh_3 complexes. Reactions of the molecular COS complexes with other small molecules result in the replacement of COS.

IN earlier papers^{1,2} we discussed reactions of carbonyl sulphide (COS) with $\text{Pt}(\text{PPh}_3)_3$, $\text{RhCl}(\text{PPh}_3)_3$ and other rhodium(I) complexes and with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in the presence of PPh_3 , AsPh_3 or SbPh_3 . It was shown that COS acted as a good carbonylating agent and easily formed SPPh_3 or SAsPh_3 . In this paper we report the reactions of COS with PdCl_2 , $\text{Pd}(\text{PPh}_3)_4$ and $\text{Pd}(\text{PPh}_3)_2\text{O}_2$ in the presence and absence of PPh_3 or AsPh_3 . The reactions of resulting COS complexes with other small molecules like O_2 , I_2 , CH_3I , HgCl_2 , HCl are also described.

Materials and Methods

Chemically pure reagents were used. $\text{Pd}(\text{PPh}_3)_4$ (ref. 3), $\text{Pd}(\text{PPh}_3)_2\text{O}_2$ (ref. 4), and saturated solutions of COS (ref. 5) in methanol, ethanol, isopropanol and benzene were prepared by the standard methods. A fresh solution of COS was used in every reaction.

(a) *Reaction of PdCl_2 with COS in methanol*— PdCl_2 (0.1 g) was dissolved in hot DMSO (5 ml) and cooled to room temperature. To this was added COS solution (100 ml) in methanol at room temperature ($\sim 20^\circ\text{C}$) and shaken for 20 min. until the solution turned turbid. The brick-red precipitate was allowed to settle, filtered, washed with methanol, ether and dried *in vacuo*.

The filtrate was allowed to stand until a brownish black compound separated out (~ 12 hr). It was filtered, washed with methanol, ether and dried *in vacuo*. If the above reaction was repeated by adding 50 ml of COS solution in place of 100 ml and the mixture was kept at room temperature without shaking for about two days, pure brownish black compound $\text{PdCl}_2(\text{COS}) \cdot 2\text{MeOH}$ was obtained.

The brick-red complex (0.2g) was dissolved in DMSO (15ml) by little warming and a large excess of methanol was added when a brown compound separated out which was centrifuged, washed with methanol, ether and dried *in vacuo*.

(b) *Reaction of PdCl_2 with COS in ethanol*—This reaction was carried at 0° as described in (a) above.

The reddish-brown compound was collected and washed with ethanol, ether and dried *in vacuo*.

(c) *Reactions of PdCl_2 with COS in ethanol, isopropanol and benzene*—The same method as in (a) above was adopted but the temperature was kept at 35° . In the case of ethanol and isopropanol almost instantaneous decomposition of the initially formed reddish-brown compound resulted whereas in case of benzene, the initially formed yellowish-brown complex decomposed slowly. The final product was PdS in every case.

(d) *Reactions of $\text{PdS}(\text{COS}) \cdot 3\text{MeOH}$ with PPh_3 , AsPh_3 and SbPh_3* — $\text{PdS}(\text{COS}) \cdot 3\text{MeOH}$ (0.2 g) in DMSO (15 ml) was treated at room temperature with PPh_3 , AsPh_3 or SbPh_3 (1 g each) in methanol (100 ml). The mixture was refluxed for 5 min, when a bright-yellow to orange complex separated out in about 70% yield. It was filtered, washed with methanol, ether, and recrystallized from benzene.

In all the cases, the filtrate on concentration followed by extraction with pet. ether gave white needle shaped crystals of SPPh_3 , SAsPh_3 or OSbPh_3 as the case may be.

In the case of PPh_3 , the brown filtrate upon concentration and on addition of excess ether yielded a brown compound which was filtered, washed with excess ether, purified by reprecipitation from ether and ethanol.

The brownish black and the brown compounds under similar conditions failed to give similar products with PPh_3 , AsPh_3 or SbPh_3 .

$\text{Pd}(\text{PPh}_3)_2\text{COS}$ (0.2 g) dissolved in benzene (20 ml) and methanol (10 ml) was refluxed for 25 hr, when the colour of the solution changed to brown. It was concentrated to half the volume and on the addition of excess ether, a brown complex $[\text{Pd}(\text{SPPh}_3)(\text{PPh}_3\text{S})]_2$ separated out which was centrifuged, washed with ether and dried *in vacuo*.

In cases of $\text{Pd}(\text{AsPh}_3)_2\text{COS}$ and $\text{Pd}(\text{SbPh}_3)_2\text{COS}$, PdS was formed in place of the corresponding arsine and stibine sulphide complexes.

(e) *Reaction of Pd(PPh₃)₄ with COS* — (i) Dichloromethane solution (10 ml) of Pd(PPh₃)₄ (0.2 g) was added to methanol solution (30 ml) of COS. It was allowed to concentrate in air at room temperature. After a few days a yellow crystalline complex separated out which was filtered, washed with ethanol, ether and dried *in vacuo*.

(ii) Pd(PPh₃)₄ (0.2 g) in dichloromethane (10 ml) was mixed with COS saturated methanol (30 ml) and the mixture refluxed for 2-3 hr. The yellow crystalline compound which formed, was separated as above. On analysis it was found to be Pd(PPh₃)₂(COS)₂. The brown filtrate after the separation of yellow compound was concentrated either on a water-bath or by keeping in air. An orange-yellow compound separated out, which was filtered, washed with excess ether and dried *in vacuo*.

Pd(PPh₃)₂(COS)₂ (0.2 g) in benzene (25 ml) and methanol (10 ml) was refluxed for 2 hr when a brown solution was obtained. This was concentrated to 5 ml, and addition of excess ether yielded a brown complex, [Pd (SPPPh₃)₂S]₂.

(f) *Reactions of [Pd(SPPPh₃)₂S]₂ and [Pd(SPPPh₃)(PPh₃)S]₂ with excess PPh₃* — The complex (0.2 g) in CH₂Cl₂ (15 ml) was treated with 2.5 and 1.5 equivalents of PPh₃ respectively and the mixture refluxed for 18 hr followed by concentration to 5 ml. A large excess of ether was then added when a brown compound which analyzed for [Pd(PPh₃)₂S]₂ precipitated out. It was centrifuged and the centrifugate dried to a white mass which on repeated fractional crystallization from pet. ether gave SPPPh₃. Products SPPPh₃ and [Pd(PPh₃)₂S]₂ were characterized by their m.p., m.m.p., IR spectra and the chemical analyses.

(g) *Reactions of Pd(PPh₃)₂(COS)₂, Pd(PPh₃)₂COS, Pd(AsPh₃)₂COS and Pd(SbPh₃)₂COS with other small molecules* : (i) *Reactions with I₂* — In a typical reaction a solution of the complex (0.2 g) in benzene (20 ml) was treated with a slight excess than the equivalent amount (1:1 mol) of iodine and the mixture gently heated to reduce the volume to 3-5 ml. Addition of a large excess of pet. ether to it yielded the desired reaction product, which was separated, washed with methanol, ether and dried *in vacuo*.

Pd(PPh₃)₂(COS)₂ and Pd(PPh₃)₂COS gave a reddish brown compound, Pd(PPh₃)₂I₂ (m.p. 250°), characterized by its IR spectrum, the elemental analyses and m.m.p. (ref. 6). Pd(AsPh₃)₂COS gave a brown complex. Pd(SbPh₃)₂COS after reaction yielded a very little amount of a mixture of the black decomposed products which could not be characterized.

(ii) *Reactions with CH₃I* — The general reaction procedure involved the addition of an excess of CH₃I to a benzene solution (20 ml) of the complex (0.2 g). The mixture was allowed to stay overnight at room temperature or at 0°C and the volume of the reaction mixture reduced to 3-5 ml by slow evaporation of the solvent. The compound was precipitated by adding a large excess of pet. ether to the concentrated solution, centrifuged, precipitate washed with methanol, ether and dried *in vacuo*. In this manner Pd(PPh₃)₂(COS)₂ gave a reddish-

brown compound [Pd(PPh₃)₂I₂] and Pd(PPh₃)₂COS gave Pd(PPh₃)₂I₂ (ref. 6).

Pd(AsPh₃)₂COS and Pd(SbPh₃)₂COS did not react, giving the original compounds after the reaction.

(iii) *Reactions with oxygen* — Oxygen was bubbled for 15 min through a solution of the compound (0.2 g) in benzene [CH₂Cl₂ in case of Pd(PPh₃)₂(COS)₂]. The solution was allowed to evaporate in air, extracted with CH₂Cl₂ and precipitated with ether. The solid mass was collected by filtration, washed with methanol, ether and dried *in vacuo*.

Pd(PPh₃)₂(COS)₂ gave Pd(PPh₃)₂O₂ as a yellow complex which was characterized by its IR spectrum, the elemental analyses and by comparing with a standard sample⁴. Pd(PPh₃)₂COS and Pd(AsPh₃)₂COS did not react. Pd(SbPh₃)₂COS did not react with O₂ but OSbPh₃ was recovered from the filtrate.

(iv) *Reactions with HgCl₂* — Compound (0.2 g) in benzene (20 ml) was treated with an excess of HgCl₂ in methanol and the solution concentrated on a water-bath when a yellow to orange yellow compound separated out. It was separated by centrifugation, washed with methanol, ether and dried *in vacuo*.

Pd(PPh₃)₂(COS)₂ gave a pale yellow complex [Pd(HgCl)Cl(PPh₃)₂], Pd(PPh₃)₂(COS) and Pd(AsPh₃)₂(COS) gave Pd(PPh₃)₂Cl₂ and Pd(AsPh₃)₂Cl₂ respectively which were characterized by comparison (co-IR) with the authentic samples⁷.

Pd(SbPh₃)₂COS yielded a decomposed product.

(v) *Reactions with excess HCl* — In a typical reaction, compound (0.2 g) was dissolved in acetone (15 ml) to which 3-4 drops of conc. HCl was added, the whole mixture heated gently on a water-bath with occasional shaking. When the volume was reduced to 3-4 ml, a yellow to orange yellow complex separated out, which was filtered, washed with methanol, ether and dried *in vacuo*.

Pd(PPh₃)₂(COS)₂ and Pd(PPh₃)₂COS gave the known compound Pd(PPh₃)₂Cl₂ which was characterized by its elemental analyses and IR spectrum.

Pd(AsPh₃)₂COS yielded the known compound Pd(AsPh₃)₂Cl₂, identical (CO-IR) with an authentic specimen.

Pd(SbPh₃)₂COS was decomposed.

(vi) *Reaction of Pd(PPh₃)₂(COS)₂ with NO* — Dry NO gas was allowed to bubble through a benzene solution (20 ml) of Pd(PPh₃)₂(COS)₂ at room temperature for 1 hr. The solution was concentrated at room temperature in air to 3-4 ml and a large excess of ether added to obtain Pd(PPh₃)₂(NO₂)₂, as a brown precipitate, which was filtered, washed with methanol, ether, dried *in vacuo*. Comparison (co-IR) with an authentic sample⁸ confirmed the identity.

(h) *Reaction of Pd(PPh₃)₂O₂ with COS in the presence of PPh₃* — Through a solution of Pd(PPh₃)₄ (0.2 g) in CH₂Cl₂ (15 ml) and ether (45 ml) was bubbled O₂ for 5 min when the colour of the solution changed to red owing to the formation of Pd(PPh₃)₂O₂. PPh₃ (0.2 g) and a methanolic solution (50 ml) of COS was added to it and concentrated on a water-bath when a yellow precipitate of Pd(PPh₃)₂COS (known previously) separated out

which was filtered, washed with methanol, ether and dried *in vacuo*. A direct comparison (m.m.p. and co-IR) with an authentic sample of $\text{Pd}(\text{PPh}_3)_2\text{COS}$ confirmed its identity. The brown filtrate was concentrated on a water-bath to 5 ml and excess pet. ether (60-80°) added to it to give a brown compound, which was filtered, washed with pet. ether and ether. It was purified by recrystallization from CHCl_3 -ether and dried *in vacuo*.

(i) *Reaction of COS with PdCl_2 in the presence of PPh_3 or AsPh_3* — PdCl_2 (0.2 g) was dissolved in DMSO (5 ml) and saturated methanol solution (50 ml) of COS added to it. The mixture was shaken for 2-3 min, followed by the addition of PPh_3 or AsPh_3 (0.12 g). The mixture was refluxed for 2.5 hr and the resulting brown solution concentrated to afford a yellow to orange yellow crystalline compound. It was filtered, washed with ethanol, ether and dried *in vacuo*. The yellow compound was found to be a mixture of $\text{Pd}(\text{MPh}_3)_2\text{Cl}_2$ and

$\text{Pd}(\text{MPh}_3)_2\text{COS}$ (M=P, As) which was separated by column chromatography and the individual compounds characterized by comparison (CO-IR) with authentic specimens, prepared by alternate methods.

All the compounds reported here were purified by recrystallization from suitable solvents. The purity of the complexes were further tested by preparing them a number of times and analysing them. In each case the experimental and calculated value of the analytical results corroborates the purity of the compounds.

Results and Discussion

The compounds obtained by the reactions of COS and PdCl_2 or $\text{Pd}(\text{PPh}_3)_4$ in the presence or absence of PPh_3 , AsPh_3 or SbPh_3 are given in Table 1. Scheme 1 illustrates the interrelationship amongst the various compounds. It appears that COS acts as mono- or bi-dentate ligand in these compounds.

TABLE 1 — ANALYTICAL DATA, MELTING POINTS, MOLECULAR WEIGHTS AND IMPORTANT INFRARED BANDS OF THE COMPLEXES

Formula	m.p. (°C)	Found (Calc.) (%)					Mol. wt	Important IR bands (cm ⁻¹)
		C	H	S	Pd	Cl/I		
$[\text{PdS}(\text{COS})_2 \cdot 3\text{CH}_3\text{OH}]_2$	165	16.8 (16.32)	3.1 (4.0)	20.0 (21.7)	36.4 (36.1)	—	—	$\nu_{\text{as}}(\text{C}=\text{O})$, 1710; $\nu_{\text{s}}(\text{C}=\text{O})$, 1422; $\nu_{\text{as}}(\text{C}-\text{O})$, 1188; $\nu(\text{C}=\text{S})$, 1118; $\nu_{\text{s}}(\text{C}-\text{O})$, 935; $\nu(\text{C}-\text{S})$, 802; $\nu(\text{C}-\text{H})$, 2950; $\nu(\text{O}-\text{H})$, 3400; 679, 409.
$\text{PdCl}_2(\text{COS}) \cdot 2\text{CH}_3\text{OH}$	>300	11.9 (12.0)	2.7 (2.7)	11.2 (10.6)	34.6 (34.6)	23.2 (23.6)	—	$\nu_{\text{as}}(\text{C}-\text{O})$, 1190; $\nu(\text{C}=\text{S})$, 1135; $\nu(\text{M}-\text{O})$, 1020; $\nu_{\text{s}}(\text{C}-\text{O})$, 945; $\nu(\text{C}-\text{S})$, 808; 670, 411.
$\text{PdS} \cdot 3\text{CH}_3\text{OH}$	>300	16.1 (15.3)	3.7 (5.1)	13.5 (13.7)	43.6 (45.3)	—	—	$\nu(\text{C}-\text{H})$, 2942; $\nu(\text{O}-\text{H})$, 3455; $\nu(\text{C}-\text{O})$, 1188, 679, 418.
$\text{Pd}_2(\text{COS})_2\text{Cl}_2\text{S}_2 \cdot 2\text{C}_2\text{H}_5\text{OH}$	—	13.8 (13.7)	2.3 (1.9)	18.4 (18.2)	40.4 (40.2)	14.0 (13.5)	—	$\nu(\text{O}-\text{H})$, 3440; $\nu(\text{C}-\text{H})$, 2968; $\nu(\text{C}=\text{O})$, 1700; $\nu(\text{C}-\text{O})$, 1170; $\nu(\text{C}=\text{S})$, 1125; $\nu(\text{M}-\text{O})$, 1012; $\nu(\text{C}-\text{S})$, 840.
$\text{Pd}(\text{PPh}_3)_2\text{COS}$	196	63.6 (64.3)	5.0 (4.4)	5.0 (4.6)	15.1 (15.4)	—	716	$\nu(\text{C}=\text{O})$, 1642; $\nu(\text{C}-\text{O})$, 1180; $\nu(\text{C}=\text{S})$, 1120; $\nu(\text{C}-\text{O})$, 850; $\nu(\text{C}-\text{S})$, 810.
$\text{Pd}(\text{AsPh}_3)_2\text{COS}$	203	56.9 (57.0)	3.8 (3.9)	4.5 (4.1)	12.6 (13.6)	—	762	$\nu(\text{C}=\text{O})$, 1640; $\nu(\text{C}-\text{O})$, 1185; $\nu(\text{C}=\text{O})$, 1128; $\nu(\text{C}-\text{O})$, 845; $\nu(\text{C}-\text{S})$, 815.
$\text{Pd}(\text{SbPh}_3)_2\text{COS}$	165	50.5 (50.9)	3.6 (3.4)	4.2 (3.7)	13.1 (12.2)	—	—	$\nu(\text{C}=\text{O})$, 1632; $\nu(\text{C}-\text{O})$, 1180; $\nu(\text{C}=\text{S})$, 1120; $\nu(\text{C}-\text{O})$, 850; $\nu(\text{C}-\text{S})$, 811.
$\text{Pd}(\text{PPh}_3)_2(\text{COS})_2$	155	61.2 (60.8)	4.1 (4.0)	7.9 (8.5)	14.2 (14.1)	—	—	$\nu(\text{C}=\text{O})$, 1670; $\nu(\text{C}-\text{S})$, 1000sh; $\nu(\text{C}-\text{S})$, 828; $\nu(\text{CO})$, 900.
$[\text{Pd}(\text{SPPH}_3)_2\text{S}]_2$	160	58.5 (59.5)	4.3 (4.2)	14.0 (13.3)	14.6 (14.6)	—	649	No extra bands other than PPh_3 bands.
$[\text{Pd}(\text{SPPH}_3)(\text{PPh}_3)\text{S}]_2$	210	61.5 (62.2)	4.6 (4.3)	9.1 (9.2)	16.5 (15.3)	—	630	No extra bands other than PPh_3 bands.
$\text{Pd}(\text{AsPh}_3)_2\text{I}_2(\text{COS})$	135	42.9 (43.0)	3.1 (2.9)	4.0 (3.1)	9.3 (10.3)	23.7 (24.6)	—	$\nu(\text{C}=\text{O})$, 1710, 1658; $\nu(\text{C}-\text{O})$, 1188; $\nu(\text{C}=\text{S})$, 1122; $\nu(\text{C}-\text{O})$, 900; $\nu(\text{C}=\text{S})$, 810.
$[\text{Pd}(\text{PPh}_3)(\text{CO}_2\text{S})]_2$	160	52.0 (51.4)	3.5 (3.4)	6.6 (7.2)	24.3 (23.9)	—	—	$\nu(\text{C}=\text{O})$, 1640, 1605; $\nu(\text{C}-\text{O})$, 1185; $\nu(\text{C}-\text{S})$, 1110sh, 1020; $\nu(\text{C}-\text{O})$, 970; $\nu(\text{C}-\text{S})$, 848.
$[\text{Pd}(\text{PPh}_3)_2\text{I}_2\text{Cl}]_2$	225	35.2 (34.7)	2.8 (2.4)	—	16.5 (17.0)	38.9 (40.8)	—	No extra bands other than PPh_3 bands.
$[\text{Pd}(\text{PPh}_3)(\text{HgCl})\text{Cl}]$	185	33.3 (33.8)	3.0 (2.3)	—	15.9 (16.6)	12.0 (11.1)	—	No extra bands other than PPh_3 bands.

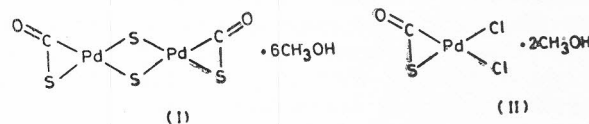
Chloride and sulphur were estimated by standard methods (ref. 9) after decomposing the complexes with aqua regia or $\text{NaOH} + \text{NaNO}_3$ mixture.

In some cases it functions as a π -donor. All the compounds are diamagnetic and non-conducting in solution, indicating that palladium is present in +2, or zero oxidation state. The mono-, di- or polymeric nature is ascertained by determining their molecular weight by cryoscopic method. In a number of cases either the complexes are insufficiently soluble or behave erratically in solution, hence their molecular weights could not be determined and therefore, not reported.

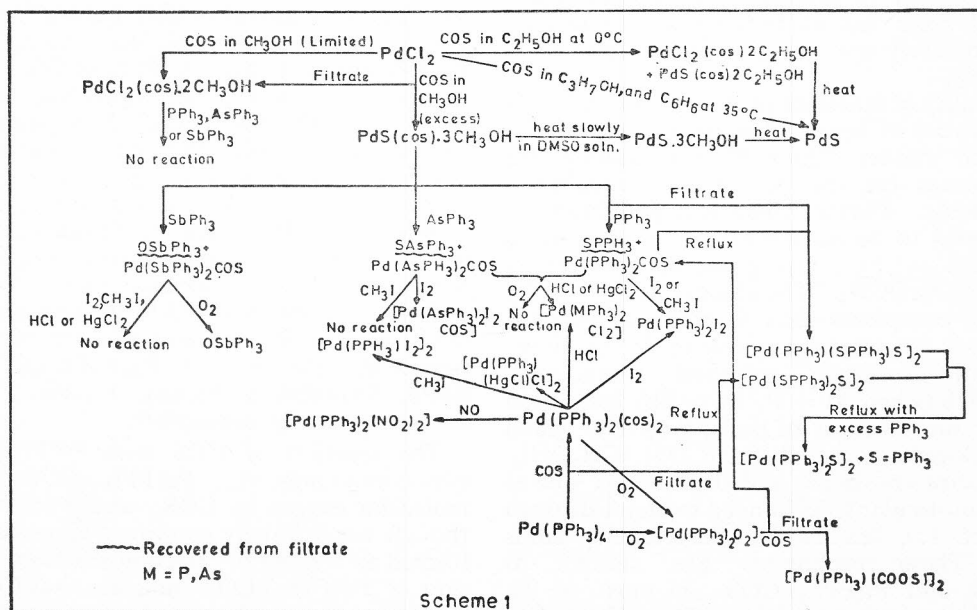
In all these complexes COS group has been identified by the presence of four characteristic^{10,11} bands of medium intensity around 1650, 1600, 840 and 800 cm^{-1} in their IR spectra in KBr (Perkin-Elmer model 580 or 537), and SPPH_3 by the presence of medium intense bands due to ν (P=S) at 530 cm^{-1} (ref. 12). In phosphine, arsine and stibine containing complexes, the IR spectra of the complexes showed characteristic bands^{12,13} of PPh_3 , AsPh_3 and SbPh_3 .

It is obvious from the formulae of the various complexes that in the presence of excess of COS, palladium ion is able to extract one sulphur atom from COS and gets linked up with one molecule of COS to precipitate $[\text{PdS}(\text{COS}) \cdot 3\text{CH}_3\text{OH}]_2$. Another complex, $\text{PdCl}_2(\text{COS}) \cdot 2\text{CH}_3\text{OH}$ has been isolated from the filtrate. When the amount of COS is comparatively less, the only complex $\text{PdCl}_2(\text{COS}) \cdot 2\text{CH}_3\text{OH}$ separates out. Thus, it appears that in the presence of a large excess of COS, both the complexes, $[\text{PdS}(\text{COS}) \cdot 3\text{CH}_3\text{OH}]_2$ and $\text{PdCl}_2(\text{COS}) \cdot 2\text{CH}_3\text{OH}$ are formed, $[\text{PdS}(\text{COS}) \cdot 3\text{CH}_3\text{OH}]_2$ being relatively less soluble precipitates out first. In a relatively less amount of COS, sulphide ions are not able to compete with Cl^- ions and $\text{PdCl}_2(\text{COS}) \cdot 2\text{CH}_3\text{OH}$ is the only reaction product. Further, $[\text{PdS}(\text{COS}) \cdot 3\text{CH}_3\text{OH}]_2$ is unstable in solution and decomposes to $\text{PdS} \cdot 3\text{CH}_3\text{OH}$ after losing one molecule of COS. It is however, stable in the solid state. All these compounds have been fully charac-

terised by elemental analyses and the presence of bands at 3400 (ν OH), 2950 (ν C-H), 1700 (ν_{as} C=O), 1420 (ν C=O), 1190 (ν_{as} C-O), 1120 (ν C=S), 940 (ν_{as} C-O) and 810 cm^{-1} (ν C-S). The absence of bands around 1020 cm^{-1} excludes the possibility of the presence of coordinated methanol molecule in the complex¹⁴. It is, therefore, assumed that methanol in the complexes is present as methanol or crystallisation only. However, attempts to replace the methanol with other molecules, like acetone, nitrobenzene, or nitromethane have not succeeded. Because of relatively less solubility of $[\text{PdS}(\text{COS}) \cdot 3\text{CH}_3\text{OH}]_2$ and the peculiar behaviour of the other complexes in the solvents, their molecular weights could not be determined. Since, $[\text{PdS}(\text{COS}) \cdot 3\text{CH}_3\text{OH}]_2$ is comparatively less soluble than $\text{PdCl}_2(\text{COS}) \cdot 2\text{CH}_3\text{OH}$, it is assumed that the former complex is at least a dimer (see structure I) with Pd-S-Pd linkage and $\text{PdCl}_2(\text{COS}) \cdot 2\text{CH}_3\text{OH}$ is a monomer (see structure II).



It is quite possible that the complexes $[\text{PdS}(\text{COS}) \cdot 3\text{CH}_3\text{OH}]_2$ and $\text{PdS} \cdot 3\text{CH}_3\text{OH}$ may be palladium(0) complexes having the formulae $\text{Pd}(\text{COS})_2 \cdot 2\text{CH}_3\text{OH}$ and $\text{Pd}(\text{COS}) \cdot 2\text{CH}_3\text{OH}$. But these possibilities have not been favoured over the ones having sulphide linkage, because in the complex $\text{Pd}(\text{COS})_2 \cdot 2\text{CH}_3\text{OH}$, it is highly improbable to have one of the COS groups more labile than the other. Further, the reaction of COS with PdCl_2 in all the alcohols and benzene give the same final product, PdS. In some of the higher alcohols the final reaction product, PdS is formed instantaneously.



In order to understand the role of methyl alcohol in the reaction, the same reaction has been carried out in other higher aliphatic alcohols and benzene in place of CH_3OH . The reaction of PdCl_2 in DMSO at 0° and ethanol saturated with COS at 0° yields a reddish brown solid which is possibly a mixture of $\text{PdS}(\text{COS}) \cdot 2\text{C}_2\text{H}_5\text{OH}$ and $\text{PdCl}_2(\text{COS}) \cdot 2\text{C}_2\text{H}_5\text{OH}$. It has practically the same IR spectrum as that of $[\text{PdS}(\text{COS}) \cdot 3\text{CH}_3\text{OH}]_2$, except a band at 1420 cm^{-1} which may be assigned to $\nu_s\text{C}=\text{O}$. It also resembles the black $\text{PdCl}_2(\text{COS}) \cdot 2\text{CH}_3\text{OH}$ in all the physical and chemical properties. The compound is decomposed on prolonged standing in solid state to a black mass, containing PdS as one of the decomposition product.

The reactions of COS with PdCl_2 in other alcohols and benzene ultimately lead to PdS as the only and the final product. In the case of higher alcohols instantaneous reactions occur leading to red to reddish brown solution which is instantaneously decomposed with the formation of PdS at room temperature. It appears that the reactions of COS and PdCl_2 in the presence of various alcohols are temperature dependent. The higher the molecular weight of alcohol, the more the instability of the complex at higher temperature. Thus, at room temperature around 35° the reaction of COS in methanol with PdCl_2 yields only blackish brown $\text{PdCl}_2(\text{COS}) \cdot 2\text{CH}_3\text{OH}$ while ethanolic COS affords PdS. At 0° ethanolic COS reacts with PdCl_2 in DMSO to give a reddish brown compound while methanolic COS even around 15° furnishes only a brick-red complex $[\text{PdS}(\text{COS}) \cdot 3\text{CH}_3\text{OH}]_2$ (if large excess of COS is present the yield is quantitative). Further the brick-red complex in DMSO solution on heating decomposes slowly to PdS.

Similarly in benzene solution of COS and PdCl_2 in DMSO around 35° the yellowish brown compound first formed in solution slowly decomposes to PdS over a period of several hours, the behaviour is strikingly similar to that of alcohols cases. These experimental facts led us to suggest that alcohol molecules possibly are present as molecules of solvation only.

The possibility of reactions of PdCl_2 and alcohols to give aldehydes or ketones has been ruled out by analysing the mother liquor after separating the metal complexes for the presence of aldehydes, ketones or acids. Further there is a possibility of these complexes to be having alkoxy group. It is however, ruled out by carrying out the reaction in the presence of NaOCH_3 . The absence of any alkoxy group in the complexes thus formed suggest that OCH_3 group is not playing any role in the reactions.

The yellow to orange coloured compounds, $\text{Pd}(\text{MPh}_3)_2\text{COS}$ (where $\text{M} = \text{P}, \text{As}$ or Sb) have been obtained by the reaction of the appropriate ligand with the brick-red compound $[\text{PdS}(\text{COS}) \cdot 3\text{CH}_3\text{OH}]_2$. Their IR spectra are similar and show bands due to coordinated molecular COS bonded to metal through C and S (ref. 15), besides the characteristic bands of MPh_3 . These compounds are similar to $\text{Pd}(\text{PPh}_3)_2\text{CS}_2$ and $\text{Pt}(\text{PPh}_3)_2\text{COS}$ in most of the chemical and physical properties. The $\nu(\text{CO})/\nu(\text{CS})$

ratio in $\text{Pd}(\text{PPh}_3)_2\text{COS}$ and $\text{Pd}(\text{PPh}_3)_2\text{CS}_2$ is almost 1.5 which further corroborates the assignment¹⁶. The structure of these complexes like $\text{Pt}(\text{C}_2\text{H}_2)(\text{PPh}_3)_2$ complex¹⁷ contain a three-membered ring with Pd-C and Pd-S bonds, the metal then being in +2 oxidation state¹⁵.

The stability of these complexes decreases as we go from phosphine to stibine, as indicated by the time taken to convert these complexes in benzene or methanol to a brown solution ensuring decomposition ($\text{PPh}_3 : \text{AsPh}_3 : \text{SbPh}_3 = 24 : 3 : 1$ hr). The time of reactions with other small molecules shows similar variation.

The reaction of $\text{Pd}(\text{PPh}_3)_4$ with COS is quite similar to that of $\text{Pt}(\text{PPh}_3)_3$. The IR spectrum also resembles that of $\text{Pt}(\text{COS})_2(\text{PPh}_3)_2$ reported earlier¹. The yellow compound $\text{Pd}(\text{PPh}_3)_2(\text{COS})_2$ is unstable and decomposes in solution on prolonged standing in air, which renders it difficult to measure its molecular weight. The reaction product $\text{Pd}(\text{PPh}_3)_2(\text{COS})_2$ is however, independent of the solvent used and the presence of O_2 . The same results are also obtained in an inert atmosphere indicating that it is not a carbonato or thiocarbonato complex. This is further proved by the reaction with O_2 where ligand replacement occurs.

The reaction of $\text{Pd}(\text{AsPh}_3)_4$ with COS proceeds in the same way but ultimately leads to an intractable brown mixture of solids which could not be characterized. This however, do not have any coordinated molecular COS group.

The orange-yellow complex obtained in the reaction of $\text{Pd}(\text{PPh}_3)_4$ with COS and a brown complex obtained from the reaction of PPh_3 with $[\text{PdS}(\text{COS}) \cdot 3\text{CH}_3\text{OH}]_2$ do not show characteristic bands except those of PPh_3 in their IR spectra. These compounds analyse for $\text{Pd}(\text{PPh}_3)_2\text{S}_3$ and $\text{Pd}(\text{PPh}_3)_2\text{S}_2$ respectively. It is quite possible that they are SPPH_3 complex, because PPh_3 is a well known sulphur acceptor¹⁸ and forms SPPH_3 easily by reaction with COS. Further, SPPH_3 complexes of palladium are also well known¹⁹. Since these compounds are also obtained simply by refluxing $\text{Pd}(\text{PPh}_3)_2(\text{COS})_2$ and $\text{Pd}(\text{PPh}_3)_2\text{COS}$, these should be the result of the decomposition of the parent molecular COS complexes. It appears that COS first decomposes into CO and S, sulphur being a soft base preferentially reacts with palladium, a soft acid, to form the required product. Also, the isolation of SPPH_3 from the filtrate of the reactions of these compounds with excess PPh_3 indicates the presence of SPPH_3 in these complexes. We, therefore, assign their formula as $[\text{Pd}(\text{SPPH}_3)_2\text{S}]_2$ and $[\text{Pd}(\text{SPPH}_3)(\text{PPh}_3)\text{S}]_2$. Again the nonexistence of similar compound in the case of $\text{Pd}(\text{AsPh}_3)_2\text{COS}$ confirms SPPH_3 formulation, because SAsPh_3 complexes if formed are very unstable¹⁹.

The reaction of COS with $\text{Pd}(\text{PPh}_3)_2\text{O}_2$ affords two compounds, viz., $\text{Pd}(\text{PPh}_3)_2\text{COS}$, by replacing molecular oxygen by COS, and $[\text{Pd}(\text{PPh}_3)(\text{COOS})]_2$, though not definitely confirmed appears to have been formed as a result of insertion reaction. The formation of $\text{Pd}(\text{PPh}_3)_2\text{COS}$ indicates that COS probably forms a more stable complex as compared to that

of molecular oxygen. This is also evident from the inability of molecular oxygen to replace COS from $\text{Pd}(\text{PPh}_3)_2\text{COS}$. The brown compound $[\text{Pd}(\text{PPh}_3)_2(\text{CO}_2\text{S})]_2$ could possibly be a result of the decomposition of the initially formed unstable peroxide complex, $\text{Pd}(\text{PPh}_3)_2\text{O}_2\cdot\text{COS}$, which is more unstable compared to its CO_2 analogue²⁰, viz. $\text{Pd}(\text{PPh}_3)_2\text{CO}_4$. The initial insertion of COS in palladium-oxygen bond followed by decomposition of the product thus formed and then dissociation of one molecule of PPh_3 will give the required product. It is soluble in many organic solvents.

The reactions of $\text{Pd}(\text{PPh}_3)_2(\text{COS})_2$, $\text{Pd}(\text{PPh}_3)_2\text{COS}$, $\text{Pd}(\text{AsPh}_3)_2\text{COS}$ and $\text{Pd}(\text{SbPh}_3)_2\text{COS}$ have been studied with various small molecules like O_2 , I_2 , CH_3I , HCl and HgCl_2 . In every case wherever reaction occurs the coordinated COS groups are replaced. In all these reactions COS molecule does not react with the small molecule. This fact has also been previously reported in the case of an analogous complex, $\text{Pd}(\text{PPh}_3)_2\text{CS}_2$ (ref. 21). $\text{Pd}(\text{AsPh}_3)_2\text{COS}$ appears to be more inert regarding the replacement reactions. $\text{Pd}(\text{SbPh}_3)_2\text{COS}$ being least stable decomposes almost in every reaction. The behaviour of $\text{Pd}(\text{PPh}_3)_2(\text{COS})_2$ and $\text{Pd}(\text{PPh}_3)_2\text{COS}$ towards small molecules is almost similar. It is interesting to note that molecular oxygen replaces both the COS groups in $\text{Pd}(\text{PPh}_3)_2(\text{COS})_2$ while no reaction takes place with $\text{Pd}(\text{PPh}_3)_2\text{COS}$. Further CS_2 fails to replace COS from $\text{Pd}(\text{PPh}_3)_2(\text{COS})_2$ even on prolonged refluxing. The reaction of NO with $\text{Pd}(\text{PPh}_3)_2(\text{COS})_2$ is however, difficult to explain, where a NO_2 complex has been isolated. It might be that $\text{Pd}(\text{PPh}_3)_2\text{O}_2$ is first formed which then reacts with NO to give the required product. However, the reaction of initially formed NO complex might as well give in the presence of atmospheric oxygen NO_2 complex which should be more stable than NO complex⁸. It is difficult to choose preferentially one mechanism over the other without further study.

The reaction with aqueous HCl in every case gives $\text{Pd}(\text{MPh}_3)_2\text{Cl}_2$ ($\text{M} = \text{P, As}$), except in the case of $\text{Pd}(\text{SbPh}_3)_2\text{COS}$ which decomposes during the reaction, $\text{Pd}(\text{MPh}_3)_2\text{COS}$ ($\text{M} = \text{P, As}$) fails to react with molecular oxygen whereas $\text{Pd}(\text{SbPh}_3)_2\text{COS}$ gives OSbPh_3 , $\text{Pd}(\text{AsPh}_3)_2\text{COS}$ and $\text{Pd}(\text{SbPh}_3)_2\text{COS}$ fails to react with CH_3I but $\text{Pd}(\text{PPh}_3)_2\text{COS}$ and $\text{Pd}(\text{PPh}_3)_2(\text{COS})_2$ yield $\text{Pd}(\text{PPh}_3)_2\text{I}_2$ and $[\text{Pd}(\text{PPh}_3)_2\text{I}_2]_2$ respectively. Reactions with HgCl_2 afford $\text{Pd}(\text{MPh}_3)_2\text{Cl}_2$ with $\text{Pd}(\text{MPh}_3)_2\text{COS}$ ($\text{M} = \text{P, As}$). $\text{Pd}(\text{SbPh}_3)_2\text{COS}$ decomposes in the reaction

and $\text{Pd}(\text{PPh}_3)_2(\text{COS})_2$ gives a typical product $[\text{Pd}(\text{PPh}_3)_2(\text{HgCl})\text{Cl}]_2$. With I_2 , $\text{Pd}(\text{PPh}_3)_2(\text{COS})_2$ and $\text{Pd}(\text{PPh}_3)_2\text{COS}$ produce identical product. $\text{Pd}(\text{PPh}_3)_2\text{I}_2$ but $\text{Pd}(\text{AsPh}_3)_2\text{COS}$ gives $\text{Pd}(\text{AsPh}_3)_2\text{I}_2\cdot\text{COS}$ which is a very unusual product, the formation of which is difficult to explain. $\text{Pd}(\text{SbPh}_3)_2\text{COS}$ decomposes to a black mass after the reaction.

In general these reactions mostly involve oxidative addition of small molecules formed by ligand dissociation. In some exceptional cases like, $\text{Pd}(\text{PPh}_3)_2(\text{COS})_2$ with molecular oxygen simple ligand displacement reaction occurs. $\text{Pd}(\text{AsPh}_3)_2\text{COS}$ with I_2 gives the oxidative addition product without ligand dissociation.

References

- PODDAR, R. K. & AGARWALA, U. C., *J. coord. Chem.*, **6** (1977), 207.
- DATTA, S., PANDEY, K. K. & AGARWALA, U., *Inorg. chim. Acta*, **40** (1980), 65.
- COULSON, D. R., *Inorganic synthesis*, Vol. 13, edited by F. A. COTTON (McGraw Hill, New York), 1972, 121.
- WILKE, G., SCOTT, H. & HEIMBACH, P., *Angew. Chim. Int. Edn.*, **6** (1967), 92.
- BRAUER, G., *Handbook of preparative inorganic chemistry*, Vol. 1, 2nd Edn (Academic Press, New York), 1963.
- CHATT, J. & MANN, F. G., *J. chem. Soc.*, (1939), 1622.
- BURMEISTER, J. L. & BASOLO, F., *Inorg. Chem.*, **3** (1964), 1587.
- BURMEISTER, J. L. & TIMMER, R. C., *J. inorg. nucl. Chem.*, **28** (1966), 1973.
- VOGEL, A. I., *A text book of quantitative inorganic analysis*, 3rd Edn (Longmans Green, London), 1961.
- CALLOMON, H. F., MCKEAN, D. C. & THOMSON, H. W., *Proc. R. Soc. Lond.*, **A-208** (1951), 321.
- MAKI, A., PLYLER, E. K. & TIDWELL, F. D., *J. res. natl. bur. Stand.*, **66A** (1962), 163.
- KOSOLAPOFF, G. M. & MAIER, L., *Organic phosphorous compounds*, Vol. 4 (Wiley-Interscience, New York), 1972.
- DOAK, G. O. & FREEDMAN, L. D., *Organometallic compounds of arsenic, antimony and bismuth* (Wiley-Interscience, New York), 1970.
- STEPHENSON, T. A. & WILKINSON, G., *J. inorg. nucl. Chem.*, **28** (1966), 945.
- BAIRD, M. C. & WILKINSON, G., *J. chem. Soc. (A)*, (1967), 865.
- GILBERT, J. D., BAIRD, M. C. & WILKINSON, G., *J. chem. Soc. (A)*, (1968), 2198.
- CHATT, J., ROWE, G. A. & WILLIAM, A. A., *Proc. chem. Soc.*, (1957), 208; GLANVILLE, J. O., STEWART, J. M. & GUIM, S. O., *J. organomet. Chem.*, **7** (1967), 9.
- BAIRD, M. C., HARTWELL, G. & WILKINSON, G., *J. chem. Soc. (A)*, (1967), 2037.
- KING, M. G. & MCQUILLAN, G. P., *J. chem. Soc. (A)*, (1967), 898; BANNISTER, E. & COTTON, F. A., *J. chem. Soc.*, (1960), 1959.
- HAYWORD, P. J., BLAKE, D. M., WILKINSON, G. & NYMAN, C. J., *J. Am. chem. Soc.*, **92** (1970), 5873.
- FEHLHAMMER, W. P. & STOLZENBERG, H., *Inorg. chim. Acta*, **44** (1980), L-151.