Metal Complexes of Sulphur Ligands. Part 17.[1] Reaction of Palladium(II) and Platinum(II) Monothiobenzoates with Various Lewis Bases and Further Studies on Complexes containing related Ligands

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Reaction of palladium(II) acetate with an excess of monothiobenzoic acid in benzene gives $[\{Pd(SOCPh)_2\}_n]$ formulated as a sulphur-bridged polymer ($n \geqslant 3$) on the basis of i.r. and molecular-weight studies. In contrast, various forms of $[\{Pt(SOCPh)_2\}_n]$ are obtained by reaction of $Na_2[PtCl_4]$ and $Na[SOCPh]$ in ethanolic or aqueous media. All these materials, however, react with an excess of various Lewis bases L or L–L {L = PPh_3, $PMePh_2$, PMe_2Ph, $AsPh_3$, $SbPh_3$, or C_5H_5N; L–L = 2,2′-bipyridyl, $Ph_2P[CH_2]_xPPh_2$ (x = 1 or 2)} to give the neutral monomeric $[M(SOCPh)_2L_2]$ or $[M(SOCPh)_2(L–L)]$ complexes which contain unidentate $[SOCPh]^-$ groups. For L = $PMePh_2$ or PMe_2Ph, ^1H and ^{31}P n.m.r. studies indicate a *trans* configuration whereas the related $[Pd(O_2CMe)_2(PR_3)_2]$ complexes have a *cis* configuration. Unlike related complexes of carboxylate and dithioacidate ligands, no evidence has been found here for either the neutral 1 : 1 or ionic 1 : 2 complexes $[\{M(SOCPh)_2L\}_n]$ or $[M(SOCPh)L_2][SOCPh]$ respectively.

THE reaction of $[M(S\text{-}S)_2]$ complexes (M = Pd or Pt; $S\text{-}S^-$ = $[S_2PR_2]^-$, $[S_2P(OR)_2]^-$, $[S_2CNR_2]^-$, or $[S_2COR]^-$) with various tertiary phosphines [2] and phosphinites [3] has been discussed in detail in earlier parts of this series and some work on the reactions of $[\{Pd(O_2CR)_2\}_n]$ with various Lewis bases has also been published.[4,5] In this paper we report on the reactions of $[\{M(SOCPh)_2\}_n]$ complexes (M = Pd or Pt) with various Lewis bases and compare the results with those for complexes of related carboxylate and dithioacidate ligands.

RESULTS AND DISCUSSION

Dropwise addition of monothiobenzoic acid to a benzene solution of palladium(II) acetate gave an immediate red-brown precipitate of palladium(II) monothiobenzoate, obtained in higher yield by further treatment of the filtrate with light petroleum (b.p. 60—80 °C). The platinum complex was best obtained, albeit in low yield, by prolonged shaking at room temperature of a mixture of $Na_2[PtCl_4]$ and an excess of $Na[SOCPh]$ in ethanol and then filtering off the insoluble products. Although the platinum species was not sufficiently soluble for molecular-weight studies, osmometric molecular-weight measurements on the palladium complex in chloroform at 37 °C over a range of concentration (1.0—4.0 g dm^{-3}) produced concentration-dependent molecular weights varying from 1 100 to 1 700 respectively. Similar concentration-dependent association phenomena have been observed for various metal thiophosphinato- and selenophosphinato-complexes in benzene or chloroform and ascribed to differing amounts of ligand bridge formation.[6] Since *X*-ray

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[1] Part 16, R. O. Gould, T. A. Stephenson, and M. A. Thomson, *J.C.S. Dalton*, 1978, 769.

[2] See M. C. Cornock and T. A. Stephenson, *J.C.S. Dalton*, 1977, 501 and refs. therein.

[3] M. C. Cornock, R. O. Gould, C. L. Jones, and T. A. Stephenson, *J.C.S. Dalton*, 1977, 1307.

[4] T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, and G. Wilkinson, *J. Chem. Soc.*, 1965, 3632.

[5] T. A. Stephenson and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1967, **29**, 2122.

[6] See W. Küchen and H. Hertel, *Angew. Chem. Internat. Edn.*, 1969, **8**, 89 and refs. therein.

structural analyses have shown that both $[\{Pd(O_2CMe)_2\}_3]$ [7] and $[\{Pd(S_2CPh)_2\}_3]$ [8] are trimeric in the solid state (although of quite different molecular structure) * and ebullioscopic molecular-weight studies on $[\{Pd(O_2CPh)_2\}_3]$ indicate a trimer,[4] it seems reasonable to expect that $[\{Pd(SOCPh)_2\}_n]$ would also possess *at least* a trimeric structure in the solid state.

As discussed elsewhere,[10] the most useful method for establishing the mode of bonding of the monothiobenzoate group is i.r. spectroscopy. Thus, Savant *et al.*[10] showed that for Na[SOCPh] ν(CO) occurs at 1 500 and ν(CS) at 960 cm^{-1}. Furthermore, when $[SOCPh]^-$ acts as a bidentate ligand and the bonding in the M–O and M–S linkages is more or less symmetrical, then ν(CO) and ν(CS) are expected to remain almost unaffected, *e.g.* for $[Ru(SOCPh)_2(PPh_3)_2]$ ν(CO) occurs at 1 500 and ν(CS) at 965 cm^{-1}.[1] However, as the interaction with the metal through sulphur increases and that through oxygen decreases, it is expected that ν(CO) will increase and ν(CS) will decrease in energy. Thus, for $[\{Pd(SOCPh)_2\}_n]$ strong bands are observed at 1 670 and 875 cm^{-1} (broad) suggesting a strong Pd–S interaction and *at best* a very weak Pd–O interaction. For PhCOSH ν(CO) occurs at 1 690 cm^{-1} but the absence of a band at 2 560 cm^{-1} [ν(SH)] shows that no free monothiobenzoic acid is present here.

Without *X*-ray structural information, the exact structure of this monothiobenzoato-complex must remain a matter of conjecture and unfortunately all attempts to date to grow single crystals have been unsuccessful. However, the i.r. spectrum of $[\{Pd(SOCPh)_2\}_n]$ is similar to that of $[\{Hg(SOCPh)_2\}_n]$ [ν(CO) at 1 630, ν(CS) at 912 cm^{-1}] for which a polymeric sulphur-bridged structure has been suggested.[10] A polymeric sulphur-bridged structure has also been suggested for the very insoluble red-brown $[\{Pd(OSCNR_2)_2\}_n]$ complexes.[11]

For $[\{Pt(SOCPh)_2\}_n]$ strong bands were also observed in the i.r. spectrum at 1 660 and 880 cm^{-1} but, in addition, strong peaks appeared at 1 595, 1 575, and 920 cm^{-1}. These latter bands could also be attributed to ν(CO) and ν(CS) vibrations respectively of $[SOCPh]^-$ groups and again suggest appreciable Pt–S and weak Pt–O interactions. The presence of these additional peaks might signify either that the *overall* structure is different from that of the palladium complex or that the material consists of several rather insoluble complexes of stoicheiometry $[\{Pt(SOCPh)_2\}_n]$ one of which has the same structure as $[\{Pd(SOCPh)_2\}_n]$. There is a precedent for the first suggestion since both platinum(II) acetate and aryldithiocarboxylates have been shown by *X*-ray analysis to have *different* molecular structures from the corresponding palladium complexes. Platinum(II) acetate has a tetrameric structure containing strong metal–metal interactions [12] whereas platinum(II) *p*-isopropyldithiobenzoate has a dimeric structure with strong metal–metal bonds.[13] The i.r. spectrum of $[\{Pt(S_2CPh)_2\}_2]$ indicates that it has a similar dimeric structure.[13]

However, further work has shown that the latter suggestion is more likely and that the reaction products here are very sensitive to both the reaction conditions and work-up procedure. Thus, work-up of the filtrate from the $Na_2[PtCl_4]$–Na[SOCPh] reaction in ethanol gave a yellow solid (which analysed quite closely for $[\{Pt(SCOPh)_2(HOEt)\}_n]$ whose i.r. spectrum showed *strong* peaks at 1 590, 1 570, and 920 cm^{-1} but only *weak* peaks at 1 660 and 880 cm^{-1}. Additional peaks occurred at 1 530 and 950 cm^{-1}. Reaction of $Na_2[PtCl_4]$ and Na[SOCPh] in aqueous solution also produced several products (see Experimental section), one of which contained strong bands in its i.r. spectrum at 1 530 and 950 cm^{-1} and weak peaks at 1 590, 1 570, and 920 cm^{-1}. Furthermore, in a closely related study, it has recently been shown that reaction of $K_2[PdCl_4]$ with $MeCS_2H$ produced several structural variations of $[\{Pd(S_2CMe)_2\}_n]$ which exhibit different multiplicities of ligand vibrations in their i.r. spectra.[14]

Without *X*-ray structural analyses further speculation on the structure of these various complexes is unwarranted, although by analogy with $[\{Ni(SOCPh)_2\}_2]\cdot EtOH$ [ν(CO) at 1 508; ν(CS) at 958 cm^{-1}] [15] the platinum complex exhibiting i.r. bands at 1 530 and 950 cm^{-1} may also have a dimeric structure with bridging $[SOCPh]^-$ groups. In fact Oro *et al.*[16] reported that reaction of $PdCl_2$ with Na[SOCPh] in water gave $[\{Pd(SOCPh)_2\}_2]$ [ν(CO) at 1 530 cm^{-1}] which was dimeric in benzene. In our hands, however, reaction of $Na_2[PdCl_4]$ and Na[SOCPh] in water gave a material with strong peaks in its i.r. spectrum at 1 660 and 880 cm^{-1} plus very weak peaks at 1 590 and 920 cm^{-1}.

Although *complete* characterisation of these $[\{M(SOCPh)_2\}_n]$ complexes was not possible, all these materials react with an excess of a variety of Lewis bases (L) in either benzene or dichloromethane to give monomeric non-conducting complexes of stoicheiometry $[M(SOCPh)_2L_2]$ (M = Pd or Pt; L = PPh_3, $PMePh_2$, PMe_2Ph, $AsPh_3$, $SbPh_3$, or C_5H_5N). The i.r. spectra of all these complexes show ν(CO) bands between 1 550 and

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* Palladium(II) dithiobenzoate has a stacked trimeric structure in the solid state but osmometric molecular-weight measurements in benzene [9] reveal a monomeric structure in solution, whereas palladium(II) acetate has a cyclic trimeric structure which osmometric molecular-weight studies [4] in benzene at 37 °C indicate is retained in solution.

[7] A. C. Skapski and M. L. Smart, *Chem. Comm.*, 1970, 658.

[8] M. Bonamico and G. Dessy, *Chem. Comm.*, 1968, 483.

[9] C. Furlani and M. L. Luciani, *Inorg. Chem.*, 1968, **7**, 1586.

[10] V. V. Savant, J. Gopalakrishnan, and C. C. Patel, *Inorg. Chem.*, 1970, **9**, 748.

[11] J. G. M. van der Linden, W. Blommerde, A. H. Dix, and F. W. Pijpers, *Inorg. Chim. Acta*, 1977, **24**, 261.

[12] M. A. A. F. de C. T. Carrondo and A. C. Skapski, *J.C.S. Chem. Comm.*, 1976, 410.

[13] J. M. Burke and J. P. Fackler, jun., *Inorg. Chem.*, 1972, **11**, 3000.

[14] O. Piovesana, L. Sestili, C. Bellitto, A. Flamini, M. Tomassini, P. F. Zanazzi, and A. R. Zanzari, *J. Amer. Chem. Soc.*, 1977, **99**, 5190.

[15] G. A. Melson, P. T. Greene, and R.F. Bryan, *Inorg. Chem.*, 1970, **9**, 1116; G. A. Melson, N. P. Crawford, and B. J. Geddes, *ibid.*, p. 1123.

[16] L. A. Oro, F. Gómez Beltran, and F. J. Tejel, *Anales de Quim.*, 1972, **68**, 1461.

1 600 cm^{-1} and ν(CS) bands between 900 and 940 cm^{-1} (Table 1) indicative of strong M–S and weak M–O interactions {*cf.* [$Ru(CO)_2(PMe_2Ph)_2(SOCPh)_2$], ν(CO)(SOCPh) at 1 600 and 1 570, ν(CS) at 945 cm^{-1}, which has *S*-bonded [SOCPh]$^-$ groups[1]}. Furthermore, the electronic spectra of these complexes are similar to those of other well established square-planar metal(II) complexes, and this fact, together with the i.r. evidence, suggests they have structure (1) and/or (2).*

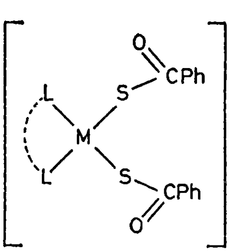
TABLE 1

Analytical data and some characteristic i.r. bands (Nujol mull) for some palladium(II) and platinum(II) monothiobenzoates

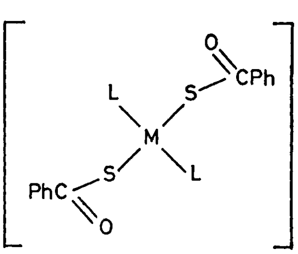
Complex	Colour	M.p. (θc/°C)	Analysis (%) Found C	Found H	Found N	Calc. C	Calc. H	Calc. N	M [a]	Infrared bands (cm^{-1}) ν(CO)	ν(CS)
[$Pd(SOCPh)_2(PPh_3)_2$]	Yellow	215—220	67.3	4.7		66.3	4.4			1 595s, 1 570s	910vs
[$Pd(SOCPh)_2(PMePh_2)_2$]	Yellow	190—192	61.6	4.7		61.5	4.6			1 590s, 1 565s	930 (sh), 915vs
[$Pd(SOCPh)_2(PMe_2Ph)_2$]	Yellow	168	54.1	5.3		54.8	4.9			1 595s, 1 560s	910vs [b]
[$Pd(SOCPh)_2(AsPh_3)_2$]·CH_2Cl_2	Pale brown	173—174	56.5	3.9		56.8	3.9		1 045 (1 077)	1 590s, 1 560s	925 (sh), 910vs
[$Pd(SOCPh)_2(SbPh_3)_2$]·CH_2Cl_2	Yellow	175	52.3	3.7		52.3	3.6		1 160 (1 171)	1600s, 1 570s	910vs
[$Pd(SOCPh)_2(C_5H_5N)_2$]	Pale brown	129	53.5	3.9	5.6	53.5	3.7	5.3		1 590s, 1 565s	935m, 912s
[$Pd(SOCPh)_2$(bipy)]	Yellow	280 (decomp.)	54.8	3.5	5.0	53.7	3.4	5.2		1 600vs, 1 570m	930s, 910vs
[$Pd(SOCPh)_2(Ph_2PCH_2PPh_2)$]	Brown	194—196	61.4	4.3		61.3	4.2			1 595vs, 1 560s	930 (sh), 910vs
[$Pd(SOCPh)_2\{Ph_2P(CH_2)_2PPh_2\}$]	Pale brown	231	61.9	4.4		61.7	4.1			1 590s, 1 560s	925 (sh), 911vs
[$Pt(SOCPh)_2(PPh_3)_2$]	Yellow	263—264	59.4	4.2		59.4	4.0			1 600s, 1 575s	915vs
[$Pt(SOCPh)_2(PMePh_2)_2$]	Pale yellow	160—164	55.0	4.1		55.2	4.1			1 593s, 1 570s	930s, 910vs
[$Pt(SOCPh)_2(PMe_2Ph)_2$]	Pale yellow	203	48.2	4.5		48.3	4.3			1 600s, 1 570m	910vs [b]
[$Pt(SOCPh)_2(AsPh_3)_2$]·CH_2Cl_2	Pale brown	250—252	53.0	3.7		52.5	3.6			1 590s, 1 570s	925 (sh), 905vs
[$Pt(SOCPh)_2$(bipy)]	Pale brown	>300	45.3	2.9	4.0	46.1	2.9	4.5		1 595s, 1 565s	935 (sh), 920vs
[$Pt(SOCPh)_2(Ph_2PCH_2PPh_2)$]·$CH_2Cl_2$	Pale brown	148—155	50.7	3.6		49.9	3.4		929 (937)	1 595s, 1 570s	925 (sh), 910vs
[$Pt(SOCPh)_2\{Ph_2P(CH_2)_2PPh_2\}$]	Yellow	228	55.0	4.0		55.4	3.9		895 (866)	1 590s, 1 565s	910vs

[a] Osmometrically at 37 °C in chloroform; calculated values are given in parentheses. [b] Partially masked by strong PMe_2Ph vibration at 900 cm^{-1}.

Examination of the ^{31}P and ^1H n.m.r. spectra of the complexes [$M(SOCPh)_2L_2$] (L = PMe_2Ph or $PMePh_2$) has enabled the isomeric form to be established. Thus, the ^{31}P-{^1H} n.m.r. spectra in each instance showed either a singlet (Pd) or a 1 : 4 : 1 triplet (Pt) [$J(PtP) \simeq 2\,600$ Hz] indicative of a single isomer with directly bonded PR_3 groups. The ^1H n.m.r. spectra showed a 'virtually-coupled' triplet pattern for the methyl resonances of the phosphine indicative of the *trans* structure (2).[17,†] A *trans* configuration has also been established by ^1H n.m.r. studies for [$Pd(pyrm)_2(PMe_2Ph)_2$] (pyrm = *N*-pyrrolidin-1-ylmonothiocarbamate).[18]



(1)



(2)

Earlier,[4] the analogous [$Pd(O_2CMe)_2(NEt_2H)_2$] was also assigned the *trans* configuration (3) on the basis of dipole-moment measurements. However, clearly the isomer formed here depends on the Lewis base used since the ^1H n.m.r. spectra of [$Pd(O_2CMe)_2(PR_3)_2$] (PR_3 = PMe_2Ph or $PMePh_2$), made by reaction of [$Pd(O_2CMe)_2]_3$ with excess of PR_3, both show a 'pseudo-doublet' ‡ pattern for the methyl resonance indicative of the *cis* configuration (4). The ^{31}P-{^1H} n.m.r. spectrum of [$Pd(O_2CMe)_2(PMe_2Ph)_2$] showed a singlet at δ 5.3 p.p.m. consistent with only one isomer in solution. For [$Pt(O_2CCF_3)_2(PMe_2Ph)_2$], however, made by reaction of [$PtCl_2(PMe_2Ph)_2$] with Ag[O_2CCF_3], the ^1H n.m.r. spectrum showed a 'virtually-coupled' triplet pattern indicating the *trans* structure (3).[19]

The complex [$Pd(O_2CMe_2)_2$(bipy)] (bipy = 2,2′-bipyridyl) reported earlier[4] must of course have the *cis*

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* The complex [$Pd(SOCPh)_2(C_5H_5N)_2$] has been briefly reported elsewhere[16] although the ν(CO) band was assigned to a peak at 1 700 cm^{-1} which was not found in the i.r. spectrum of our sample.

† *Note added in proof.* This *trans* structure (2) with *S*-bonded $PhCOS^-$ groups has recently been verified by *X*-ray analysis for [$Pd(SOCPh)_2(PMe_2Ph)_2$] (R. O. Gould, personal communication).

‡ A 'pseudo-doublet' is a sharp doublet with additional signal intensity situated between the doublet. This spectral pattern is indicative of a small but non-zero J(PP) value when compared to $|J(PH) + J(PH)'|$.

[17] P. R. Brookes and B. L. Shaw, *J. Chem. Soc.* (*A*), 1967, 1079.

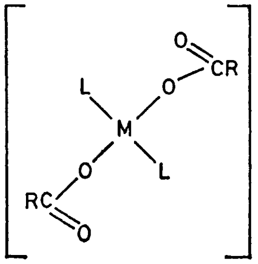
[18] E. M. Krankovits, R. J. Magee, and M. J. O. O'Connor, *Austral. J. Chem.*, 1973, **26**, 1645.

[19] D. M. Barlex and R. D. W. Kemmitt, *J.C.S. Dalton*, 1972, 1436.

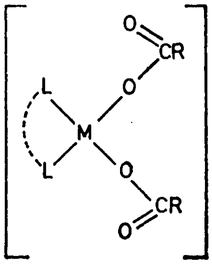
configuration (4). Similarly, reaction of $[\{M(SOCPh)_2\}_n]$ with various bidentate Lewis bases (L–L) gave the monomeric non-conducting complexes $[M(SOCPh)_2(L\text{–}L)]$ (M = Pd or Pt; L–L = bipy, $Ph_2PCH_2PPh_2$, or $Ph_2P[CH_2]_2PPh_2$) which must have the *cis* configuration (1).

An interesting feature here is the big difference between the positions of the ^{31}P n.m.r. resonances in $[M(SOCPh)_2(Ph_2PCH_2PPh_2)]$ [δ −37.3 (Pd) and −49.1 p.p.m. (Pt)] and $[M(SOCPh)_2\{Ph_2P(CH_2)_2PPh_2\}]$ [δ 57.0 (Pd) and 45.8 p.p.m. (Pt)]. Such a difference between ^{31}P n.m.r. chemical shifts in four- and five-membered phosphorus ring compounds has been found elsewhere [20] but an acceptable explanation has not yet been suggested.

Comparison of the platinum–phosphorus coupling constants in the various complexes indicates that the *trans* influence of the $[SOCPh]^-$ group is slightly lower than that of PMe_2Ph or $PMePh_2$, but considerably greater than chloride. Thus, *trans*-$[Pt(SOCPh)_2(PMe_2Ph)_2]$ and *trans*-$[Pt(SOCPh)_2(PMePh_2)_2]$ have $^1J(PtP)$ values of 2 546 and 2 655 Hz respectively compared to 2 761 and 3 018 Hz in *cis*-$[Pt(SOCPh)_2(Ph_2PCH_2PPh_2)]$ and *cis*-$[Pt(SOCPh)_2\{Ph_2P(CH_2)_2PPh_2\}]$ respectively. The complexes *cis*-$[PtCl_2(PMe_2Ph)_2]$ and *cis*-$[PtCl_2(PMePh_2)_2]$ have $^1J(PtP)$ values of 3 549 and 3 616 Hz respectively.[21]



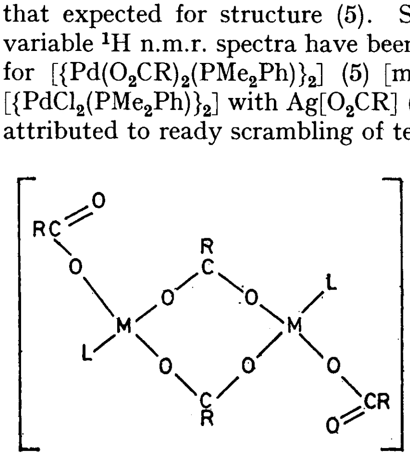
(3)



(4)

In contrast to the reaction of $[\{Pd(O_2CMe)_2\}_3]$ with stoicheiometric amounts of EPh_3 (E = P or As) which gave the dimeric complexes $[\{Pd(O_2CMe)_2(EPh_3)\}_2]$ (5) [5] and of $[M(S\text{–}S)_2]$ with PR_3 which gave the monomers $[M(S\text{–}S)_2(PR_3)]$ (6),* attempts to obtain the analogous $[\{M(SOCPh)_2L\}_n]$ have been unsuccessful. Thus, reaction of $[\{M(SOCPh)_2\}_n]$ with stoicheiometric amounts of L only led to the isolation of $[M(SOCPh)_2L_2]$ and unchanged $[\{M(SOCPh)_2\}_n]$. Furthermore, monitoring the reaction between $[\{Pd(SOCPh)_2\}_n]$ and small amounts of $PMePh_2$ in benzene confirmed that only the bis(phosphine) complex was generated in spectroscopically detectable amounts.

For $[\{Pd(O_2CMe)_2(AsPh_3)\}_2]$ only one methyl resonance is observed in the ^1H n.m.r. spectrum at ambient temperature. On cooling to 223 K the singlet splits into two resonances of equal intensity consistent with that expected for structure (5). Similar temperature-variable ^1H n.m.r. spectra have been observed elsewhere for $[\{Pd(O_2CR)_2(PMe_2Ph)\}_2]$ (5) [made by reaction of $[\{PdCl_2(PMe_2Ph)\}_2]$ with $Ag[O_2CR]$ (1 : 4 mol ratio)] and attributed to ready scrambling of terminal and bridging carboxylate groups by a solvent-assisted ring-opening mechanism.[26] Attempts to synthesise pure samples of $[\{Pd(O_2CMe)_2(PR_3)\}_2]$ (PR_3 = PMe_2Ph or $PMePh_2$) by reaction of $[\{Pd(O_2CMe)_2\}_3]$ with stoicheiometric amounts of PR_3 were unsuccessful, giving inseparable mixtures of the dimers and $[Pd(O_2CMe)_2(PR_3)_2]$. Furthermore, unlike $[Pd(O_2CMe)_2(PPh_3)_2]$ which rearranged to $[\{Pd(O_2CMe)_2(PPh_3)\}_2]$ when left in benzene for 12 h, $[Pd(O_2CMe)_2(PR_3)_2]$ (PR_3 = PMe_2Ph or $PMePh_2$) were recovered unchanged from benzene solution. This reluctance to lose a PR_3 group can be correlated with the higher basicity and smaller size of these alkyl-substituted phosphines compared to PPh_3 {*cf.* rearrangement of $[PdX_2L_2]$ to $[(PdX_2L)_2]$ which takes place far more readily for $X = I^-$ than for Cl^-}.[26]



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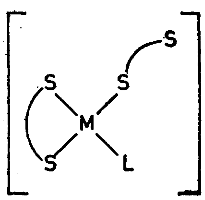
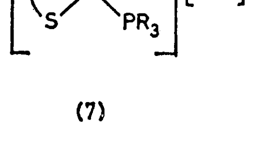


(6)

Unlike the reactions of $[M(S\text{–}S)_2]$ with excess of PR_3 in polar solvents which gave the ionic complexes $[M(S\text{–}S)(PR_3)_2][S\text{–}S]$ (7),[2] no ionic species have been detected in any reactions of $[\{M(SOCPh)_2\}_n]$. Thus reaction of $[\{M(SOCPh)_2\}_n]$ with various L in acetone led to no increase in the conductivity of the solution and only neutral $[M(SOCPh)_2L_2]$ were isolated from the



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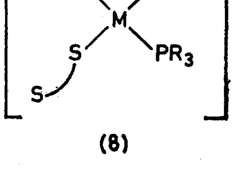

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* Structure (6) has now been established by *X*-ray analysis for $[Pd(S_2PPh_2)_2(PPh_3)]$,[22,23] $[Pt(S_2CC_6H_5C_3H_7)_2(PMePh_2)]$,[24] $[Pt(S_2CNEt_2)_2(PPh_3)]$,[23,25] $[Pt\{S_2P(OEt)_2\}_2(PPh_3)]$,[25] and $[Pt(S_2COEt)_2(PPh_3)]$.[25]

[20] See D. A. Slack and M. C. Baird, *Inorg. Chim. Acta*, 1977, **24**, 277 and refs. therein.

[21] S. O. Grim, R. L. Keiter, and W. McFarlane, *Inorg. Chem.*, 1967, **6**, 1133.

[22] J. M. C. Alison, T. A. Stephenson, and R. O. Gould, *J. Chem. Soc.* (*A*), 1971, 3690.

[23] J. M. C. Alison, Ph.D. Thesis, University of Edinburgh, 1975.

[24] D. R. Swift, Ph.D. Thesis, Case Western Reserve University, 1970.

[25] I. J. B. Lin, H. W. Chen, and J. P. Fackler, jun., *Inorg. Chem.*, 1978, **17**, 394.

[26] T. R. Jack and J. Powell, *Canad. J. Chem.*, 1975, **53**, 2558.

reaction mixture. In contrast, reaction of $[\{Pd(O_2CMe)_2\}_3]$ with an excess of PR_3 in acetone did produce a highly conducting solution. However, only neutral $[Pd(O_2CMe)_2(PR_3)_2]$ were isolated from the reaction mixtures and attempts to ' trap out ' an ionic species by addition of $[AsPh_4]Cl{\cdot}HCl$ or $Na[BPh_4]$ were unsuccessful. By analogy with the reaction of $K_2[PtCl_4]$ and PR_3 in water which gives initially $[M(PR_3)_4][MCl_4]$ and then rearranges to $[MCl_2(PR_3)_2]$,[27] the ionic species here are probably $[Pd(PR_3)_4][Pd(O_2CMe)_4]$.

Finally, contrary to earlier reports,[28] there is some very recent evidence for the formation of *neutral* 1 : 2 dithioacidato-complexes $[M(S\text{-}S)_2L_2]$. Thus, Fackler [25] has shown by *X*-ray analysis that the reaction product from $[Pt(S_2CNBu^i{}_2)_2]$ treated with excess of PMe_2Ph in acetone–diethyl ether is the neutral monomer $[Pt(S_2CNBu^i{}_2)_2(PMe_2Ph)_2]$ (8) with *trans* unidentate bonded $[S_2CNBu^i{}_2]^-$ ligands. However, in solution, even at low temperatures, this complex rapidly rearranges to an ionic species of structure (7). Clearly, the nature of the product *isolated* by reaction of $[M(S\text{-}S)_2]$ with excess of PR_3 is very sensitive to such variables as the nature of the phosphine, the dithioacid, the solvent used, and the method of work-up. Similarly with $[Ni(S\text{-}S)_2]$, where it is well established that the five- and six-co-ordinate adducts $[Ni(S\text{-}S)_2L]$ and $[Ni(S\text{-}S)_2L_2]$ respectively are readily formed with a range of nitrogen-donor ligands,[29] very recent work has shown that reaction of $[Ni(S_2COR)_2]$ (R = Et or Bu^i) with $PBu^n{}_3$ gives red square-planar $[Ni(S_2COR)_2(PBu^n{}_3)_2]$ containing unidentate dithiocarbonate groups.[30] Also, reaction of $[Ni\{S_2P(OMe)_2\}_2]$ with $Ph_2PC_2H_4AsPh_2$ gives $[Ni\{S_2PO(OMe)\}(Ph_2PC_2H_4AsPh_2)]{\cdot}0.5C_6H_6$, probably *via* the ionic intermediate $[Ni\{S_2P(OMe)_2\}(Ph_2PC_2H_4AsPh_2)][S_2P(OMe)_2]$.[31]

Thus, reaction of $[M(S_2PR_2)_2]$ with an excess of PR_3 such as PMe_2Ph, PEt_3, PPh_3, *etc.*, appear to give only ionic complexes as shown by the *X*-ray structural analysis of $[Pd(S_2PPh_2)(PEt_3)_2][S_2PPh_2]$ [22,32] together with the observation of identical mull and solution i.r. spectra.[22,33] A re-examination of the i.r. spectra of the dithiocarbamato-complexes prepared as reported in ref. 28 also confirms that these are *genuine ionic species* $[Pt(S_2CNR_2)(PMePh_2)_2][S_2CNR_2]$ (R = Me or Et) in the *solid state* and *not* neutral $[Pt(S_2CNR_2)_2(PMePh_2)_2]$ which rapidly rearrange to the ionic species in solution. Thus, ν(CN) in the i.r. spectra (mull and KBr disc) of these complexes and of $[Pt(S_2CNR_2)(PMePh_2)_2]Y$ (Y = $[BPh_4]^-$, $[PF_6]^-$, or Cl^-) [28] occur at *ca.* 1 560 cm^{-1} (bidentate $[S_2CNR_2]^-$ co-ordination) [34] whereas for $[Pt(S_2CNBu^i{}_2)_2(PMe_2Ph)_2]$ ν(CN) occurs [25] at 1 465 cm^{-1} (unidentate $[S_2CNR_2]^-$ co-ordination).[34]

However, reaction of $[M(S_2PPh_2)_2]$ with the more bulky phosphines $P(C_8H_{17}{}^n)_3$ and $PBu^n{}_3$ give yellow solids whose mull i.r. spectra contain strong bands at *ca.* 540 cm^{-1}, indicative of unidentate $[S_2PPh_2]^-$ co-ordination,[22] but no bands at 560 or 570 cm^{-1} characteristic of ionic or bidentate $[S_2PPh_2]^-$ ligands.[22] These products are very unstable, readily rearranging in solution to give ionic $[M(S_2PPh_2)(PR_3)_2][S_2PPh_2]$.

Conclusion.—Although the reaction of $[\{Pd(O_2CMe)_2\}_3]$ with various Lewis bases (L) gives both the 1 : 1 and 1 : 2 adducts $[\{Pd(O_2CMe)_2L\}_2]$ and $[Pd(O_2CMe)_2L_2]$ and likewise, with $[M(S\text{-}S)_2]$, reaction with tertiary phosphines gives $[M(S\text{-}S)_2(PR_3)]$, $[M(S\text{-}S)(PR_3)_2][S\text{-}S]$, or $[M(S\text{-}S)_2(PR_3)_2]$, reaction of $[\{M(SOCPh)_2\}_n]$ with a variety of Lewis bases gives only the neutral $[M(SOCPh)_2L_2]$ or $[M(SOCPh)_2(L\text{-}L)]$.

EXPERIMENTAL

Microanalyses were by the University of Edinburgh Chemistry Department. Molecular weights were determined on a Mechrolab vapour-pressure osmometer (model 301) calibrated with benzil. Infrared spectra were recorded in the 250—4 000 cm^{-1} region on a Perkin-Elmer 557 grating spectrometer using Nujol and hexachlorobutadiene mulls on caesium iodide plates. Electronic spectra were obtained on a Unicam SP 800 spectrophotometer using unmatched silica cells. Hydrogen-1 n.m.r. spectra were recorded on a Varian Associates HA-100 spectrometer equipped with a variable-temperature probe, proton-noise-decoupled ^{31}P n.m.r. spectra on a Varian XL100 spectrometer operating in the pulse and Fourier-transform modes at 40.5 MHz (^{31}P chemical shifts quoted in p.p.m. to high frequency of 85% H_3PO_4). Conductivity measurements were obtained on a Portland Electronics 310 conductivity bridge at 298 K. Melting points were determined with a Kofler hot-stage microscope and are uncorrected. Palladium(II) chloride, potassium tetrachloroplatinate(II) (Johnson, Matthey Ltd), monothiobenzoic acid (Aldrich), triphenylphosphine (B.D.H.), dimethylphenylphosphine, and methyldiphenylphosphine (Maybridge Chemical Co.) were obtained as indicated. The compounds Na[SOCPh],[1] $Ph_2PCH_2PPh_2$,[35] $Ph_2P[CH_2]_2PPh_2$,[36] $[Pd(O_2CMe)_2]_3$,[4] $[\{Pd(O_2CMe)_2(AsPh_3)\}_2]$,[5] and $[Pt(S_2CNR_2)(PMePh_2)_2]Y$ (Y = $[S_2CNR_2]^-$, Cl^-, $[BPh_4]^-$, or $[PF_6]^-$) [28] were prepared as described earlier. Analytical data and characteristic i.r. bands for various monothiobenzoato-complexes are given in Table 1 and ^1H and ^{31}P-{^1H} n.m.r. data for selected monothiobenzoato- and acetato-complexes in Table 2. Reactions involving tertiary phosphines were carried out under a nitrogen atmosphere.

Bis(monothiobenzoato)palladium(II).—Palladium(II) acetate (0.40 g) was dissolved in a minimum volume of cold benzene (30 cm^3) and monothiobenzoic acid (2.0 cm^3) added dropwise to the resulting red-brown solution to give an immediate red-brown *precipitate*. Complete precipitation was induced by the addition of an excess of light petroleum (b.p. 60—80 °C). The product was then filtered off, washed

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[27] G. B. Kauffman and L. A. Teter, *Inorg. Synth.*, 1963, **7**, 245.

[28] J. M. C. Alison and T. A. Stephenson, *J.C.S. Dalton*, 1973, 254.

[29] For detailed references see D. Coucouvanis, *Progr. Inorg. Chem.*, 1970, **11**, 233; J. R. Wasson, G. M. Woltermann, and H. J. Stoklosa, *Topics Current Chem.*, 1973, **35**, 65.

[30] J. Zagal and J. A. Costamagna, *Inorg. Nuclear Chem. Letters*, 1977, **13**, 411.

[31] L. Gastaldi, P. Porta, and A. A. G. Tomlinson, *J.C.S. Dalton*, 1974, 1424.

[32] A. J. F. Fraser, Ph.D. Thesis, University of Edinburgh, 1973.

[33] D. F. Steele and T. A. Stephenson, *J.C.S. Dalton*, 1973, 2124.

[34] See D. C. Bradley and M. H. Gitlitz, *J. Chem. Soc. (A)*, 1969, 1152 and refs. therein.

[35] W. Kuchen, W. Strolenberg, and J. Metten, *Chem. Ber.*, 1963, **96**, 1753.

[36] W. Hewertson and H. R. Watson, *J. Chem. Soc.*, 1962, 1490.

with diethyl ether to remove any free PhCOSH, and then dried *in vacuo* at 40 °C, m.p. 118—121 °C (yield 0.30 g) [Found: C, 43.3; H, 2.7%; *M* in $CHCl_3$ 1 125 (0.90), 1 504 (2.08), 1 672 (4.08 g dm^{-3}). Calc. for $C_{14}H_{10}O_2PdS_2$: C, 44.2; H, 2.6%; *M* 380 (monomer)]. Infrared spectrum (Nujol mull): 1 670vs [ν(CO)] and 875vs cm^{-1} [ν(CS)].

Bis(monothiobenzoato)platinum(II).—The compound $Na_2[PtCl_4]$ (0.50 g), prepared by passing $K_2[PtCl_4]$ down a cation exchange column, was suspended in ethanol (25 cm^3)–water (5 cm^3) and treated with Na[SOCPh] (0.40 g) dissolved in ethanol (40 cm^3). This mixture was shaken at room temperature for 5 d and then the resulting yellow-brown *precipitate* was filtered off, washed with ethanol, and dried *in vacuo* at 40 °C, m.p. 194 °C (decomp.) (Found: C, 35.6; H, 2.2. Calc. for $C_{14}H_{10}O_2PtS_2$: C, 35.8; H, 2.1%). Infrared spectrum (Nujol mull): 1 660s, 1 595s, and 1 575s [ν(CO)]; 920s, and 880s cm^{-1} [ν(CS)].

TABLE 2

Hydrogen-1 and $^{31}P-\{^1H\}$ n.m.r. data in $CDCl_3$ for various palladium(II) and platinum(II) complexes at 300 K

Complex	^1H N.m.r. (δ) [a]			^{31}P N.m.r.	
	Me (carboxylate)	Me (phosphine)	Ph	δ [b]	*J*(PtP)/Hz
$[Pd(SOCPh)_2(PMePh_2)_2]$		2.14 (t) [c]	7.0—8.2 (m)	12.3 (s)	
$[Pd(SOCPh)_2(PMe_2Ph)_2]$		1.79 (t) [c]	7.0—7.8 (m)	−2.6 (s)	
$[Pd(SOCPh)_2(Ph_2PCH_2PPh_2)]$		4.10 (t) [d]	7.0—8.0 (m)	−37.3 (s)	
$[Pd(SOCPh)_2\{Ph_2P(CH_2)_2PPh_2\}]$		2.33 (m) [e]	7.0—8.2 (m)	57.0 (s)	
$[Pd(O_2CMe)_2(PMe_2Ph)_2]$	2.00 (s)	1.42 (pd) [f]	7.0—8.0 (m)	5.3 (s)	
$[Pd(O_2CMe)_2(PMePh_2)_2]$	1.64 (s)	1.68 (pd) [f]	7.0—8.0 (m)		
$[Pd(O_2CMe)_2(PPh_3)_2]$	0.85 (s)		7.0—7.8 (m)	14.8 (s)	
$[\{Pd(O_2CMe)_2(AsPh_3)\}_2]$	1.44 (s), 1.47 (s), 1.41 (s) [g]		7.0—8.0 (m)		
$[\{Pd(O_2CMe)_2(PPh_3)\}_2]$	1.42 (s)		7.0—8.0 (m)	19.7 (s)	
$[Pt(SOCPh)_2(PMePh_2)_2]$		2.23 (t of t) [c,h]	7.0—7.9 (m)	8.2 (t) [i]	2 655.2
$[Pt(SOCPh)_2(PMe_2Ph)_2]$		1.86 (t of t) [c,h]	7.0—8.0 (m)	−6.2 (t) [i]	2 546.2
$[Pt(SOCPh)_2(Ph_2PCH_2PPh_2)]$		4.43 [j]	7.0—8.0 (m)	−49.1 (t) [i]	2 761.7
$[Pt(SOCPh)_2\{Ph_2P(CH_2)_2PPh_2\}]$		2.18 (m) [e]	7.0—8.0 (m)	45.8 (t) [i]	3 017.8

s = Singlet, pd = pseudo-doublet, t = triplet, and m = multiplet.

[a] ±0.01 p.p.m. [b] ±0.05 p.p.m. [c] $|^2J(PH) + {}^4J(PH)|$ 7.0 Hz. [d] CH_2 resonance, $^2J(PH)$ 10.0 Hz. [e] CH_2 resonance. [f] $|^2(PH) + {}^4J(PH)|$ 11.0 Hz. [g] At 223 K. [h] $^2J(PtH)$ 28.0 Hz. [i] 1 : 4 : 1 Triplet. [j] Too insoluble to determine splitting pattern.

The remaining red filtrate was evaporated almost to dryness and then treated with an excess of light petroleum to give a yellow *precipitate* which was washed with more light petroleum and dried *in vacuo* at 40 °C (Found: C, 38.3, H, 2.6. Calc. for $[\{Pt(SOCPh)_2(HOEt)\}_n]$: C, 37.3; H, 3.1%). Infrared spectrum (Nujol mull): 1 660w, 1 590vs, and 1 570—1 520vs, br [ν(CO)]; 950—920vs, br and 880w cm^{-1} [ν(CS)].

When $Na_2[PtCl_4]$ (1.00 g) was dissolved in hot water (15 cm^3) and treated with an aqueous solution (40 cm^3) of Na[SOCPh] (2.00 g) a brown precipitate was produced. After filtering, extracting into dichloromethane, and drying over $Mg[SO_4]$ for 12 h the solution was filtered, solvent partially removed, and excess of light petroleum added to give a pinkish *solid* (Found: C, 40.6; H, 2.6%). Infrared spectrum (Nujol mull): 1 580w and 1 530vs [ν(CO)]; 950vs and 920w cm^{-1} [ν(CS)]. On leaving the aqueous solution which remained after removal of the brown solid, a yellow solid precipitated out after 2 d and was filtered off and dried *in vacuo* (Found: C, 38.1; H, 2.4%). Infrared spectrum (Nujol mull): 1 660s and 1 590—1 520vs, br [ν(CO)]; 950—920 vs, br and 880w cm^{-1} [ν(CS)]. Qualitative analysis showed that none of these platinum monothiobenzoates contained any chlorine.

General Method of Preparation of $[\{M(SOCPh)_2L_2]$ *and* $[M(SOCPh)_2(L{-}L)]$ *Complexes*.—The complexes $[\{M(SOCPh)_2\}_n]$ (M = Pd or Pt) were dissolved or suspended in benzene or dichloromethane and treated with an excess of Lewis base (L). After shaking for 2—3 h the volume was reduced and light petroleum added to precipitate out the products. These were filtered off, washed with diethyl ether, and dried *in vacuo* at 40 °C. For L = $SbPh_3$ or $AsPh_3$ the dichloromethane solutions were heated for 2—3 h to induce complete reaction and the complexes which then crystallised out contained one molecule of dichloromethane of solvation. For the bidentate ligands (L–L) an excess of ligand was avoided in order to help prevent complete displacement of the monothiobenzoate groups.

cis-*Bis(acetato)bis(dimethylphenylphosphine)palladium*(II).—The complex $[\{Pd(O_2CMe)_2\}_3]$ in benzene was treated with an excess of dimethylphenylphosphine under nitrogen to give a yellow solution. Addition of light petroleum gave a cream crystalline *precipitate* which was washed with diethyl ether and light petroleum and dried in air (Found: C, 47.8; H, 5.8. Calc. for $C_{20}H_{28}O_4P_2Pd$: C, 48.0; H, 5.6%). Infrared spectrum (Nujol mull): $\nu_{asym}(CO_2^-)$ at 1 590, ν_{sym} at 1 330 cm^{-1}. cis-*Bis(acetato)bis(methyldiphenylphosphine)palladium*(II) was similarly prepared from $[\{Pd(O_2CMe)_2\}_3]$ and an excess of $PMePh_2$ (Found: C, 57.5; H, 5.1. Calc. for $C_{30}H_{32}O_4P_2Pd$: C, 57.7; H, 5.1%). Infrared spectrum (Nujol mull): $\nu_{asym}(CO_2^-)$ at 1 580; ν_{sym} at 1 315 cm^{-1}.

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