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 $(n \ge 3)$ 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, SDPh_3, or C_5H_5N; L-L = 2.2'-bipyridyI, Ph_2P[CH_2]_xPPh_2 (x = 1 or 2)} to give the neutral monometric $[M(SOCPh)_2L_2]$ or $[M(SOCPh)_2(L-L)]$ complexes which contain unidentate $[SOCPh]^-$ groups. For L = PMePh_2 or PMe_2Ph, ¹H and ³¹P 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 $[M(S-S)_2]$ complexes $(M = Pd \text{ or } Pt; S-S^- = [S_2PR_2]^-, [S_2P(OR)_2]^-, [S_2CNR_2], - \text{ or } [S_2COR]^-)$ 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 Na₂[PtCl₄] 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 concentrationdependent 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

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(O₂- CMe_{2}_{3} ⁷ and $[{Pd(S_{2}CPh)_{2}_{3}}^{8}$ are trimeric in the solid state (although of quite different molecular structure) * and ebullioscopic molecular-weight studies on [{Pd(O₂- $(CPh)_{2}_{3}$ 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 v(CS) are expected to remain almost unaffected, e.g. for [Ru(SOCPh)₂(PPh₃)₂] v(CO) occurs at 1500 and $\nu(CS)$ at 965 cm^{-1.1} However, as the interaction with the metal through sulphur increases and that through oxygen decreases, it is expected that $\nu(CO)$ will increase and $\nu(CS)$ will decrease in energy. Thus, for [{Pd- $(SOCPh)_{2n}$ 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 $2560 \text{ cm}^{-1} [v(SH)]$ 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 $[\{Hg(SOCPh)_{2}_{n}\}]$ $[\nu(CO) \text{ at } 1 \text{ } 630, \nu(CS) \text{ at } 912 \text{ cm}^{-1}]$ 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- $(OSCNR_2)_2$] 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 v(CO) and $\nu(CS)$ 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

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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 metalmetal interactions ¹² whereas platinum(II) p-isopropyldithiobenzoate has a dimeric structure with strong metal-metal bonds.13 The i.r. spectrum of [{Pt- $(S_2CPh)_2$ 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 Na₂[PtCl₄]-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 Na₂[PtCl₄] 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 K₂[PdCl₄] with MeCS₂H 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 $[{Ni(SOCPh)_2}_2]$. 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 $\rm cm^{-1}$ may also have a dimeric structure with bridging [SOCPh]⁻ groups. In fact Oro et al.¹⁶ reported that reaction of PdCl₂ with Na[SOCPh] in water gave [{Pd(SOCPh)₂}] $[\nu(CO) \text{ at } 1 \text{ 530 cm}^{-1}]$ which was dimeric in benzene. In our hands, however, reaction of Na₂[PdCl₄] 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 = PPh₃, PMePh₂, PMe₂Ph, AsPh₃, SbPh₃, or C₅H₅N). The i.r. spectra of all these complexes show $\nu(CO)$ bands between 1 550 and

^{*} Palladium(II) dithiobenzoate has a stacked trimeric structure in the solid state but osmometric molecular-weight measurements in benzene⁹ 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.

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(PMe₂Ph)₂(SOCPh)₂], v(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)

groups. The ¹H n.m.r. spectra showed a 'virtuallycoupled ' 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 = Npyrrolidin-1-ylmonothiocarbamate).¹⁸

Earlier,⁴ the analogous [Pd(O₂CMe)₂(NEt₂H)₂] was

TABLE 1

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

			Analysis (%)								
		Mn	Found		Calc.			Infrared bands (cm ⁻¹)			
Complex	Colour	$(\theta_c/^{\circ}C)$	c	H	N	c	H	N	M^{a}	$\tilde{\nu(CO)}$	$\nu(CS)$
[Pd(SOCPh), (PPh ₃),]	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 ₂ Ph) ₂]	Yellow	168	54.1	5.3		54.8	4.9			1 595s, 1 560s	910vs b
[Pd(SOCPh) ₂ (AsPh ₃) ₂]·CH ₂ Cl ₂	Pale brown	173—174	56.5	3.9		56.8	3.9		1045 (1077)	1 590s, 1 560s	925 (sh), 910vs
$[\mathrm{Pd}(\mathrm{SOCPh})_2(\mathrm{SbPh}_3)_2] \cdot \mathrm{CH}_2\mathrm{Cl}_2$	Yellow	175	52.3	3.7		52.3	3.6		1 160 (1 171)	1600s, 1 570s	910vs
$[\mathrm{Pd}(\mathrm{SOCPh})_2(\mathrm{C_5H_5N})_2]$	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 ₂ PCH ₂ PPh ₂)]	Brown	`194—1 ¹ 96	61.4	4.3		61.3	4.2			1 595vs, 1 560s	930 (sh), 910vs
$[Pd(SOCPh)_{2}\{Ph_{2}P(CH_{2})_{2}PPh_{2}\}]$	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 vellow	203	48.2	4.5		48.3	4.3			1 600s, 1 570m	910vs ^b
$[Pt(SOCPh)_2(AsPh_3)_2] \cdot CH_2Cl_2$	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 ₂ PCH ₂ PPh ₂)]· CH ₂ Cl ₂	Pale brown	148155	50.7	3.6		49.9	3.4		929 (937)	1 595s, 1 570s	925 (sh), 910vs
$[Pt(\tilde{SOCPh})_{2}\{Ph_{2}P(CH_{2})_{2}PPh_{2}\}]$	Yellow	228	55.0	4.0		55.4	3.9		895	1 590s, 1 565s	910vs

^a Osmometrically at 37 °C in chloroform; calculated values are given in parentheses. ^b Partially masked by strong PMe₂Ph vibration at 900 cm⁻¹.

complexes, and this fact, together with the i.r. evidence, suggests they have structure (1) and/or (2).*

Examination of the ³¹P and ¹H n.m.r. spectra of the complexes $[M(SOCPh)_2L_2]$ (L = PMe₂Ph or PMePh₂) has



enabled the isomeric form to be established. Thus, the ³¹P-{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 PR₃

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 $[Pd(O_2CMe)_2(PR_3)_2]$ (PR₃ = PMe_2Ph or $PMePh_2$), made by reaction of $[Pd(O_2 -$ CMe)₂]₃ with excess of PR₃, both show a 'pseudodoublet ' ‡ pattern for the methyl resonance indicative of the cis configuration (4). The ${}^{31}P-{}^{1}H$ n.m.r. spectrum of [Pd(O₂CMe)₂(PMe₂Ph)₂] showed a singlet at δ 5.3 p.p.m. consistent with only one isomer in solution. For [Pt(O₂CCF₃)₂(PMe₂Ph)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 earlier⁴ must of course have the cis

^{*} 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(PMe₂Ph)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 $[M(SOCPh)_2(L-L)]$ (M = Pd or Pt; L-L = bipy, Ph₂PCH₂PPh₂, or Ph₂P[CH₂]₂PPh₂) which must have the *cis* configuration (1).

An interesting feature here is the big difference between the positions of the ³¹P n.m.r. resonances in $[M(SOCPh)_2(Ph_2PCH_2PPh_2)] [\delta -37.3 (Pd) and -49.1$ p.p.m. (Pt)] and $[M(SOCPh)_2\{Ph_2P(CH_2)_2PPh_2\}] [\delta 57.0$ (Pd) and 45.8 p.p.m. (Pt)]. Such a difference between ³¹P 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 PMe₂Ph or PMePh₂, but considerably greater than chloride. Thus, *trans*-[Pt(SOCPh)₂(PMe₂-Ph)₂] and *trans*-[Pt(SOCPh)₂(PMePh₂)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(Ph₂PCH₂PPh₂)] and cis-[Pt(SOCPh)₂{Ph₂P(CH₂)₂PPh₂}] respectively. The complexes cis-[PtCl₂(PMe₂Ph)₂] and cis-[PtCl₂(PMePh₂)₂] have ${}^{1}J$ (PtP) values of 3 549 and 3 616 Hz respectively.²¹

In contrast to the reaction of $[\{Pd(O_2CMe)_2\}_3]$ with stoicheiometric amounts of EPh₃ (E = P or As) which gave the dimeric complexes $[\{Pd(O_2CMe)_2-(EPh_3)\}_2]$ (5) ⁵ and of $[M(S-S)_2]$ with PR₃ which gave the monomers $[M(S-S)_2(PR_3)]$ (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 PMePh₂ 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

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

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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 temperaturevariable 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 $[\{Pd(O_2CMe)_2(PR_3)\}_2]$ (PR₃ = PMe₂Ph or PMePh₂) by reaction of $[\{Pd(O_2CMe)_2\}_3]$ with stoicheiometric amounts of PR₃ 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, $[Pd(O_2CMe)_2(PPh_3)_2]$ when left in benzene for 12 h, $[Pd(O_2CMe)_2(PPh_3)_2]$ (PR₃ = PMe₂Ph or PMePh₂) were recovered unchanged from benzene solution. This reluctance to lose a PR₃ group can be correlated with the higher basicity and smaller size of these alkyl-substituted phosphines compared to PPh₃ (*cf.* rearrangement of $[PdX_2L_2]$ to $[(PdX_2L)_2]$ which takes place far more readily for X = I⁻ than for Cl⁻.²⁶

Unlike the reactions of $[M(S-S)_2]$ with excess of PR_3 in polar solvents which gave the ionic complexes $[M(S-S)(PR_3)_2][S-S]$ (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

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

^{*} 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 $[Pt(S_2CNEt_2)_2(PPh_3)]$,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.

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

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

reaction mixture. In contrast, reaction of [{Pd(O₂- CMe_{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 [AsPh₄]Cl·HCl or Na[BPh₄] 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 [MCl₂(PR₃)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-S)₂L₂]. Thus, Fackler ²⁵ has shown by X-ray analysis that the reaction product from [Pt(S₂CNBuⁱ₂)₂] treated with excess of PMe₂Ph in acetone-diethyl ether is the neutral monomer [Pt- $(S_2CNBu_2^i)_2(PMe_2Ph)_2$ (8) with trans unidentate bonded [S₂CNBuⁱ₂]⁻ 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 $[M(S-S)_2]$ with excess of PR_a 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 $[Ni(S-S)_2]$, where it is well established that the five- and six-co-ordinate adducts $[Ni(S-S)_{2}L]$ and $[Ni(S-S)_{2}L_{2}]$ respectively are readily formed with a range of nitrogen-donor ligands,²⁹ very recent work has shown that reaction of [Ni(S₂- COR_{2} (R = Et or Buⁱ) with PBuⁿ₃ gives red squareplanar $[Ni(S_2COR)_2(PBu^n_3)_2]$ containing unidentate dithiocarbonate groups.³⁰ Also, reaction of $[Ni\{S_2P (OMe)_2$] with $Ph_2PC_2H_4AsPh_2$ gives $[Ni{S_2PO(OMe)}]$ -(Ph₂PC₂H₄AsPh₂)]·0.5C₆H₆, 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 PR₃ such as PMe₂Ph, PEt₃, PPh₃, 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(S2CNR2)2(PMePh2)2] which rapidly rearrange to the ionic species in solution. Thus, $\nu(CN)$ in the i.r. spectra (mull and KBr disc) of these complexes and of $[Pt(S_2CNR_2)(PMePh_2)_2]Y$ (Y = [BPh₄]⁻, [PF₆],⁻ or Cl⁻)²⁸ occur at ca. 1 560 cm⁻¹ (bidentate $[S_2CNR_2]^$ co-ordination) ³⁴ whereas for $[Pt(S_2CNBu^i{}_2)_2(PMe_2Ph)_2]$ v(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 $P(C_{8}H_{17}{}^{n})_{3}$ and $PBu^{n}{}_{3}$ give yellow

solids whose mull i.r. spectra contain strong bands at ca. 540 cm⁻¹, indicative of unidentate [S₂PPh₂]⁻ coordination,²² but no bands at 560 or 570 cm⁻¹ characteristic of ionic or bidentate [S2PPh2]- 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 $[{Pd}(O_2 - O_2)]$ CMe)₂₃] with various Lewis bases (L) gives both the 1:1 and 1:2 adducts $[{Pd(O_2CMe)_2L}_2]$ and $[Pd(O_2-Me)_2]_2$ $CMe_{2}L_{2}$ and likewise, with $[M(S-S)_{2}]$, reaction with tertiary phosphines gives [M(S-S)₂(PR₃)], [M(S-S)- $(PR_3)_2[S-S]$, or $[M(S-S)_2(PR_3)_2]$, reaction of $[\{M (SOCPh)_{2}_{n}$ with a variety of Lewis bases gives only the neutral [M(SOCPh)₂L₂] or [M(SOCPh)₂(L-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 ³¹P n.m.r. spectra on a Varian XL100 spectrometer operating in the pulse and Fourier-transform modes at 40.5 MHz (³¹P chemical shifts quoted in p.p.m. to high frequency of 85% H₃PO₄). 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 Ph₂PCH₂PPh₂,³⁵ 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 ${}^{31}\mathrm{P-}\{{}^{1}\mathrm{H}\}\,n.m.r.$ 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 cm³) and monothiobenzoic acid (2.0 cm³) 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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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,

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³² A. J. F. Fraser, Ph.D. Thesis, University of Edinburgh, 1973.
³³ D. F. Steele and T. A. Stephenson,</sup> *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 CHCl₃ 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 $\lceil v(CO) \rceil$ and 875vs cm⁻¹ $\lceil v(CS) \rceil$.

Bis(monothiobenzoato)platinum(II).—The compound Na₂- $[PtCl_4]$ (0.50 g), prepared by passing K₂ $[PtCl_4]$ down a cation exchange column, was suspended in ethanol (25 cm³)water (5 cm³) and treated with Na[SOCPh] (0.40 g) dissolved in ethanol (40 cm³). This mixture was shaken at room temperature for 5 d and then the resulting yellowbrown precipitate was filtered off, washed with ethanol, and tative analysis showed that none of these platinum monothiobenzoates contained any chlorine.

General Method of Preparation of $[\{M(\mathrm{SOCPh})_2L_2]$ 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

TABLE 2	2
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Hydrogen-1 and ³¹P-{¹H} n.m.r. data in CDCl₃ for various palladium(II) and platinum(II) complexes at 300 K

		¹ H N.m.r. (δ) ^a	217. 37		
	Me	Me	Ph	³¹ P N.m.r.	
Complex	(carboxylate)	rboxylate) (phosphine)		80	/(PtP)/Hz
[Pd(SOCPh) ₂ (PMePh ₂) ₂]		2.14 (t) °	7.0-8.2 (m)	12.3 (s)	5 1
[Pd(SOCPh) ₂ (PMe ₂ Ph) ₂]		1.79 (t) °	7.0—7.8 (m)	-2.6 (s)	
[Pd(SOCPh) ₂ (Ph ₂ PCH ₂ PPh ₂)]		4.10 (t) ^d	7.0—8.0 (m)	-37.3 (s)	
$[Pd(SOCPh)_{2}{Ph_{2}P(CH_{2})_{2}PPh_{2}}]$		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),		7.08.0 (m)		
	1.47 (s),				
	1.41 (s) g				
$[{\rm Pd}(O_2CMe)_2({\rm PPh}_3)\}_2]$	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	7.08.0 (m)	-49.1 (t) ⁱ	$2\ 761.7$
$[Pt(SOCPh)_{2}{Ph_{2}P(CH_{2})_{2}PPh_{2}}]$		2.18 (m) e	7.0—8.0 (m)	45.8 (t) i	$3\ 017.8$
s - Singlet nd - nseudo-doublet	t = triplet and t	m - multiplet			

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

* ± 0.01 p.p.m. * ± 0.05 p.p.m. * $|{}^{2}J(\text{PH}) + {}^{4}J(\text{PH})|$ 7.0 Hz. * CH₂ resonance, ${}^{2}J(\text{PH})$ 10.0 Hz. * CH₂ resonance. * $|{}^{2}(\text{PH})|$ + ${}^{4}J(\text{PH})|$ 11.0 Hz. * At 223 K. * ${}^{2}J(\text{PH})$ 28.0 Hz. * 1 : 4 : 1 Triplet. * Too insoluble to determine splitting pattern.

dried in vacuo at 40 °C, m.p. 194 °C (decomp.) (Found: C, 35.6; H, 2.2. Calc. for C₁₄H₁₀O₂PtS₂: C, 35.8; H, 2.1%). Infrared spectrum (Nujol mull): 1 660s, 1 595s, and 1 575s $[\nu(CO)]$; 920s, and 880s cm⁻¹ $[\nu(CS)]$.

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 [v(CO)]; 950-920vs, br and 880w cm^{-1} [v(CS)].

When Na₂[PtCl₄] (1.00 g) was dissolved in hot water (15 cm³) and treated with an aqueous solution (40 cm³) of Na[SOCPh] (2.00 g) a brown precipitate was produced. After filtering, extracting into dichloromethane, and drying over Mg[SO₄] 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): 1580w and 1530vs [v(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 [v(CO)]; 950–920 vs, br and 880w cm⁻¹ [v(CS)]. Qualiof 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 C₂₀H₂₈O₄P₂Pd: C, 48.0; H, 5.6%). Infrared spectrum (Nujol mull): $\nu_{asym}(CO_2^-)$ at 1 590, v_{sym} at 1 330 cm⁻¹. cis-Bis(acetato)bis(methyldiphenylphosphine)palladium(II) was similarly prepared from [{Pd- $(O_2CMe)_2$] and an excess of PMePh₂ (Found: C, 57.5; H, 5.1. Calc. for C₃₀H₃₂O₄P₂Pd: C, 57.7; H, 5.1%). Infrared spectrum (Nujol mull): $v_{asym}(CO_2^-)$ at 1 580; v_{sym} at 1 315 cm⁻¹.

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