Metal Complexes of Sulphur Ligands. Part 11.[1] Reactions of Platinum(II) and Palladium(II) Dithiocarbonates with Dithiocarbonate Ions

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Reaction of the complexes $[Pt(S_2COR)_2]$ with $K[S_2COR]$ (R = Et or Pr^i) followed by addition of $[AsPh_4]Cl$ generates $[AsPh_4][Pt(S_2COR)_3]$. Variable-temperature ^1H n.m.r. studies indicate rapid unidentate–bidentate exchange at ambient temperature. Attempted recrystallisation from CH_2Cl_2 or $CDCl_3$ results in an intramolecular rearrangement to give $[AsPh_4][Pt(S_2CO)(S_2COR)]$. Reaction of $[Pd(S_2COEt)_2]$ with $K[S_2COEt]$ and $[AsPh_4]Cl$ gives $[AsPh_4][Pd(S_2CO)(S_2COEt)]$ as the main product. Reaction of $[Pt(S_2COR)_2]$ with $K[S_2COR]$ (R = Me, or CH_2Ph) and $[AsPh_4]Cl$ generates $[AsPh_4][Pt(S_2CO)(S_2COMe)]$ or $[AsPh_4]_2[Pt(S_2CO)_2]$, both of which give $[PtL_2(S_2CO)]$ on addition of various Lewis bases L (L = PPh_3, PMe_2Ph, or $\frac{1}{2}Ph_2PC_2H_4PPh_2$). The salt $[AsPh_4]$-$[Pt(S_2COEt)_3]$ is shown by *X*-ray diffraction analysis to have square-planar stereochemistry with one bi- and two uni-dentate $[S_2COEt]^-$ groups. The crystals are monoclinic, space group $P2_1/c$ with a = 9.95, b = 14.26, c = 25.82 Å, β = 99.3°.

It is now well established that when reaction occurs between $[Ni(S\text{-}S)_2]$ $\{S\text{-}S^- = [S_2CNR_2]^-, [S_2COR]^-, [S_2P(OR)_2]^-, [S_2PR_2]^-,$ *etc.*$\}$ and most nitrogen- or phosphorus-donor ligands (L) either five-co-ordinate $[NiL(S\text{-}S)_2]$ and/or six-co-ordinate $[NiL_2(S\text{-}S)_2]$ adducts are formed, depending on the nature of the ligand used.[2] Furthermore, it has been shown that reaction of $NiCl_2\cdot6H_2O$, $Na[S_2COEt]$, and $[NMe_3Ph]Cl$ gives the dark green complex $[NMe_3Ph][Ni(S_2COEt)_3]$ which was assigned a six-co-ordinate octahedral structure on the basis of electronic-spectral evidence[3] and preliminary *X*-ray studies.[4] In contrast, some of the earlier papers in this series[5] have shown that the reaction of the isomorphous $[M(S\text{-}S)_2]$ complexes (M = Pd or Pt) with tertiary phosphines occurs by stepwise cleavage of metal–sulphur bonds to generate the four-co-ordinate square-planar complexes $[M(PR'_3)(S\text{-}S)_2]$ and $[M(PR'_3)_2(S\text{-}S)][S\text{-}S]$ which exhibit unidentate–bidentate and bidentate–ionic modes of bonding of the dithioacid groups respectively.

In this paper, we report the full results[6] of reactions between various platinum(II) and palladium(II) dithiocarbonates with dithiocarbonate ion which provide further evidence for the substantial differences in chemistry exhibited by nickel on the one hand and palladium and platinum on the other.

RESULTS AND DISCUSSION

Reaction of $[Pt(S_2COEt)_2]$ with excess of $[AsPh_4]$-$[S_2COEt]$ in dichloromethane followed by the addition of diethyl ether gave a yellow crystalline solid which was a 1 : 1 electrolyte in nitromethane and analysed closely for $[AsPh_4][Pt(S_2COEt)_3]$ (1). This complex could also be prepared by treating $[Pt(S_2COEt)_2]$ with excess of

[1] Part 10, D. J. Cole-Hamilton and T. A. Stephenson, *J.C.S. Dalton*, 1976, 2396.

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

[3] D. Coucouvanis and J. P. Fackler, jun., *Inorg. Chem.*, 1967, **6**, 2047.

[4] A. D'Addario, Ph.D. Thesis, 1970, University Microfilms, Ann Arbor, Michigan.

[5] For detailed references see D. F. Steele and T. A. Stephenson, *J.C.S. Dalton*, 1973, 2124.

[6] Preliminary communication: M. C. Cornock, D. F. Steele, and T. A. Stephenson, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 785.

$K[S_2COEt]$ in acetone followed by addition of methanolic $[AsPh_4]Cl\cdot HCl$. An *X*-ray structural analysis of (1) (see below) shows that, unlike the nickel analogue, the platinum(II) ion remains four-co-ordinate and square planar by binding to one bidentate and to two unidentate dithiocarbonate groups {*cf.* $[Au(S_2CNEt_2)_3]$ [7]}. The complex $[AsPh_4][Pt(S_2COPr^i)_3]$ (2) could be similarly prepared. Furthermore, the close similarity of the mull and solution i.r. spectra of these complexes together with the similarity between their electronic spectra and those of well established square-planar platinum(II) complexes strongly suggests that this four-co-ordinate structure is retained in solution.

Further evidence for this statement comes from the low-temperature (233 K) ^1H n.m.r. spectrum of (1) in $CDCl_3$ which consisted of two sharp methyl triplets at δ 1.45 and 1.28 p.p.m. of relative intensity 1 : 2. Two overlapping methylene quartets centred at δ 4.43 p.p.m. were also observed. Similarly, for (2) at 223 K, two sharp doublets were observed for the methyl protons at δ 1.47 and 1.29 p.p.m. also of relative intensity 1 : 2, in addition to a weak multiplet at δ 4.50 p.p.m. from the methine protons. The ^{19}F n.m.r. spectrum of a related complex $[NPr_4][Pd(S_2PF_2)_3]$ at 209 K also shows two doublets of relative intensity 1 : 2 with P–F coupling constants consistent with bi-and uni-dentate co-ordination of the $[S_2PF_2]^-$ groups respectively.[8]

On warming (1) to higher temperatures (303 K), broadening of the methyl signals occurred and these n.m.r. changes were reversible and concentration independent. For (2), the two methyl doublets also broadened on raising the temperature. For the $[Pd(S_2PF_2)_3]^-$ ion, the ^{19}F n.m.r. spectrum at ambient temperature consisted of a single broad doublet and again this change was reversible.[8] Hence, these observations are indicative of a facile intramolecular unidentate–bidentate scrambling process at higher temperatures, similar to that already proposed to explain the temperature-dependent n.m.r. changes of the neutral $[M(PR'_3)(S\text{–}S)_2]$ complexes.[5] Unfortunately, because of decomposition and irreversible rearrangement processes which occur before the coalescence temperatures of complexes (1) and (2) could be reached (>320 K) (see below), useful kinetic information was not obtained from the limited data available.

Crystal Data for $[AsPh_4][Pt(S_2COEt)_3]$ (1).—$C_{33}H_{35}AsO_3PtS_6$, $M = 942$, yellow monoclinic needles, $a = 9.95(1)$, $b = 14.26(1)$, $c = 25.82(2)$ Å, $\beta = 99.3(2)°$, $U = 3\,615$ Å^3, $D_m = 1.70$, $Z = 4$, $D_c = 1.73$ g cm^{-3}. Space group $P2_1/c$, No. 14; Cu-K_α radiation, $\lambda = 1.541\,8$ Å, μ(Cu-K_α) = 119 cm^{-1}.

TABLE 1

Fractional co-ordinates ($\times 10^4$) and thermal parameters ($\times 10^3$/Å^2) for (1). Mean standard deviations for atomic positions are: Pt, 0.003; As, 0.007; S, 0.02; O, 0.05; C, 0.08; ring centres, 0.03 Å

Atom	x	y	z	U	Atom	x	y	z	U
Pt(1)	3 648	1 196	992	*	C(12)	−1 330	2 297	4 096	91
As(1)	−90	1 019	3 452	*	C(13)	1 088	1 869	3 164	31
S(1)	5 679	1 312	658	59	C(14)	1 622	2 683	3 421	109
S(2)	1 465	957	1 168	76	C(15)	2 553	3 234	3 204	85
S(3)	3 358	4 594	559	111	C(16)	2 951	2 971	2 728	93
S(4)	3 225	2 768	1 068	66	C(17)	2 419	2 157	2 471	71
S(5)	4 391	−326	991	63	C(18)	1 487	1 605	2 688	71
S(6)	−120	−163	1 718	113	C(19)	396	−299	3 499	25
O(1)	2 446	−301	1 799	96	C(20)	−137	−1 207	3 436	93
O(2)	4 125	3 011	263	103	C(21)	732	−1 984	3 521	79
O(3)	6703	−366	644	64	C(22)	2 136	−1 850	3 670	112
C(1)	−1 795	983	3 018	47	C(23)	2 669	−942	3 733	103
C(2)	−1 959	1 210	2 484	63	C(24)	1 799	−166	3 648	123
C(3)	−3 228	1 096	2 167	58	C(25)	4 420	3 728	−198	174
C(4)	−4 335	754	2 384	40	C(26)	4 667	3 090	−582	144
C(5)	−4 171	527	2 917	67	C(27)	2 430	−1 259	2 165	240
C(6)	−2 901	641	3 235	108	C(28)	3 809	−1 733	2 294	156
C(7)	−442	1 537	4 087	26	C(29)	1 488	156	1 540	89
C(8)	244	1 164	4 558	65	C(30)	3 559	3 570	609	50
C(9)	41	1 551	5 038	66	C(31)	7 814	12	388	61
C(10)	−847	2 310	5 046	32	C(32)	8 657	−1 011	274	71
C(11)	−1 533	2 682	4 576	81	C(33)	5 556	96	736	40

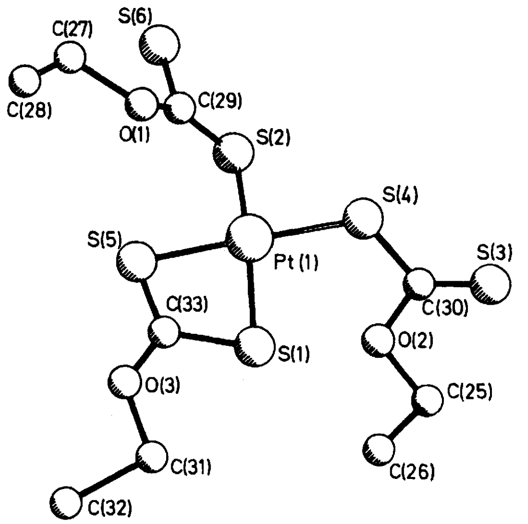
* Anisotropic thermal parameters

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt(1)	56	163	37	8	4	−3
As(1)	57	117	35	0	−6	−6

Structure determination. Considerable difficulty was experienced in choosing a suitable crystal. Layers $h0$—$5l$ were eventually collected by the equi-inclination Weissenberg method using multiple film packs. Intensities were estimated photometrically, using a Saab rotating-drum film scanner, and 1 292 independent data were taken as significant above background. No absorption corrections were made. From the Patterson function, positions could be assigned to the platinum and arsenic atoms. Subsequent difference-Fourier syntheses gave approximate positions for the sulphur and oxygen atoms. Carbon atoms were generally ill defined, and alternative positions were tried for ethyl groups. Idealised phenyl rings, with C–C 1.40 Å, were fitted to regions

[7] J. H. Noordik, *Crystal Struct. Comm.*, 1973, **2**, 81.
[8] F. N. Tebbe and E. L. Muetterties, *Inorg. Chem.*, 1970, **9**, 629.

of electron density near the arsenic atom, and these were refined as groups. Layer scale factors were initially allowed to refine, but were fixed in the last few cycles when the platinum and arsenic atoms were given anisotropic thermal parameters. Reflections were given unit weight except for those with $|F_o| > 125$, which were



Perspective view of the anion of (1)

given a weight of $125/|F_o|$. At convergence, by full-matrix refinement, R was 0.12. Final values of the fractional co-ordinates and thermal parameters are given

is essentially planar, the maximum deviation from the plane of Pt(1),S(1),S(2),S(4),S(5) being 0.18 Å. The unco-ordinated sulphur atoms of the unidentate groups are almost at the maximum possible distance from Pt(1), and lie 0.9 and 0.6 Å from the plane of co-ordination. There are no other platinum–sulphur distances of less than 5 Å. The oxygen atoms of these molecules approximate very roughly to axial ligands, but are still >3 Å

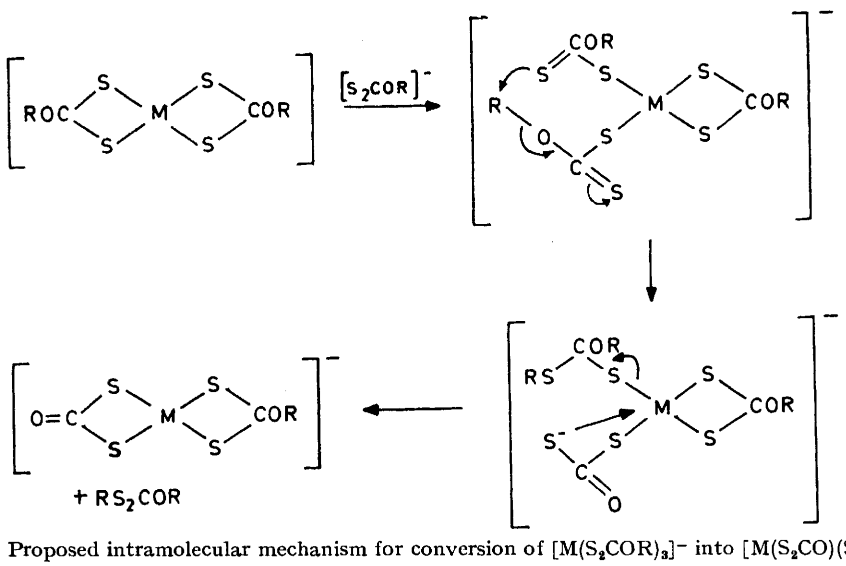
Table 2

Bond lengths (Å) and angles (°) for the platinum co-ordination in (1)

(*a*) Bond lengths			
Pt(1)–S(1)	2.327(17)	Pt(1)–S(5)	2.293(27)
Pt(1)–S(2)	2.315(19)	Pt(1) · · · S(6)	4.85(3)
Pt(1) · · · S(3)	4.97(3)	Pt(1) · · · O(1)	3.34(6)
Pt(1)–S(4)	2.294(32)	Pt(1) · · · O(2)	3.28(6)
(*b*) Angles			
S(1)–Pt(1)–S(2)	169.0(6)	S(2)–Pt(1)–S(4)	86.3(9)
S(1)–Pt(1)–S(4)	98.3(10)	S(2)–Pt(1)–S(5)	99.9(9)
S(1)–Pt(1)–S(5)	76.5(10)	S(4)–Pt(1)–S(5)	171.1(6)

from the platinum. They both lie 1.5 Å from the plane of co-ordination, but make angles of *ca.* 60 or 120° at Pt(1) with the co-ordinated sulphur atoms. Within the very large standard deviations of the determination, the arsenic co-ordination and the geometry of the dithiocarbonate groups are normal.

Thus, crystallographic and spectroscopic evidence clearly show that these tris(dithiocarbonato)platinate(II) anions contain both bi- and uni-dentate dithiocarbonate



Scheme 1 Proposed intramolecular mechanism for conversion of $[M(S_2COR)_3]^-$ into $[M(S_2CO)(S_2COR)]^-$

in Table 1, and the table of structure factors is deposited as Supplementary Publication No. SUP 21964 (4 pp.).*

Description of the structure. Distances and angles relating to the co-ordination of the platinum atom are given in Table 2, and a view of the complex anion is shown in the Figure. The co-ordination of the platinum

groups in both the solid and solution states. Although several main-group dithiocarbonates such as $[NEt_4][Cd(S_2COEt)_3]$ [9] and $[NEt_4][Te(S_2COEt)_3]$ [10] have recently been shown to possess five-co-ordinate structures with two bi- and one uni-dentate *O*-ethyl dithiocarbonate groups, complexes (1) and (2) are two of the few examples of transition-metal complexes shown *unequivocally* to

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue (items less than 10 pp. are supplied as full-size copies).

[9] B. F. Hoskins and B. P. Kelly, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 875.

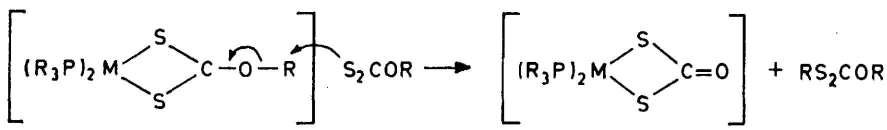
[10] R. D. MacDonald and G. Winter, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 305; B. F. Hoskins and C. D. Pannan, *J.C.S. Chem. Comm.*, 1975, 408.

contain unidentate dithiocarbonate groups. Other recent possible examples are $[M(PPh_3)(S_2COEt)_2]$ (M = Pd or Pt),[11] $[Pd(1—3\text{-}\eta\text{-}2\text{-methylallyl})(PMe_2Ph)(S_2COMe)]$,[12] and $[RhCl_2(PMe_2Ph)_3(S_2COEt)]$.[13]

Attempted recrystallisation of (1) from either dichloromethane or chloroform solutions gave an orange-yellow crystalline complex (3) containing extra i.r. bands at 1 678m, 1 600s, and 1 576m cm^{-1}. These values are reasonably close to the characteristic frequencies reported for the dithiocarbonate ion in $[Pt(PMePh_2)_2(S_2CO)]$[1 696s, 1 681(sh), and 1 615s cm^{-1}] [14] and *trans*-$[Rh(PMe_2Ph)_2(S_2CO)(S_2COEt)]$ (1 670br and 1 698s cm^{-1}),[13] and analytical data confirm that (3) is $[AsPh_4][Pt(S_2CO)(S_2COEt)]$. A similar complex $[AsPh_4][Pt(S_2CO)(S_2COPr^i)]$ (4) was formed from (2) either by recrystallisation from CH_2Cl_2 or $CHCl_3$ or by leaving methanol–diethyl ether or acetone solutions of (2) to stand for 24 h.

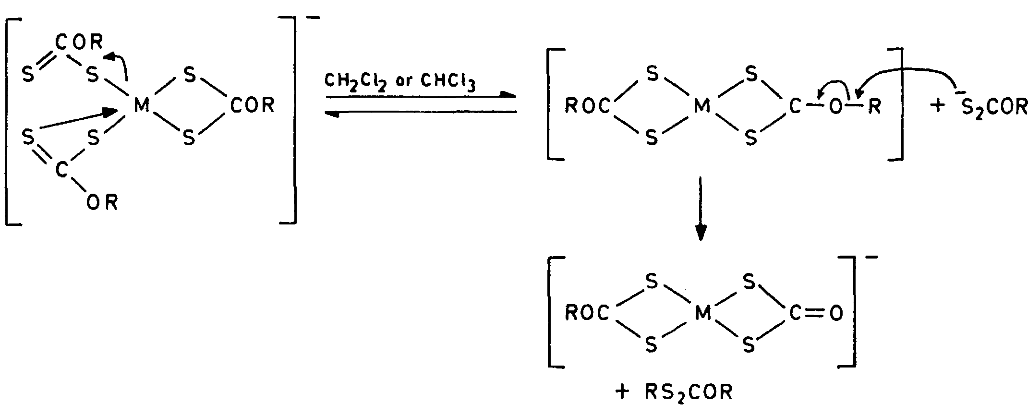
Reaction of $[Pd(S_2COEt)_2]$ with excess of $K[S_2COEt]$ in acetone followed by filtration into a methanolic solution of $[AsPh_4]Cl{\cdot}HCl$ gave a bright orange-yellow precipitate with an i.r. spectrum almost identical to that of (3) and the formulation $[AsPh_4][Pd(S_2CO)(S_2COEt)]$ was confirmed by elemental analyses. However, on carrying out the same reaction in methanol, a very small yield of a buff powder with an i.r. spectrum almost identical to (1) was obtained. These observations suggest that the $[Pd(S_2COEt)_3]^-$ anion rearranges very rapidly to $[Pd(S_2CO)(S_2COEt)]^-$ which is consistent with the known lability of Pd–S compared to Pt–S bonds.

A possible mechanism of formation of these various species which is consistent with the above evidence is outlined in Scheme 1. Thus, initial nucleophilic attack of dithiocarbonate ion on a M–S bond gives the tris-(dithiocarbonato) complex and this is followed by intramolecular generation of a dithiocarbonate group accompanied by the formation of a dithiocarbonate ester. The following related rearrangement process has been described earlier: [11]



As expected, this intramolecular rearrangement is inhibited in more solvating solvents since increasing solvation of the unidentate dithiocarbonate groups will decrease the nucleophilicity of the free sulphur atoms. The alternative intermolecular mechanism shown in Scheme 2 is considered unlikely because if true some rearranged product would be expected to form *immediately* on reaction of $[Pt(S_2COR)_2]$ with $K[S_2COR]$.

Attempts to extend the range of $[Pt(S–S)_3]^-$ anions were unsuccessful. For *O*-benzyl dithiocarbonate, the only complex which could be isolated at all molar ratios of $[Pt(S_2COCH_2Ph)_2]$ to $K[S_2COCH_2Ph]$ (from 1 : 1 to 1 : 5) was $[AsPh_4]_2[Pt(S_2CO)_2]$ (5). The i.r. spectrum of this yellow crystalline solid showed no bands between 1 200 and 1 300 cm^{-1} (dithiocarbonate) [2a] but strong absorptions at 1 690(sh), 1 670m, 1 590s, and 1 574s cm^{-1} indicative of dithiocarbonato-ligands. Confirmation of this formulation was obtained from the high conductivity value of (5) in nitromethane, characteristic of a 1 : 2 electrolyte,[15] and the reactions of (5) with various Lewis bases L (L = PPh_3, PMe_2Ph, or $\frac{1}{2}Ph_2PC_2H_4PPh_2$) which readily gave $[PtL_2(S_2CO)]$ {*cf.* the reaction of $[Pt(S_2CS)_2]^{2-}$ with $PMePh_2$ giving $[Pt(PMePh_2)_2(S_2CS)]$ [16]}. The same complexes were obtained



SCHEME 2 Alternative intermolecular mechanism for conversion of $[M(S_2COR)_3]^-$ into $[M(S_2CO)(S_2COR)]^-$

[11] See J. M. C. Alison and T. A. Stephenson, *J.C.S. Dalton*, 1973, 254 and refs. therein.
[12] J. Powell and A. W. L. Chan, *J. Organometallic Chem.*, 1972, **35**, 203.
[13] D. J. Cole-Hamilton and T. A. Stephenson, *J.C.S. Dalton*, 1974, 1818.
[14] J. M. Burke and J. P. Fackler, jun., *Inorg. Chem.*, 1972, **11**, 2744.
[15] R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 1964, 4587.
[16] J. P. Fackler, jun., and W. C. Seidel, *Inorg. Chem.*, 1969, **8**, 1631.

from the reactions of $[AsPh_4][Pt(S_2CO)(S_2COEt)]$ and excess of L.

For $[Pt(S_2COMe)_2]$ and $K[S_2COMe]$ (1 : 5 molar ratio), the only product isolated was the bis(dithiocarbonato)-anion (5). However, when 1 : 1 or 1 : 2 molar ratios were used, orange-yellow crystals of $[AsPh_4][Pt(S_2CO)(S_2COMe)]$ were deposited. Presumably, the inability to isolate the $[Pt(S_2COCH_2Ph)_3]^-$ and $[Pt(S_2COMe]^-$ anions is a reflection of the great stability of the benzylcarbonium ion generated in the transition state in the mechanism shown in Scheme 1 and of the high nucleophilicity of the $[S_2COMe]^-$ group. The final step in formation of (5) is probably intermolecular attack of $[S_2COR]^-$ on the co-ordinated alkoxy-group in $[Pt(S_2CO)(S_2COR)]^-$.

Finally, reactions of $[Pt(S-S)_2]$ ($S-S^- = [S_2PMe_2]^-$, $[S_2PPh_2]^-$, or $[S_2CNEt_2]^-$) with Na[S-S] under similar conditions gave only starting materials and, unlike the recent synthesis of $[NBu_4][Zn(S_2CNR_2)_2(S_2CNMe_2)]$ (R = Me or Et) by reaction of $[Zn(S_2CNR_2)_2]$ and $[NBu_4][S_2CNMe_2]$,[17] no reaction was observed between $[Pd(S_2CNEt_2)_2]$ and $[NBu_4][S_2CNEt_2]$ or $[Pt(S_2CNMe_2)_2]$ and $[NBu_4][S_2CNMe_2]$.

EXPERIMENTAL

Microanalyses were by A. Bernhardt, West Germany, and the University of Edinburgh Chemistry Department. Infrared spectra were recorded in the 250—4 000 cm^{-1} region on Perkin-Elmer 225 and 457 grating spectrometers using Nujol and hexachlorobutadiene mulls on caesium iodide plates. Solution spectra were run in potassium bromide cells. Conductivity measurements were made on a Portland Electronics 310 conductivity bridge in nitromethane at 298 K. Hydrogen-1 n.m.r. spectra were obtained on a Varian Associates HA-100 spectrometer equipped with a variable-temperature probe. Electronic spectra were recorded on a Unicam SP 800 spectrophotometer using unmatched silica cells. Melting points were determined with a Köfler hot-stage microscope and are uncorrected.

Potassium tetrachloroplatinate(II) and palladium(II) chloride (Johnson Matthey Ltd.), $[AsPh_4]Cl\cdot HCl$ (Koch Light Ltd.), PPh_3 and $K[S_2COEt]$ (B.D.H.) were used as obtained. The salts $K[S_2COR]$ (R = Me, Pr^i, or CH_2Ph) were synthesised as described in ref. 2*a* and $[M(S_2COR)_2]$ (M = Pd or Pt) as described earlier.[18] Operations were carried out under nitrogen and in degassed solvents.

Tetraphenylarsonium Tris(O-ethyl dithiocarbonato)platinate(II) (1).—An excess of $K[S_2COEt]$ (0.50 g) was added to $[Pt(S_2COEt)_2]$ (0.20 g) in acetone (10 cm^3) and the resulting yellow solution was gently warmed and then immediately filtered into a methanolic solution (20 cm^3) of $[AsPh_4]Cl\cdot HCl$ (0.25 g). On cooling, yellow *needles* of the product formed which were filtered off, washed with water, methanol, benzene, and diethyl ether, m.p. 112 °C (Found: C, 41.9; H, 3.8; S, 20.2. Calc. for $C_{33}H_{35}AsO_3PtS_6$: C, 42.1; H, 3.7; S, 20.4%), Λ (1×10^{-3} mol dm^{-3}) in $MeNO_2$ = 59.5 S cm^2 mol^{-1}, ν(C–O) (S_2COEt^-) at 1 285s and 1 200s cm^{-1} (mull).

Tetraphenylarsonium tris(O-isopropyl dithiocarbonato)platinate(II) (2) was similarly prepared from $K[S_2COPr^i]$ and $[Pt(S_2COPr^i)_2]$, m.p. 117—119 °C (Found: C, 43.9; H, 4.2; S, 19.3. Calc. for $C_{36}H_{41}AsO_3PtS_6$: C, 43.9; H, 4.2; S, 19.5%), Λ(1×10^{-3} mol dm^{-3}) in $MeNO_2$ = 51.0 S cm^2 mol^{-1}, ν(C–O) (S_2COPr^{i-}) at 1 280s and 1 210s cm^{-1} (mull), 1 280s and 1 205s cm^{-1} (in CH_2Cl_2). *Tetraphenylarsonium tris(O-ethyl dithiocarbonato)palladate*(II) was prepared in like manner using methanol instead of acetone. The very small amount of buff *product* was characterised by i.r. spectroscopy.

Tetraphenylarsonium (Dithiocarbonato)(O-ethyl dithiocarbonato)platinate(II) (3).—This complex was formed as orange-yellow crystals by the recrystallisation of $[AsPh_4][Pt(S_2COEt)_3]$ from CH_2Cl_2 or $CHCl_3$ or by leaving methanol–diethyl ether or acetone solutions of $[AsPh_4][Pt(S_2COEt)_3]$ to stand for 24 h, m.p. 141 °C (Found: C, 42.5; H, 3.1; S, 15.9. Calc. for $C_{28}H_{25}AsO_2PtS_4$: C, 42.5; H, 3.2; S, 16.2%), Λ(1×10^{-3} mol dm^{-3}) in $MeNO_2$ = 57.5 S cm^2 mol^{-1}, ν(C–O) (S_2COEt^-) at 1 250s cm^{-1}, ν(C=O) (S_2CO^{2-}) at 1 678m, 1 600s, and 1 575m cm^{-1} (mull).

Tetraphenylarsonium (dithiocarbonato)(O-isopropyl dithiocarbonato)platinate(II) (4) was similarly prepared from $[AsPh_4][Pt(S_2COPr^i)_3]$, m.p. 122—124 °C (Found: C, 42.8; H, 3.2; S, 15.7. Calc. for $C_{29}H_{27}AsO_2PtS_4$: C, 43.2; H, 3.3; S, 15.9%) Λ(1×10^{-3} mol dm^{-3}) in $MeNO_2$ = 43.4 S cm^2 mol^{-1}, ν(C–O) (S_2COPr^{i-}) at 1 270s and 1 210s cm^{-1}, ν(C=O) (S_2CO^{2-}) at 1 680w, 1 600s, and 1 575m cm^{-1} (mull).

Tetraphenylarsonium (Dithiocarbonato)(O-methyl dithiocarbonato)platinate(II).—The complex $[Pt(S_2COMe)_2]$ and $K[S_2COMe]$ (1 : 1 or 1 : 2 molar ratio) were dissolved in acetone and the resulting yellow solution was filtered into a methanolic solution of $[AsPh_4]Cl\cdot HCl$. Potassium chloride was then filtered off and the filtrate evaporated almost to dryness to produce orange *crystals* of the product which were filtered off and washed with water, methanol, and diethyl ether, m.p. 136—138 °C (Found: C, 41.5; H, 3.1; S, 16.6. Calc. for $C_{27}H_{23}AsO_2PtS_4$: C, 41.7; H, 3.0; S, 16.5%), Λ(1×10^{-3} mol dm^{-3}) in $MeNO_2$ = 54.2 S cm^2 mol^{-1}, ν(C–O) (S_2COMe^-) at 1 270s cm^{-1}, ν(C=O) (S_2CO^{2-}) at 1 680s, 1 600s, and 1 575(sh) cm^{-1} (mull).

Tetraphenylarsonium Bis(dithiocarbonato)platinate(II) (5).—The complex $[Pt(S_2COCH_2Ph)_2]$ and $K[S_2COCH_2Ph]$ (1 : 1 to 1 : 5 molar ratio) were dissolved with heating in acetone. The hot solution was then filtered into a methanolic solution of $[AsPh_4]Cl\cdot HCl$ to give a yellow *precipitate* on cooling. This was filtered off and washed with water, methanol, and diethyl ether, m.p. 255—258 °C (decomp.) (Found: C, 52.1; H, 3.9; S, 11.4. Calc. for $C_{50}H_{40}As_2O_2PtS_4$: C, 52.4; H, 3.5; S, 11.2%), Λ(1×10^{-3} mol dm^{-3}) in $MeNO_2$ = 137.6 S cm^2 mol^{-1}, ν(C=O) (S_2CO^{2-}) at 1 690(sh), 1 670m, 1 590s, and 1 574s cm^{-1} (mull). The same product was obtained from the reaction of $[Pt(S_2COMe)_2]$ and a fivefold excess of $K[S_2COMe]$.

Tetraphenylarsonium (Dithiocarbonato)(O-ethyl dithiocarbonato)palladate(II).—This complex was prepared from $[Pd(S_2COEt)_2]$, $K[S_2COEt]$, and $[AsPh_4]Cl\cdot HCl$ using the same method as used for $[AsPh_4][Pt(S_2COEt)_3]$. The product precipitated as orange-yellow *crystals* which were washed and dried as before, m.p. 155 °C (Found: C, 47.8, H, 3.6, S, 18.3. Calc. for $C_{28}H_{25}AsO_2PdS_4$: C, 47.9, H, 3.6, S, 18.3%), ν(C–O) (S_2COEt^-) at 1 250s cm^{-1}, ν(C=O) (S_2CO^{2-}) at 1 678m, 1 600s, and 1 575m cm^{-1} (mull).

Dithiocarbonatobis(triphenylphosphine)platinum(II).—The salt $[AsPh_4]_2[Pt(S_2CO)_2]$ and excess of PPh_3 were heated under reflux in dichloromethane for 3 h to give a pale yellow

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[18] G. W. Watt and B. J. McCormick, *J. Inorg. Nuclear Chem.*, 1965, **27**, 898.

solution. Removal of solvent gave a yellow oil which yielded a white *solid* on addition of diethyl ether. This was filtered off and washed with water, methanol, and diethyl ether, m.p. 258—259 °C (Found: C, 54.9; H, 3.9. Calc. for $C_{37}H_{30}OP_2PtS_2$: C, 54.8; H, 3.7%), ν(C=O) (S_2CO^{2-}) at 1 690m and 1 615s cm^{-1} (mull). The same product was obtained from the reaction of [$AsPh_4$][Pt(S_2CO)(S_2COEt)] and excess of PPh_3 in dichloromethane.

Dithiocarbonatobis(dimethylphenylphosphine)platinum(II).—Excess of PMe_2Ph was added to a suspension of $[AsPh_4]_2$-$[Pt(S_2CO)_2]$ in dichloromethane and the mixture shaken for *ca.* 1 h. The resulting pale yellow solution was filtered to remove unchanged starting material and the filtrate was concentrated. Addition of diethyl ether then gave a white *solid* which was filtered off and washed with water, methanol, and diethyl ether (Found: C, 36.6; H, 4.1. Calc. for $C_{17}H_{22}OP_2PtS_2$: C, 36.2; H, 3.9%), ν(C=O) (S_2CO^{2-}) at 1 670br and 1 595m cm^{-1} (mull). Similarly, [1,2-*bis(diphenylphosphino)ethane*](*dithiocarbonato*)*platinum*(II) was obtained from $[AsPh_4]_2[Pt(S_2CO)_2]$ and $Ph_2PC_2H_4PPh_2$, m.p. 262—265 °C (Found: C, 47.2; H, 3.5. Calc. for $C_{27}H_{24}OP_2PtS_2$: C, 47.3; H, 3.5%), ν(C=O) (S_2CO^{2-}) at 1 690s and 1 620s cm^{-1} (mull).

Crystallographic calculations were made using the '*X*-Ray 74' system.[19]

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[19] '*X*-Ray' Program System, Computer Science Center, University of Maryland, Technical Report TR 192, version of January 1974.