Metal Complexes of Sulphur Ligands. Part 13.[1] Reaction of Dichloro-(η-cyclo-octa-1,5-diene)-palladium and -platinum Complexes with some Sulphur-containing Nucleophiles

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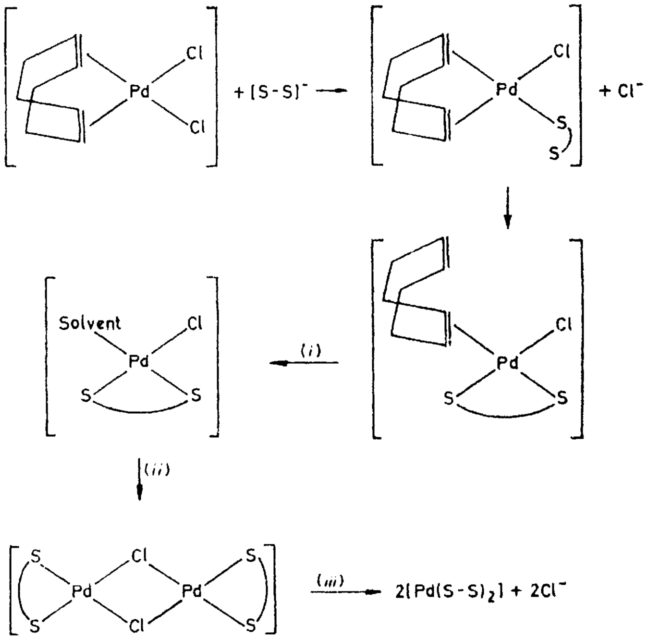
Reaction of $[Pd(C_8H_{12})Cl_2]$ (C_8H_{12} = cyclo-octa-1,5-diene) with equimolar amounts of various alkali-metal dithioacid salts ($[S{-}S^-] = [S_2CNEt_2]^-$, $[S_2COEt]^-$, or $[S_2PMe_2]^-$) gives the chloride-bridged dimers $[\{PdCl(S{-}S)\}_2]$ (1). Metathetical reactions of these give the corresponding $[\{PdX(S_2CNEt_2)\}_2]$ ($X = Br^-$ or $[SPh]^-$). Cleavage of these complexes with Lewis bases gives $[PdCl(S{-}S)L]$ (2; $L = PPh_3$, $[S{-}S^-] = [S_2CNEt_2]^-$, $[S_2COEt]^-$, or $[S_2PMe_2]^-$; $L = AsPh_3$, $SbPh_3$, or C_5H_5N, $[S{-}S^-] = [S_2CNEt_2]^-$), and with M′Cl–HCl, $M'[PdCl_2(S_2CNEt_2)]$ (3; $M' = [AsPh_4]^+$ or $[PPh_3(CH_2Ph)]^+$) are formed. Reaction of (1; $[S{-}S]^- = [S_2CNEt_2]^-$) with $Na[S_2PMe_2]\cdot 2H_2O$ gives $[Pd(S_2CNEt_2)(S_2PMe_2)]$ (4a) which partially disproportionates in solution to $[Pd(S_2CNEt_2)_2]$ and $[Pd(S_2PMe_2)_2]$. Complex (4a) reacts with PPh_3 to give $[Pd(PPh_3)(S_2CNEt_2)(S_2PMe_2)]$ (5a) which possesses bidentate $[S_2CNEt_2]^-$ and unidentate $[S_2PMe_2]^-$ groups. In contrast, reaction of $[Pt(C_8H_{12})Cl_2]$ and $Na[S_2CNEt_2]\cdot 3H_2O$ (1 : 1 mol ratio) gives $[\{PtCl(S_2CNEt_2)\}_2C_8H_{12}]$ (6a) which in turn reacts with PPh_3 to give $[PtCl(PPh_3)(S_2CNEt_2)]$ and with excess of PPh_3 to give $[Pt(PPh_3)_2(S_2CNEt_2)]Cl\cdot H_2O$. Reaction of (6a) and $Na[S_2PMe_2]\cdot 2H_2O$ gives $[Pt(S_2CNEt_2)(S_2PMe_2)]$ (4b) which on treatment with PPh_3 gives $[Pt(PPh_3)(S_2CNEt_2)(S_2PMe_2)]$ (5b).

THE activation of olefins towards nucleophilic attack by co-ordination to palladium(II) and platinum(II) is now well established and of commercial importance. Extensive studies on reactions of $[M(diene)Cl_2]$ complexes (M = Pd or Pt) with various nucleophiles containing oxygen- or nitrogen-donor atoms (*e.g.* [OR] , $[O_2CR]^-$, NRH_2, *etc.*) show that, usually, attack on one of the co-ordinated double bonds occurs to give substituted alkenyl complexes.[2] In contrast, in the only previously reported reaction of $[M(diene)Cl_2]$ complexes with sulphur-containing nucleophiles, reaction of $[Pt(C_7H_8)Cl_2]$ with $Ag[SCF_3]$ gives $[Pt(C_7H_8)(SCF_3)_2]$ whereas with $[Pd(C_7H_8)Cl_2]$ the nortricyclyl derivatives $[Pd_2(C_7H_8SCF_3)_2Cl_2]$ and $[Pd(C_7H_8SCF_3)_2Cl(SCF_3)]$ are obtained.[3]

In this paper, we report the full results[4] of reactions between $[M(C_8H_{12})Cl_2]$ (M = Pd or Pt; C_8H_{12} = cyclo-octa-1,5-diene) and various dithioacid anions where quite different behaviour from that previously observed with other nucleophiles has been found.

RESULTS AND DISCUSSION

(*a*) *Palladium Complexes*.—Addition of an acetone solution of $Na[S_2CNEt_2]\cdot 3H_2O$ to $[Pd(C_8H_{12})Cl_2]$ in methylene chloride (1 : 1 mol ratio) gave an orange solution from which an orange solid of empirical formula $[\{PdCl(S_2CNEt_2)\}_n]$ was isolated.† With excess of $Na[S_2CNEt_2]\cdot 3H_2O$, the well known[6] $[Pd(S_2CNEt_2)_2]$ was obtained. Molecular-weight measurements in chloroform indicated that $n = 2$ and thus this complex was formulated with the square-planar chloride-bridged structure (1). Further evidence for this formulation came from the far-i.r. spectrum which showed a strong band at 300 cm^{-1} [bridging ν(PdCl)],[7] not present in $[\{PdBr(S_2CNEt_2)\}_2]$ which can be prepared either by reaction of $[PdBr_2(C_8H_{12})]$ with $Na[S_2CNEt_2]\cdot 3H_2O$ (1 : 1 mol ratio) or by reaction of $[\{PdCl(S_2CNEt_2)\}_2]$ with excess of lithium bromide. Similarly, the chloride



(1)

SCHEME Mechanism of formation of $[\{PdCl(S{-}S)\}_2]$ ($[S{-}S]^- = [S_2CNEt_2]^-$, $[S_2COEt]^-$, or $[S_2PMe_2]^-$). (*i*) $- C_8H_{12}$; (*ii*) Dimerisation; (*iii*) excess of $[S{-}S]^-$

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† Fackler[5] very recently synthesised the complex $[\{PdCl(S_2CNBu^i_2)\}_2]$ both by reaction of $[Pd(S_2CNBu^i_2)_2]$ with $K_2[PdCl_4]$ (1 : 1 mol ratio) in aqueous acetone and by direct reaction of $Na[S_2CNBu^i_2]\cdot 3H_2O$ with $K_2[PdCl_4]$ (< 1 : 1 mol ratio) in aqueous acetone.

[1] Part 12, M. C. Cornock and T. A. Stephenson, *J.C.S. Dalton*, 1977, 501.

[2] For detailed references see (*a*) F. R. Hartley, 'The Chemistry of Platinum and Palladium,' Applied Science Publishers, 1973, p. 386; (*b*) P. M. Henry, *Adv. Organometallic Chem.*, 1973, **13**, 363; (*c*) M. Green, *M.T.P. Internat. Rev. Sci. Inorg. Chem. Ser.* 1, 1972, **6**, 183.

[3] R. B. King and A. Efraty, *Inorg. Chem.*, 1971, **10**, 1376.

[4] Preliminary communication, M. C. Cornock, R. C. Davis, D. Leaver, and T. A. Stephenson, *J. Organometallic Chem.*, 1976, **107**, C43.

[5] J. P. Fackler, jun., personal communication.

[6] C. K. Jørgensen, *J. Inorg. Nuclear Chem.*, 1962, **24**, 1571.

[7] J. R. Allkins and P. J. Hendra, *J. Chem. Soc.* (*A*), 1967, 1325.

bridges in (1) were readily exchanged for $[SPh]^-$ by treatment with Na[SPh] to give $[\{Pd(SPh)(S_2CNEt_2)\}_2]$ The ^1H n.m.r. spectra of these complexes (Table 1), which showed magnetically equivalent ethyl groups, also support the proposed structure (1). However, with $[Pd(C_8H_{12})Cl_2]$ and $Na[S_2CNMe_2]\cdot 2H_2O$, the only product isolated was $[Pd(S_2CNMe_2)_2]$ which can almost certainly be attributed to the high insolubility of $[Pd(S_2CNMe_2)_2]$.*

TABLE 1

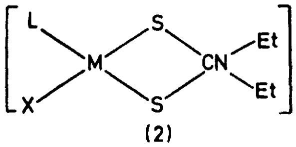
Hydrogen-1 n.m.r. data in $CDCl_3$ at 301 K for some palladium(II) and platinum(II) dithioacid complexes

Complex	$\delta \pm 0.01$ p.p.m.[a]		
	Dithio ligand		
	CH_3[b]	CH_2[b]	Other ligand resonances
$[\{PdCl(S_2CNEt_2)\}_2]$	1.33 (t)	3.69 (q)[c]	
$[\{PdCl(S_2COEt)\}_2]$	1.53 (t)	4.67 (q)	
$[\{PdBr(S_2CNEt_2)\}_2]$	1.33 (t)	3.70 (q)[c]	
$[\{Pd(SPh)(S_2CNEt_2)\}_2]$	1.18 (t)	3.58 (q)	7.00—8.00 (m)[d]
$[PdCl(PPh_3)(S_2CNEt_2)]$	1.24 (t), 1.18 (t)	3.71 (q), 3.56 (q)	7.38—7.80 (m)[d]
$[Pd(AsPh_3)Cl(S_2CNEt_2)]$	1.13 (t), 1.07 (t)	3.60 (q), 3.46 (q)	7.38—7.80 (m)[d]
$[PdCl(NC_5H_5)(S_2CNEt_2)]$	1.29 (t), 1.28 (t)	3.69 (q), 3.66 (q)	7.40 (t), 7.82 (t), 8.82 (d)[e]
$[PdCl(PPh_3)(S_2COEt)]$	1.47 (t)	4.67 (q)	7.00—8.00 (m)[d]
$[Pd(PPh_3)(SPh)(S_2CNEt_2)]$	1.14 (t), 1.12 (t)	3.61 (q), 3.59 (q)	6.95—7.80 (m)[d]
$[PdCl(PPh_3)(S_2PMe_2)]$	2.03 (d)[f]		7.20—7.80 (m)[d]
$[PPh_3(CH_2Ph)][PdCl_2(S_2CNEt_2)]$	1.15 (t)	3.54 (q)	5.32 (d),[g] 7.00—7.80 (m)[d]
$[AsPh_4][PdCl_2(S_2CNEt_2)]$	1.17 (t)	3.53 (q)	7.30—7.90 (m)[d]
$[Pd(S_2CNEt_2)(S_2PMe_2)]$[h]	1.25 (t), 2.12 (d)[f]	3.65 (q)	
$[Pd(PPh_3)(S_2CNEt_2)(S_2PMe_2)]$	1.27 (t), 1.19 (t), 1.96 (d)[f]	3.70[i]	7.00—8.00 (m)[d]
$[PtCl(PPh_3)(S_2CNEt_2)]$	1.27 (t), 1.17 (t)	3.60 (q), 3.45 (q)	7.20—7.80 (m)[d]
$[Pt(PPh_3)_2(S_2CNEt_2)]Cl\cdot H_2O$	1.22 (t)	3.60 (q)	7.00—7.50 (m),[d] 2.50 (s)[c]
$[Pt(S_2CNEt_2)(S_2PMe_2)]$	1.30 (t), 2.06 (d)[f]	3.55 (q)	
$[Pt(PPh_3)(S_2CNEt_2)(S_2PMe_2)]$	1.30 (t), 1.17 (t), 1.90 (d)[f]	3.67 (q), 3.47 (q)	7.20—7.70 (m)[d]

[a] s = Singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. [b] $^2J(CH_3CH_2)$ 7.0 Hz. [c] Broad. [d] Phenyl resonances. [e] Pyridine resonances. [f] $^2J(PH)$ 13.0 Hz. [g] Methylene, $^2J(PH)$ 14.0 Hz. [h] Solution also gave resonances at 2.02 (d) $\{[Pd(S_2PMe_2)_2]\}$ and at 1.27 (t) and 3.71 (q) p.p.m. $\{[Pd(S_2CNEt_2)_2]\}$. [i] Very broad due to superimposition of some $[Pd(PPh_3)(S_2CNEt_2)_2]$.

The analogous $[\{PdCl(S_2COEt)\}_2]$ was similarly prepared by reaction of $[Pd(C_8H_{12})Cl_2]$ and $K[S_2COEt]$ (1 : 1 mol ratio). However, unlike $[\{PdCl(S_2CNEt_2)\}_2]$, this orange-red solid slowly turned brown on standing and rapidly decomposed when heated in methylene chloride. Reaction of $[Pd(C_8H_{12})Cl_2]$ with equimolar amounts of $Na[S_2PMe_2]\cdot 2H_2O$ in CH_2Cl_2–Me_2CO also gave an immediate red solution but this rapidly turned brown precipitating an intractable brown material of unknown composition. However, although attempts to isolate a compound from the red solution were unsuccessful, reactions of the red solution (see below) strongly suggest that $[\{PdCl(S_2PMe_2)\}_2]$ is initially formed. With excess of $Na[S_2PMe_2]\cdot 2H_2O$, $[Pd(S_2PMe_2)_2]$ [9] was readily isolated. In the Scheme, the probable mechanism of formation of these chloride-bridged dimers is outlined. Presumably, the difference in behaviour compared to oxygen and nitrogen nucleophiles is the class (b) (soft-base) character of the sulphur ligands and the consequent affinity for Pd^{II}.

In common with other halide-bridged dimers, *e.g.* $[\{Rh(CO)_2Cl\}_2]$,[10] these complexes were excellent precursors for a variety of reactions. For example, the chloride bridges in $[\{PdCl(S_2CNEt_2)\}_2]$ were readily cleaved by a wide range of Lewis basis (L) to give the monomeric $[PdCl(S_2CNEt_2)L]$ (L = PPh_3, $AsPh_3$, $SbPh_3$, or C_5H_5N). As reported elsewhere, these complexes (for L = tertiary phosphine) can also be synthesised by reaction of $[\{PdCl_2(PR'_3)\}_2]$ with either $SnMe_2Cl(S_2CNR_2)$ [11] or $Na[S_2CNR_2]\cdot xH_2O$.[1] However, with weaker bases in the palladium co-ordination sphere, only $[Pd(S_2CNR_2)_2]$ were formed by this route. As found earlier for $[PdX(PMe_2Ph)(S_2CNEt_2)]$ (X = Cl, Br, or I),[1] all these complexes showed two magnetically inequivalent ethyl groups at ambient temperature in their ^1H n.m.r. spectra (Table 1) confirming structure (2).



(2)

M = Pd X = Cl, L = PPh_3, $AsPh_3$, $SbPh_3$, or C_5H_5N ; X = SPh, L = PPh_3

M = Pt X = Cl, L = PPh_3

Carbon mono-oxide also reacted with $[\{PdCl(S_2CNEt_2)\}_2]$ in methylene chloride to give a yellow solution. Unfortunately, on solvent removal, only the original orange dimer was isolated. Attempts to record the ^1H n.m.r. spectrum of the expected $[PdCl(CO)(S_2CNEt_2)]$ in $CDCl_3$ even under 1 atm † of CO also failed, presumably due to ready loss of CO and reformation of (1).

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* The complex $[\{PdBr(S_2CNMe_2)\}_2]$ can however by synthesised by reaction of (dimethyldithiocarbamato)(2-phenylazophenyl)palladium(II) with bromine, the 2-phenylazophenyl ligand being removed as 2-bromoazobenzene.[8]

† Throughout this paper: 1 atm = 101 325 Pa.

[8] R. C. Davis, Ph.D. Thesis, Edinburgh University, 1976.

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

[10] L. M. Vallarino, *Inorg. Chem.*, 1965, **4**, 161; D. N. Lawson and G. Wilkinson, *J. Chem. Soc.*, 1965, 1900.

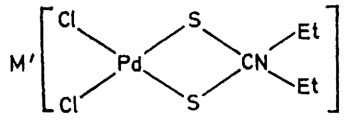
[11] N. Sonoda and T. Tanaka, *Inorg. Chim. Acta*, 1975, **12**, 261.

Reaction of $[\{Pd(SPh)(S_2CNEt_2)\}_2]$ with PPh_3 gave the red, crystalline, monomeric $[Pd(PPh_3)(SPh)(S_2CNEt_2)]$ whose ^1H n.m.r. spectrum shows the magnetically inequivalent ethyl groups expected for a structure of type (2). Earlier, Andrews *et al.*[12] synthesised $[\{M(SBu^t)(S_2CNEt_2)\}_2]$ (M = Pd or Pt) by reaction of $[\{M(SBu^t)(S_2CSBu^t)\}_2]$ with NEt_2H.[13] Reaction of these complexes with $PMePh_2$ was reported to give $[\{M(PMePh_2)(SBu^t)(S\text{-}S)\}_n]$ originally tentatively formulated from ^1H n.m.r. studies (since solid materials could not be isolated) as five-co-ordinate dimers [13] but recently reformulated [5] as four-co-ordinate monomers of structure (2).

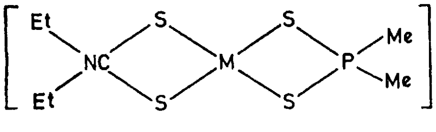
Reaction of $[\{PdCl(S_2COEt)\}_2]$ with excess of PPh_3 in methylene chloride gave a yellow solution from which the yellow solid $[PdCl(PPh_3)(S_2COEt)]$ was isolated. Treatment of the red solution {formed by reaction of $[Pd(C_8H_{12})Cl_2]$ and $Na[S_2PMe_2]\cdot 2H_2O$} with excess of PPh_3 gave an orange solution from which an orange crystalline solid was obtained. The i.r. spectrum showed the presence of PPh_3 and a band at 580 cm^{-1} assigned to a bidentate $[S_2PMe_2]^-$ group.[9] The complex analysed for $[PdCl(PPh_3)(S_2PMe_2)]$ which strongly suggests that the red solution contains $[\{PdCl(S_2PMe_2)\}_2]$.

Hence, the order of stability of the chloride-bridged dimers is $[\{PdCl(S_2CNEt_2)\}_2] > [\{PdCl(S_2COEt)\}_2] > [\{PdCl(S_2PMe_2)\}_2]$ and this can be correlated with the established order of Pd–S bond strengths, *i.e.* $[S_2CNEt_2]^- > [S_2COEt]^- > [S_2PMe_2]^-$.[9]

A typical reaction of halide-bridged dimers is reaction with halide ion to give anionic complexes, *e.g.* $[NMe_4][Rh(CO)_2Cl_2]$ from reaction of $[\{Rh(CO)_2Cl\}_2]$ and $[NMe_4]Cl$.[10] Similarly, reaction of $[\{PdCl(S_2CNEt_2)\}_2]$ with M′Cl–HCl in acetone gave $M'[PdCl_2(S_2CNEt_2)]$ (M′ = $[AsPh_4]^+$ or $[PPh_3(CH_2Ph)]^+$). The ^1H n.m.r. spectrum of this anion consisted of a single triplet (CH_3) and quartet (CH_2) pattern (Table 1) and its i.r. spectrum showed ν(PdCl) at 300 and 275 cm^{-1}, consistent with structure (3). An attempt was made to generate the complex $[AsPh_4][Pd(S_2CNEt_2)_3]$ by reaction of $[AsPh_4][PdCl_2(S_2CNEt_2)]$ with $Na[S_2CNEt_2]\cdot 3H_2O$ but the only product was $[Pd(S_2CNEt_2)_2]$.



(3) M′ = $[AsPh_4]^+$ or $[PPh_3(CH_2Ph)]^+$



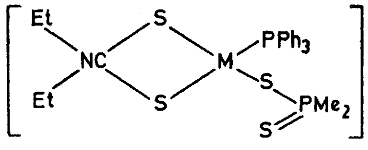
(4a) M = Pd
(4b) M = Pt

Since the chloride bridges in $[\{PdCl(S_2CNEt_2)\}_2]$ can be cleaved with excess of $[S_2CNEt_2]^-$ ion to give $[Pd(S_2CNEt_2)_2]$, the dimer was treated with $Na[S_2PMe_2]\cdot 2H_2O$ in an attempt to synthesise $[Pd(S_2CNEt_2)(S_2PMe_2)]$ (4a). However, the ^1H n.m.r. spectrum in $CDCl_3$ of the orange-yellow product contained more signals than expected for (4a). Comparison with the ^1H n.m.r. spectra of $[Pd(S_2CNEt_2)_2]$ and $[Pd(S_2PMe_2)_2]$ showed that both these products were present in solution. Hence, the remaining signals centred at 1.25 (t), 2.12 (d), and 3.65 (q) p.p.m. (Table 1) were assigned to (4a). Support for this conclusion came from the observation that mixing equimolar amounts of $[Pd(S_2CNEt_2)_2]$ and $[Pd(S_2PMe_2)_2]$ in $CDCl_3$ at 301 K gave the same ^1H n.m.r. spectrum. The equilibrium shown in equation (1) was established after *ca.* 1 h and lies predominantly to the right-hand side.

$$[Pd(S_2CNEt_2)_2] + [Pd(S_2PMe_2)_2] \rightleftharpoons 2[Pd(S_2CNEt_2)(S_2PMe_2)] \quad (1)$$

Similarly, Fackler [5] recently showed that mixing $[Ni\{S_2CN(CH_2Ph)_2\}_2]$ and $[Ni(S_2CNBu^i{}_2)_2]$ in $CDCl_3$ produced extra resonances in the ^1H n.m.r. spectrum ascribed to the mixed complex $[Ni\{S_2CN(CH_2Ph)_2\}(S_2CNBu^i{}_2)]$. In contrast, the ^1H n.m.r. spectrum of a mixture of $[Pt(S_2CNEt_2)_2]$ and $[Pt(S_2PMe_2)_2]$ in $CDCl_3$ at 301 K showed no evidence for the formation of $[Pt(S_2CNEt_2)(S_2PMe_2)]$, which can again be attributed to the decreased lability of Pt–S compared to Pd–S and Ni–S bonds. In accordance with this, $[Pt(S_2CNEt_2)(S_2PMe_2)]$ (4b) (see later) does not disproportionate at ambient temperature and showed the expected three signals centred at 1.30 (t), 2.06 (d), and 3.55 (q) p.p.m. (Table 1).

Addition of an excess of PPh_3 to a suspension of ‘ $[Pd(S_2CNEt_2)(S_2PMe_2)]$ ’ in benzene produced a yellow solid analysing closely for $[Pd(PPh_3)(S_2CNEt_2)(S_2PMe_2)]$ (5a). The i.r. spectrum of (5a) was virtually identical with that of $[Pt(PPh_3)(S_2CNEt_2)(S_2PMe_2)]$ (5b) indicating unidentate $[S_2PMe_2]^-$ [$\nu(PS_2)$ at 605 cm^{-1}] [9] and bidentate $[S_2CNEt_2]^-$ [ν(CN) at 1 515 cm^{-1}] [14] co-ordination. However, although the ^1H n.m.r. spectrum of the platinum complex was completely consistent with structure (5) (Table 1), that of the palladium complex contained small additional resonances superimposed on some of those of (5a). These appear to correspond to



(5a) M = Pd
(5b) M = Pt

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[12] J. A. M. Andrews, J. P. Fackler, jun., and D. Coucouvanis, *Inorg. Chem.*, 1972, **11**, 494.

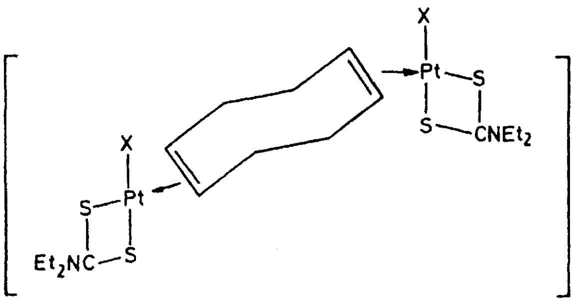
[13] J. A. M. Andrews, Ph.D. Thesis, Case Western Reserve University, 1971.

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

$[Pd(PPh_3)(S_2CNEt_2)_2]$ and $[Pd(PPh_3)(S_2PMe_2)_2]$,[9] suggesting partial disproportionation of (5a) occurs in solution [equation (2)].

$$2[Pd(PPh_3)(S_2CNEt_2)(S_2PMe_2)] \rightleftharpoons [Pd(PPh_3)(S_2CNEt_2)_2] + [Pd(PPh_3)(S_2PMe_2)_2] \quad (2)$$

(*b*) *Platinum Complexes.*—Addition of an acetone solution of $Na[S_2CNEt_2]\cdot 3H_2O$ to $[Pt(C_8H_{12})Cl_2]$ in methylene chloride (1 : 1 mol ratio) gave an immediate yellow solution and a white precipitate (NaCl), and after *ca.* 30 min a pale yellow solid was precipitated. This was too insoluble for n.m.r. spectroscopy but the i.r. spectrum showed the presence of bidentate $[S_2CNEt_2]^-$ groups and a band at 310 cm^{-1} which could be assigned to a $\nu(PtCl)$ stretching mode. Investigation of the mother liquor showed it to be a mixture of $[Pt(S_2CNEt_2)_2]$ and $[Pt(C_8H_{12})Cl_2]$. On the basis of analytical data, the insoluble yellow material was formulated as $[\{PtCl(S_2CNEt_2)\}_2C_8H_{12}]$ (6a). An analogous, insoluble, yellow complex $[\{PtMe(S_2CNEt_2)\}_2C_8H_{12}]$ (6b) * was recently prepared by Manzer[15] by the reaction of $[PtMe(C_8H_{12})(HOMe)][PF_6]$ with an equimolar amount of $Na[S_2CNEt_2]\cdot 3H_2O$. This then reacts with PPh_3 and $AsPh_3$ (L) to give the soluble neutral complexes $[PtMe(L)(S_2CNEt_2)]$ plus free cyclo-octa-1,5-diene which is consistent with the behaviour expected for a complex with structure (6b).[15] These complexes were also prepared by reaction of $[PtMe(C_8H_{12})L][PF_6]$ with an equimolar amount of $Na[S_2CNEt_2]\cdot 3H_2O$.[15] Similarly, reaction of $[\{PtCl(S_2CNEt_2)\}_2C_8H_{12}]$ with PPh_3 (1 : 1 mol ratio) readily gave $[PtCl(PPh_3)(S_2CNEt_2)]$ and free C_8H_{12} was also detected supporting our formulation (6a). As expected, the ^1H n.m.r. spectrum of the latter complex showed magnetically inequivalent ethyl groups at ambient temperature. With excess of PPh_3 in methylene chloride, $[Pt(PPh_3)_2(S_2CNEt_2)]Cl\cdot H_2O$ was isolated and this was identical in spectroscopic properties to the product obtained earlier by prolonged reaction of $[Pt(S_2CNEt_2)_2]$ with an excess of PPh_3 in methylene chloride.[17] The related $[Pt(PMe_2Ph)_2(S_2CNEt_2)]Cl\cdot H_2O$ has also been prepared by reaction of $[PtCl_2(PMe_2Ph)_2]$ with $Na[S_2CNEt_2]\cdot 3H_2O$.†



(6a) X = Cl
(6b) X = Me

Hence, unlike reactions of $[M(diene)Cl_2]$ (M = Pd or Pt) with various oxygen- and nitrogen-containing nucleophiles which give the same type of product, their behaviour with $[S_2CNEt_2]^-$ is quite different giving $[\{PdCl(S_2CNEt_2)\}_2]$ and $[\{PtCl(S_2CNEt_2)\}_2C_8H_{12}]$ respectively.‡ This difference in behaviour is presumably a consequence of the weaker palladium–olefin than platinum–olefin bonds[2a] coupled with the insolubility of complex (6a).

Reaction of (6a) with $Na[S_2CNEt_2]\cdot 3H_2O$ gave $[Pt(S_2CNEt_2)_2]$ and free C_8H_{12}. Therefore, (6a) was treated with an equimolar amount of $Na[S_2PMe_2]\cdot 2H_2O$ in acetone–methylene chloride to give a yellow solid shown by analysis and i.r. and ^1H n.m.r. spectroscopy (Table 1) to be $[Pt(S_2CNEt_2)(S_2PMe_2)]$ (4b). Unlike $[Pd(S_2CNEt_2)(S_2PMe_2)]$ (4a) reported earlier in this paper, there was no evidence for disproportionation into $[Pt(S_2CNEt_2)_2]$ and $[Pt(S_2PMe_2)_2]$ when dissolved in solution at 301 K. Reaction of (4b) with PPh_3 in benzene gave the pale yellow solid $[Pt(PPh_3)(S_2CNEt_2)(S_2PMe_2)]$ (5b) which, like the analogous $[Pt(PMePh_2)(S_2CNEt_2)(S_2PMe_2)]$ reported elsewhere,[1] has unidentate $[S_2PMe_2]^-$ and bidentate $[S_2CNEt_2]^-$ co-ordination (i.r. and ^1H n.m.r. evidence) and is stereochemically rigid even at 330 K.

EXPERIMENTAL

Microanalyses were by B.M.A.C. and the University of Edinburgh Chemistry Department. Molecular weights were determined on a Mechrolab vapour-pressure osmometer (model 301A) calibrated with benzil. Infrared spectra were recorded in the 250—4 000 cm^{-1} region on a Perkin-Elmer 457 grating spectrometer using Nujol and hexachlorobutadiene mulls on caesium iodide plates. Hydrogen-1 n.m.r. spectra were obtained on a Varian Associates HA-100 spectrometer equipped with a variable-temperature probe. Melting points were determined with a Köfler hot-stage microscope and are uncorrected.

Potassium tetrachloroplatinate(II) and palladium(II) chloride (Johnson, Matthey Ltd.) and PPh_3, $Na[S_2CNEt_2]\cdot 3H_2O$, $K[S_2COEt]$, and $[AsPh_4]Cl\cdot HCl$ (B.D.H.) were used as received. The compounds $Na[S_2PMe_2]\cdot 2H_2O$,[18] $[Pd(C_8H_{12})Cl_2]$,[19] and $[Pt(C_8H_{12})Cl_2]$[20] were synthesised as described earlier. Analytical data for the new complexes are given in Table 2 together with i.r. bands diagnostic of

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* Another structurally related complex is $[\{PtCl_2(PPh_3)\}_2C_{10}H_{12}]$ containing a bridging dicyclopentadiene group and terminal chloride groups. This reacts with Na(OMe) to give $[\{PtCl_2(PPh_3)\}_2]$.[16]

† Fackler[5] recently prepared $[Pt(PMe_2Ph)_2(S_2CNMePh)][BPh_4]$ by this method.

‡ The complex $[\{PtCl(S_2CNBu^i{}_2)\}_2]$ has in fact recently been synthesised by reaction of equimolar amounts of $[Pt(S_2CNBu^i{}_2)_2]$ and $K_2[PtCl_4]$ although higher temperatures (50 °C) and longer reaction times (24 h) than those for the analogous palladium complex were required.[5]

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the mode of co-ordination of $[S_2CNEt_2]^-$ (ref. 14) and $[S_2PMe_2]^-$ (ref. 9).

Palladium Complexes.—*Di-μ-chloro-bis*[*(diethyldithiocarbamato)palladium*(II)]. The salt $Na[S_2CNEt_2]\cdot3H_2O$ (0.30 g) in acetone was added to a methylene chloride solution of $[Pd(C_8H_{12})Cl_2]$ (0.36 g) to give a white precipitate (NaCl) and an orange solution. The solution was stirred for 30 min until it became deep orange and was then filtered through Celite. Solvent was removed *in vacuo* and a mixture of methylene chloride (15 cm^3) and water (15 cm^3) was added to the residue. The volume of the methylene chloride layer was then reduced and diethyl ether was added to precipitate the orange *product* which was washed with diethyl ether and dried in air, m.p. 236—237 °C, ν(CN) at 1 530 cm^{-1}.

TABLE 2

Analytical data for some palladium(II) and platinum(II) dithioacid complexes

	Analyses (%)								
	Found				Calc.				
Complex	C	H	N	Others	C	H	N	Others	*M* *
$[\{PdCl(S_2CNEt_2)\}_2]$	21.0	3.5	4.7	Cl, 12.1	20.7	3.5	4.8	Cl, 12.3	694 (579)
$[\{PdBr(S_2CNEt_2)\}_2]$	18.2	3.0	4.1		18.0	3.0	4.2		740 (668)
$[\{Pd(SPh)(S_2CNEt_2)\}_2]$	36.2	4.0	3.8		36.4	4.1	3.9		780 (726)
$[\{PdCl(S_2COEt)\}_2]$	14.1	1.9			13.7	1.9			
$[PdCl(PPh_3)(S_2CNEt_2)]$	50.0	4.3	2.3		50.0	4.5	2.5		
$[Pd(AsPh_3)Cl(S_2CNEt_2)]$	46.2	4.2	1.9	Cl, 6.0	46.4	4.2	2.3	Cl, 6.0	
$[Pd(SbPh_3)Cl(S_2CNEt_2)]$	42.8	3.8	1.8	Cl, 5.2	43.0	3.9	2.2	Cl, 5.5	
$[PdCl(NC_5H_5)(S_2CNEt_2)]$	32.0	4.1	7.1		32.6	4.1	7.6		
$[PdCl(PPh_3)(S_2COEt)]$	48.3	3.8			48.1	3.8			466 (524)
$[PdCl(PPh_3)(S_2PMe_2)]$	45.6	4.0			45.4	4.0			
$[Pd(PPh_3)(SPh)(S_2CNEt_2)]$	55.2	4.7	2.3		55.7	4.8	2.2		596 (625)
$[PPh_3(CH_2Ph)][PdCl_2(S_2CNEt_2)]$	52.8	4.7	2.0		53.1	4.7	2.1		
$[Pd(PPh_3)(S_2CNEt_2)(S_2PMe_2)]$	46.5	5.0	2.2		46.8	4.8	2.2		
$[\{PtCl(S_2CNEt_2)\}_2C_8H_{12}]$	25.3	3.7	3.0		25.0	3.6	3.2		
$[PtCl(PPh_3)(S_2CNEt_2)]$	43.3	3.9	2.1		43.1	3.9	2.2		
$[Pt(S_2CNEt_2)(S_2PMe_2)]$	20.1	3.5	2.9		18.0	3.4	3.0		
$[Pt(PPh_3)(S_2CNEt_2)(S_2PMe_2)]$	41.4	4.0	1.9		41.1	4.3	1.9		

* Molecular weight measured osmometrically at 37 °C in chloroform; calculated values are given in parentheses.

Di-μ-bromo-bis[*(diethyldithiocarbamato)palladium*(II)] was prepared in the same way by reaction of $[PdBr_2(C_8H_{12})]$ and $Na[S_2CNEt_2]\cdot3H_2O$ (1 : 1 mol ratio), m.p. 210—212 °C, ν(CN) at 1 535 cm^{-1}. Alternatively, $[\{PdBr(S_2CNEt_2)\}_2]$ was prepared by shaking $[\{PdCl(S_2CNEt_2)\}_2]$ with excess of lithium bromide in acetone for 24 h. The solvent was then removed and the residue was extracted into methylene chloride. Addition of diethyl ether gave an orange *powder* which was filtered off, washed with water, methanol, and diethyl ether, and dried in air.

Di-μ-phenylthio-bis[*(diethyldithiocarbamato)palladium*(II)]. Sodium benzenethiolate in acetone was added to a methylene chloride solution of $[\{PdCl(S_2CNEt_2)\}_2]$, stirred for 30 min, and then filtered through Celite. Removal of solvent and addition of methylene chloride–cyclohexane gave an orange-red *powder* which was filtered off, washed with water, methanol, and diethyl ether, and dried in air, m.p. 228—230 °C, ν(CN) at 1 510 cm^{-1}.

Di-μ-chloro-bis[O-*ethyl dithiocarbonato)palladium*(II)]. The salt $K[S_2COEt]$ (0.08 g) in acetone was added to a methylene chloride solution of $[Pd(C_8H_{12})Cl_2]$ (0.14 g) to give an orange solution and a white precipitate (KCl). After stirring for 30 min, the solution was filtered through Celite and evaporated to dryness. Recrystallisation from methylene chloride–diethyl ether gave the dark orange *product* which is unstable and darkens in colour over 24 h.

Chloro(*diethyldithiocarbamato*)(*triphenylphosphine*)*palladium*(II). Addition of excess of PPh_3 to a methylene chloride solution of $[\{PdCl(S_2CNEt_2)\}_2]$ resulted in a colour change from orange to yellow. The volume of solution was then reduced and diethyl ether was added to give a yellow *solid*. This was filtered off, washed with water, methanol, and diethyl ether, and dried in air, ν(CN) at 1 535 cm^{-1}. *Chloro*(*diethyldithiocarbamato*)(*triphenylarsine*)*palladium*(II), m.p. 133—135 °C, ν(CN) at 1 535 cm^{-1}, *chloro*(*diethyldithiocarbamato*)(*triphenylstibine*)*palladium*(II), ν(CN) at 1 535 cm^{-1}, and *chloro*(*diethyldithiocarbamato*)(*pyridine*)*palladium*(II), m.p. 154—155 °C, ν(CN) at 1 535 cm^{-1}, were similarly prepared by reaction of $[\{PdCl(S_2CNEt_2)\}_2]$ with $AsPh_3$, $SbPh_3$, and C_5H_5N respectively.

(*Diethyldithiocarbamato*)(*phenylthio*)(*triphenylphosphine*)*palladium*(II). An excess of PPh_3 was added to a methylene chloride solution of $[\{Pd(SPh)(S_2CNEt_2)\}_2]$ and shaken for 15 min. Addition of hexane and slow evaporation of the methylene chloride resulted in the formation of the red crystalline *product*, m.p. 178—179 °C, ν(CN) at 1 510 cm^{-1}.

Chloro(O-*ethyl dithiocarbonato*)(*triphenylphosphine*)*palladium*(II). The salt $K[S_2COEt]$ (0.04 g) in acetone was added to a methylene chloride solution of $[Pd(C_8H_{12})Cl_2]$ (0.07 g) and the resulting orange solution was stirred for 30 min. Triphenylphosphine (0.07 g) in methylene chloride was then added to give a bright yellow solution which was immediately filtered through Celite to remove KCl. Removal of solvent *in vacuo* and addition of methylene chloride–pentane gave the required yellow-orange *product* which was filtered off, washed with water, methanol, and pentane, and dried in air, m.p. 117 °C (decomp.).

Chloro(*dimethylphosphinodithioato*)(*triphenylphosphine*)*palladium*(II). The salt $Na[S_2PMe_2]\cdot2H_2O$ (0.09 g) in acetone was added to a methylene chloride solution of $[Pd(C_8H_{12})Cl_2]$ (0.14 g) to give a dark red solution. An excess of PPh_3 was then immediately added giving an orange solution. This was filtered through Celite and the volume of filtrate was reduced. Addition of diethyl ether–pentane gave an orange crystalline *solid* which was removed by filtration and washed with water, methanol, and diethyl ether, m.p. 203—205 °C, $\nu(PS_2)$ at 578 cm^{-1}.

Benzyl(triphenyl)phosphonium dichloro(diethyldithiocarbamato)palladate(II). The complex $[\{PdCl(S_2CNEt_2)\}_2]$ (0.28 g) in acetone was shaken with excess of $[PPh_3(CH_2Ph)]Cl$ (1.00 g) and concentrated hydrochloric acid (1 cm^3) for 24 h. The solvent was then removed *in vacuo* and the product was extracted into methylene chloride. Addition of light petroleum (b.p. 60—80 °C) precipitated a yellow-orange *solid* which was filtered off, washed with water, methanol, and diethyl ether, and dried in air, m.p. 168—170 °C, ν(CN) at 1 522 cm^{-1}. *Tetraphenylarsonium dichloro(diethyldithiocarbamato)palladate*(II) was prepared similarly by reaction of $[\{PdCl(S_2CNEt_2)\}_2]$ with excess of $[AsPh_4]Cl{\cdot}HCl$ in acetone, ν(CN) at 1 522 cm^{-1}.

' *(Diethyldithiocarbamato)(dimethylphosphinodithioato)palladium*(II).' An excess of $Na[S_2PMe_2]{\cdot}2H_2O$ in acetone was added to an acetone solution of $[\{PdCl(S_2CNEt_2)\}_2]$ to give a pale orange solution and a white precipitate (NaCl). Removal of solvent after 15 min, followed by extraction with methylene chloride and addition of diethyl ether, gave an orange *solid* which was filtered off and washed with water, methanol, and diethyl ether, ν(CN) at 1 515 and ν(PS_2) at 578 cm^{-1}.

(Diethyldithiocarbamato)(dimethylphosphinodithioato)(triphenylphosphine)palladium(II). Excess of triphenylphosphine was added to a suspension of ' $[Pd(S_2CNEt_2)(S_2PMe_2)]$ ' in benzene to give a yellow solution. The volume was reduced *in vacuo* and addition of diethyl ether–pentane gave a yellow crystalline *solid* which was filtered off and washed with water, methanol, and diethyl ether, ν(CN) at 1 515 and ν(PS_2) at 605 cm^{-1}.

Platinum Complexes.—trans-*μ-(1—2-η:5—6-η-Cyclo-octa-1,5-diene)-bis[chloro(diethyldithiocarbamato)platinum*(II)]. The salt $Na[S_2CNEt_2]{\cdot}3H_2O$ (0.11 g) in acetone was added to a methylene chloride solution of $[Pt(C_8H_{12})Cl_2]$ (0.19 g) to give an immediate white precipitate (NaCl) and a yellow solution. On further stirring, a yellow precipitate was formed and after 1 h this was filtered off, washed with water to remove NaCl, then with methanol and diethyl ether, and dried in air, m.p. 190—192 °C, ν(CN) at 1 550 cm^{-1}.

Chloro(diethyldithiocarbamato)(triphenylphosphine)platinum(II). Triphenylphosphine (0.07 g) was added to a suspension of $[\{PtCl(S_2CNEt_2)\}_2C_8H_{12}]$ (0.11 g) in methylene chloride to give a pale yellow solution. Removal of some solvent and addition of diethyl ether–pentane gave a yellow *precipitate* which was filtered off and washed with water, methanol, and diethyl ether, and dried in air, m.p. 191—194 °C, ν(CN) at 1 530 cm^{-1}.

(Diethyldithiocarbamato)bis(triphenylphosphine)platinum chloride–water (1/1). An excess of PPh_3 was added to a suspension of $[\{PtCl(S_2CNEt_2)\}_2C_8H_{12}]$ in methylene chloride to give a colourless solution. After removal of some solvent, addition of diethyl ether–pentane gave a white *precipitate* which was washed with water, methanol, and diethyl ether, m.p. 174—175 °C, ν(CN) at 1 550 cm^{-1}.

(Diethyldithiocarbamato)bis(dimethylphenylphosphine)platinum chloride–water (1/1). Excess of $Na[S_2CNEt_2]{\cdot}3H_2O$ in acetone was added to *cis*-$[PtCl_2(PMe_2Ph)_2]$ in methylene chloride and shaken for 15 min to give a very pale yellow solution and a white precipitate (NaCl). Removal of solvent and addition of methylene chloride–diethyl ether gave a white *solid* which was washed with water, methanol, and diethyl ether, and dried in air. The same complex was reported elsewhere [17] by the prolonged interaction of $[Pt(S_2CNEt_2)_2]$ and PMe_2Ph in methylene chloride.

(Diethyldithiocarbamato)(dimethylphosphinodithioato)platinum(II). An excess of $Na[S_2PMe_2]{\cdot}2H_2O$ in acetone was added to a suspension of $[\{PtCl(S_2CNEt_2)\}_2C_8H_{12}]$ in methylene chloride and stirred for *ca.* 1 h. The yellow solution was then filtered through Celite to remove NaCl and the solvent was removed *in vacuo.* The resulting yellow *product* was extracted into methylene chloride, re-precipitated by addition of pentane and washed with water, methanol, and diethyl ether, m.p. 197—200 °C (decomp.), ν(CN) at 1 528 and ν(PS_2) at 578 cm^{-1}.

(Diethyldithiocarbamato)(dimethylphosphinodithioato)(triphenylphosphine)platinum(II). Excess of PPh_3 was added to a suspension of $[Pt(S_2CNEt_2)(S_2PMe_2)]$ in benzene to give a pale yellow solution. Removal of some solvent and addition of diethyl ether–pentane gave the pale yellow crystalline *product* which was washed with water, methanol, and diethyl ether, and dried in air, m.p. 199—201 °C, ν(CN) at 1 520 and ν(PS_2) at 603 cm^{-1}.

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