Hydrides of Platinum(II) and Platinum(IV) incorporating Hydrogensulphide and Hydrogenselenide Ligands

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The complexes *trans*-[PtH(EH)(PEt$_3$)$_2$] and *trans*-[Pt(EH)$_2$(PEt$_3$)$_2$] (E = S or Se) have been prepared and characterised. Oxidative addition of H$_2$Se to *trans*-[PtH(X)(PEt$_3$)$_2$] (X = Cl Br, I, SH, SeH, or CN) produces six-co-ordinate platinum(IV) dihydrides, which, in some cases, undergo redistribution of X and EH ligands, the mechanism of which has been deduced with the aid of ^{31}P n.m.r. spectroscopy. Addition of HY (Y = Cl or I) to *trans*-[PtH(SH)(PEt$_3$)$_2$] has also been investigated. Decomposition of the platinum(IV) dihydrides leads to the formation of platinum(II) hydrogensulphido- and hydrogenselenido-complexes.

As an extension to our previous investigations of platinum hydride complexes [1-3] we have synthesised and characterised some new platinum mono- and di-hydrides incorporating hydrogensulphide and hydrogenselenide ligands. Several synthetic routes were utilised; direct exchange of chloride ligand for [HE]$^-$ (E = S or Se) in *trans*-[PtCl(H)(PEt$_3$)$_2$] afforded the complexes *trans*-[PtH(EH)(PEt$_3$)$_2$], whose triphenylphosphine analogues were prepared and characterised by Ugo and his co-workers,[4,5] using the reaction of [Pt(PPh$_3$)$_2$] with H$_2$E (E = S or Se). Recently, the synthesis of the tribenzylphosphine counterpart of *trans*-[PtH(SH)(PEt$_3$)$_2$] by reaction of the chloro-complex with Na[SH] has been reported.[6]

Although spectroscopically the triphenyl-, tribenzyl-, and triethyl-phosphine derivatives are very similar, their stabilities in the presence of air or moisture are quite different. The triethylphosphine complexes, especially the hydrogenselenide, must be handled in an inert atmosphere, whereas the triphenyl- and tribenzylphosphine complexes are reported to be stable in air.[4,6] Six-co-ordinate hydrides were formed by oxidative addition of H$_2$Se to *trans*-[PtH(X)(PEt$_3$)$_2$] (X = Cl, Br, I, CN, SH, or SeH) and of HI to *trans*-[PtH(SH)(PEt$_3$)$_2$]. Some of the platinum(IV) complexes underwent a ligand-'scrambling' process, whose mechanism was elucidated with the aid of ^{31}P Fourier-transform n.m.r. spectroscopy. The decomposition of the six-co-ordinate complexes yielded further platinum(II) hydrogensulphides and hydrogenselenides. The new complexes have been characterised by n.m.r. spectroscopy, and, in the case of *trans*-[PtH(EH)(PEt$_3$)$_2$] (E = S or Se), by i.r. and mass spectroscopy also.

RESULTS AND DISCUSSION

The complexes *trans*-[PtH(EH)(PEt$_3$)$_2$] (E = S or Se) are readily prepared by treatment of *trans*-[PtCl(H)-(PEt$_3$)$_2$] with an excess of Na[EH] in ethanol *in vacuo*. The products of the metatheses, pale yellow crystals when E = Se and white crystals when E = S, are both indefinitely stable *in vacuo* at 300 K but decompose on exposure to air and moisture. The hydrogenselenido-complex decomposes very rapidly in air to give an oily reddish brown residue and noxious fumes of H$_2$Se. In the mass spectra the parent ions of both complexes were clearly visible and the fragmentation patterns were very similar in each case. Loss of H$_2$E was followed by three successive losses of 28 mass units, presumably due to ethylene arising from the triethylphosphine ligands.

The features of interest in the i.r. spectra, which were recorded as solutions in CH$_2$Cl$_2$ and pressed Polythene discs (for the low-frequency bands), were the PtH, EH, and PtE stretching frequencies. The values obtained are given in Table 1. The EH bands were weak in comparison with the PtH absorptions, and indeed were not detected in the i.r. spectra of the corresponding triphenylphosphine complexes.[4] The values found for ν(PtH) fall in the range characteristic of platinum(II) hydrides and indeed are very close to the value found by Miyamoto [6] for *trans*-[PtH(SH){P(CH$_2$Ph)$_3$}$_2$] (2 106 cm^{-1}). There are little published data about ν(M–S) and ν(M–Se) modes for unidentate ligands with two-co-ordinate S and Se with which to compare the values found for the platinum complexes. The values do, however, accord reasonably well with the positions of ν(PtS) and ν(PtSe) recorded for thiocyanato- and selenocyanato-complexes.[7]

TABLE 1

Infrared bands (cm^{-1}) of *trans*-[PtH(EH)(PEt$_3$)$_2$]

	ν(PtH)	ν(EH)	ν(PtE)
E = S	2 108	2 561	291
Se	2 110	2 288	194

The n.m.r. data provide the most conclusive evidence as to the identity of the products. The ^{1}H n.m.r. spectra are exceedingly similar, each consisting of the usual complex patterns associated with mutually *trans* PEt$_3$ groups in platinum(II) four-co-ordinate species, and, in addition, two triplets each showing coupling to ^{195}Pt. The triplet to lower frequency in each spectrum (at δ *ca.* −11 p.p.m.) had widely spaced ^{195}Pt satellites

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[1] J. E. Bentham and E. A. V. Ebsworth, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 145.

[2] J. E. Bentham, S. Cradock, and E. A. V. Ebsworth, *J. Chem. Soc.* (*A*), 1971, 587.

[3] D. W. W. Anderson, E. A. V. Ebsworth, and D. W. H. Rankin, *J.C.S. Dalton*, 1973, 854.

[4] D. Morelli, A. Segre, R. Ugo, G. La Monica, S. Cenini, F. Conti, and F. Bonati, *Chem. Comm.*, 1967, 524.

[5] R. Ugo, G. La Monica, S. Cenini, A. Segre, and F. Conti, *J. Chem. Soc.* (*A*), 1971, 522.

[6] T. Miyamoto, *J. Organometallic Chem.*, 1977, **134**, 335.

[7] D. M. Adams, 'Metal-Ligand and Related Vibrations,' Arnold, London, 1967, p 319.

(characteristic of a hydride directly bound to the metal) with a further small doublet splitting, shown by homonuclear double resonance to be due to $^3J(H\mathrm{PtE}H)$. The higher-frequency triplet in each spectrum [at δ −4.5 (E = Se) and −1.1 p.p.m. (E = S)] had closely spaced ^{195}Pt satellites and also displayed the additional small doublet splitting; these resonances can be confidently assigned to the hydrogen bound to the Group 6 atoms. Selenium-77 satellites were also observed in the spectrum of the hydrogenselenido-complex, and their identity, and those of all the ^{195}Pt satellites, were established by heteronuclear double-resonance experiments. More accurate values for the chemical shifts of ^{195}Pt and ^{77}Se were obtained by direct observation of these nuclei. Phosphorus-31 chemical shifts and ^1J(PtP) values were also observed directly; the n.m.r. data are given in Table 2.

TABLE 2

N.m.r. parameters [a] of *trans*-[PtH(EH)(PEt$_3$)$_2$] and *trans*-[Pt(EH)$_2$(PEt$_3$)$_2$] (E = S or Se) in CH$_2$Cl$_2$ at 293 K

Complex	δ(PtH)	δ(EH)	δ(^{31}P) [b]	δ(^{195}Pt) [c]	^1J(PtH)	^1J(PtP)	^2J(PtH)	^2J(PH)	^3J(PH)	^3J(HH)
trans-[PtH(SH)(PEt$_3$)$_2$]	−11.3	−1.1	18.6	−102	1 052	2 670	−42	−15	11	3
trans-[PtH(SeH)(PEt$_3$)$_2$]	−10.7	−4.5	19.3	−205	1 108	2 654	−44	−14	13	3
trans-[Pt(SH)$_2$(PEt$_3$)$_2$]		−1.5	9.2	226		2 493	−54		10	
trans-[Pt(SeH)$_2$(PEt$_3$)$_2$]		−4.0	6.3	−75		2 457	−56		11	

The following additional parameters were obtained:

	[PtH(SeH)(PEt$_3$)$_2$]	[Pt(SeH)$_2$(PEt$_3$)$_2$]
δ(^{77}Se) [d]	−312	−232
^1J(PtSe)	322	166
^1J(SeH)	n.o. [e]	116
^2J(PSe)	*ca.* 9	12
^2J(SeH)	50	

[a] δ In p.p.m., *J* in Hz. [b] To high frequency of external 85% H$_3$PO$_4$. [c] To high frequency of external 0.5 mol dm^{-3} *trans*-[PtCl(H)(PEt$_3$)$_2$] in CH$_2$Cl$_2$. To high frequency of 10% SeMe$_2$ in CH$_2$Cl$_2$. [e] n.o. = Not observed. [f] Signs of coupling constants were not determined.

The related complexes *trans*-[Pt(EH)$_2$(PEt$_3$)$_2$] (E = S or Se) were prepared in an analogous manner by treating *trans*-[PtCl$_2$(PEt$_3$)$_2$] with an excess of Na[EH] in ethanol *in vacuo*. The complexes, both yellow crystalline solids, are readily oxidised on exposure to air but remain stable *in vacuo*. They were characterised by n.m.r. spectroscopy.

TABLE 3

N.m.r. parameters of *cis,cis,trans*-[PtH$_2$(SeH)$_{2-n}$X$_n$(PEt$_3$)$_2$] (in CH$_2$Cl$_2$ at 213 K)

Complex	δ(PtH)	δ(SeH)	δ(^{31}P)	δ(^{195}Pt)	^1J(PtH)	^1J(PtP)	^2J(PtH)	^2J(PH)	^3J(HH)
[PtH$_2$(SeH)$_2$(PEt$_3$)$_2$]	−13.1	−5.0	−1.8	−342	1 004	1 780	−22	−8	3.5
[PtClH$_2$(SeH)(PEt$_3$)$_2$]	−12.1,[a] −18.7[b]	−4.8	6.3	330	1 022,[a] 1 721[b]	1 764	n.o.	−7.5,[a] −7.5[b]	n.r.
[PtBrH$_2$(SeH)(PEt$_3$)$_2$]	−12.2,[a] −17.4[b]	−4.6	3.6	122	984,[a] 1 204[b]	1 757	n.o.	−7.5,[a] −7[b]	n.r.
[PtH$_2$I(SeH)(PEt$_3$)$_2$]	−12.5,[a] −15.6[b]	−4.3	−1.6	−247	980,[a] 1 212[b]	1 749	−20	−7.5,[a] −6[b]	n.r.
[Pt(CN)H$_2$(SeH)(PEt$_3$)$_2$]	−13.3,[a] −13.6[b]	−5.1	1.8	−405	1 020,[a] 696[b]	1 720	−22	−8,[a] −9[b]	4.5

For [PtH$_2$(SeH)$_2$(PEt$_3$)$_2$] the following additional parameters were obtained: δ(^{77}Se) −520 p.p.m.; ^1J(PtSe) 74, ^1J(SeH) 50, ^2J(SeH) 35, and ^2J(PSe) *ca.* 6 Hz.[c]

n.o. = Not observed, n.r. = not resolved.

[a] *trans* to SeH. [b] *trans* to X. [c] Signs of the coupling constants were not determined.

The ^{1}H n.m.r. spectra each showed only one resonance [at δ −4.0 (E = Se) and −1.5 p.p.m. (E = S)] apart from the signals due to the PEt$_3$ ligands. These former resonances had triplet structures with ^{195}Pt satellites and closely resemble the signals assigned to the EH hydrogens in the hydride complexes, with the difference that in this case there was no additional doublet splitting. Selenium-77 satellites were also detected in the case of the selenium complex. Platinum-195 chemical shifts were obtained by heteronuclear double resonance, but ^{77}Se and ^{31}P shifts, and values of ^1J(PtP), were obtained by direct observation. The n.m.r. data are presented in Table 2.

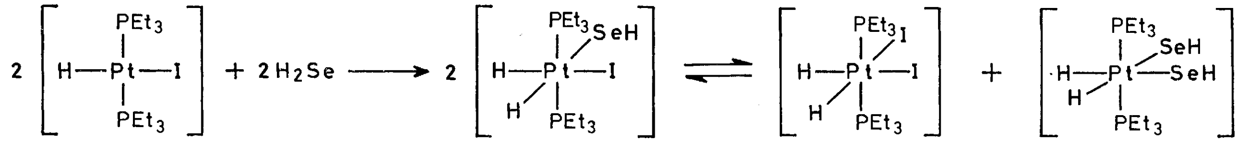
Reactions of H$_2$Se *and* H$_2$S *with Platinum Hydrides*.—(1) *Reactions of* H$_2$Se. (*a*) *With trans*-[PtH(SeH)(PEt$_3$)$_2$]. The ^{1}H n.m.r. spectrum of an equimolar mixture of H$_2$Se and *trans*-[PtH(SeH)(PEt$_3$)$_2$] in CH$_2$Cl$_2$ at 213 K showed resonances due to *trans* PEt$_3$ ligands. In addition, there was a low-frequency triplet at δ −13.1 p.p.m. with a small superimposed doublet splitting and widely spaced ^{195}Pt satellites. The value of ^2J(PH) obtained from the triplet splitting was characteristic of a platinum(IV) hydride. A broad peak with a hump on either side of the main signal appeared at δ −5.0 p.p.m. The humps were shown by heteronuclear double resonance to be ^{195}Pt satellites and the resonance was assigned to SeH protons in a platinum complex. Heteronuclear double irradiation showed that there were three ^{195}Pt frequencies which collapsed the platinum coupling on the triplet at δ −13.1 p.p.m., thus implying that the species is a dihydride. Since these frequencies also collapsed the coupling on the humps associated with the broad peak at δ −5.0 p.p.m. the two resonances clearly arise from the same complex, assigned as *cis,cis,trans*-[PtH$_2$(SeH)$_2$(PEt$_3$)$_2$]. The value of ^1J(PtP) obtained from the directly observed ^{31}P spectrum substantiates the assignment to a platinum(IV) species. The ^{77}Se chemical shift and coupling constants involving the magnetic isotope of selenium were also obtained by direct observation. The n.m.r. parameters are given in Table 3.

When the reaction mixture was allowed to warm to room temperature H_2 was evolved and the colour of the solution darkened to deep yellow. The ^{1}H n.m.r. spectrum of the resulting solution was the same as that recorded for *trans*-$[Pt(SeH)_2(PEt_3)_2]$.

(*b*) *With trans*-$[Pt(SeH)_2(PEt_3)_2]$. An attempt to obtain the species *trans*-$[PtH(SeH)_3(PEt_3)_2]$, from equimolar amounts of H_2Se and *trans*-$[Pt(SeH)_2(PEt_3)_2]$, was unsuccessful. The ^{1}H and ^{31}P n.m.r. spectra of the mixture in CH_2Cl_2 at 183 K showed that no new resonances were present, nor were any found at temperatures between 183 and 293 K; the parameters of the starting material were unaffected.

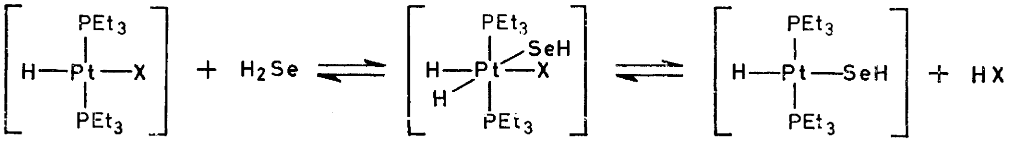
(*c*) *With trans*-$[PtH(X)(PEt_3)_2]$ (X = Cl, Br, or I). The ^{1}H n.m.r. spectrum of an equimolar mixture of *trans*-$[PtH(I)(PEt_3)_2]$ and H_2Se in CH_2Cl_2 at 213 K revealed four Pt*H* resonances, each with a basic triplet pattern and with associated platinum satellites. There were also two resonances in the Se*H* region, at δ −5.0 and −4.3 p.p.m., both broad with ^{195}Pt satellite humps. The Pt*H* signal at δ −15 p.p.m. was identified by its chemical shift, by the coupling constants, and by the associated values of $\delta(^{31}P)$ and $\delta(^{195}Pt)$ as due to *cis,cis,-trans*-$[PtH_2I_2(PEt_3)_2]$. The Pt*H* resonance at δ −13.1 p.p.m. showed a small additional doublet splitting; this peak and the one at −5.0 p.p.m. were similarly identified as arising from *cis,cis,trans*-$[PtH_2(SeH)_2(PEt_3)_2]$, described above. There remained two Pt*H* and one Se*H* resonance to be accounted for. Using heteronuclear double resonance, it was discovered that all the three peaks were associated with platinum nuclei and phosphorus nuclei having the same chemical shifts. One of the Pt*H* resonances was close to that of $[PtH_2I_2(PEt_3)_2]$; the other, which had the superimposed small doublet splitting, occurred close to the Pt*H* signal of $[PtH_2(SeH)_2(PEt_3)_2]$. The doublet splitting was collapsed by homonuclear double irradiation of the Se*H* resonance at δ −4.3 p.p.m. These three resonances can therefore be unequivocally assigned to the mixed dihydride *cis,cis,-trans*-$[PtH_2I(SeH)(PEt_3)_2]$. The Pt*H* resonance at δ −15.6 p.p.m. is assumed to be due to the hydride *trans* to I, and that at −12.5 p.p.m. to be due to the one *trans* to SeH.

The presence of the three dihydrides indicates that ligand scrambling follows the initial oxidative addition:



When the ^{1}H n.m.r. spectra of equimolar mixtures in CH_2Cl_2 of *trans*-$[PtCl(H)(PEt_3)_2]$ and H_2Se and, likewise, of *trans*-$[PtBr(H)(PEt_3)_2]$ and H_2Se, were examined at 213 K the results were similar. In each case three dihydrides were observed. The n.m.r. parameters of all the dihydrides are given in Table 3. Since little about the mechanism of the ligand-scrambling process could be deduced from the proton spectra, which were complicated by the narrow range encompassing the signals and the many couplings involved, a series of proton-decoupled ^{31}P spectra were recorded for each halide system, over a range of 183—303 K in steps of 20 K. The simplicity of the proton-decoupled phosphorus spectra enabled the resonances due to all the components of the systems to be easily distinguished, especially as the ^{31}P chemical shifts of the dihydrides had been determined from the proton spectra by double-resonance measurements. Although the initial spectra were recorded at very low temperatures and after the shortest possible time (of the order of a minute) in the liquid phase, it was impossible to obtain a spectrum in which the mixed species was the only platinum(IV) hydride present.

The ^{31}P spectra of each halide system showed that small, but significant, quantities of $[PtH(SeH)(PEt_3)_2]$ appeared as the reaction progressed and that similar quantities of the starting material, $[PtH(X)(PEt_3)_2]$, reappeared after its initial disappearance. These facts strongly indicate that the initial product, $[PtH_2(SeH)X(PEt_3)_2]$, dissociates not only into the starting materials but also to give $[PtH(SeH)(PEt_3)_2]$ and HX:

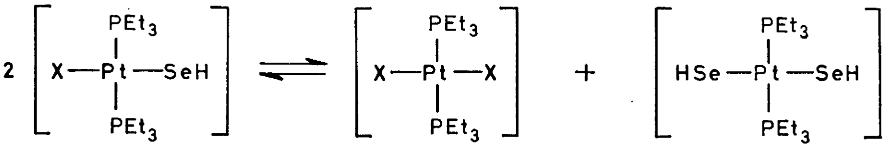


The operation of these processes explains the formation of the symmetrical dihydrides, since the oxidative addition of HX to *trans*-$[PtH(X)(PEt_3)_2]$ is well known [3] and the reaction of H_2Se and $[PtH(SeH)(PEt_3)_2]$ to give the platinum(IV) dihydride has been described above.

Although the overall reaction is qualitatively the same for each halide system there are interesting quantitative differences. The equilibrium constants obviously vary considerably from one halide system to another. The complex $[PtH_2I(SeH)(PEt_3)_2]$ is the most stable of the mixed dihydrides with respect to disproportionation, and predominates in the iodide reaction mixture, whereas when X = Cl the positions of the equilibria favour the four-co-ordinate monohydrides, and thence the symmetrical dihydrides, more than the mixed species. The bromide case is intermediate; the relative proportions of dihydrides when X = Br approximate to a purely random distribution (at 223 K), whereas values of the equilibrium constant for the disproportionation of the mixed dihydride are estimated as 0.06 for X = I and 1.0 for X = Cl at 223 K.

These reaction mixtures took a further intriguing turn when they were allowed to warm gradually to ambient temperature. Dihydrogen was evolved in each case, the resonances associated with the platinum(IV) species diminished in intensity, and three new signals appeared with ^1J(PtP) values characteristic of four-co-ordinate species. The complexes *trans*-[$\mathrm{PtX_2(PEt_3)_2}$] and *trans*-[$\mathrm{Pt(SeH)_2(PEt_3)_2}$] could be positively identified in each case, and the third 'four-co-ordinate' resonance was assigned to the mixed complex *trans*-[$\mathrm{Pt(SeH)X(PEt_3)_2}$]. The platinum(IV) dihydrides did not, however, all decompose at the same rate: [$\mathrm{PtH_2(SeH)_2(PEt_3)_2}$] was the least stable with respect to loss of dihydrogen, followed by the mixed species, and finally by the dihalide, which, in the case of X = I, still remained partially undecomposed at 303 K.

With the appearance of the four-co-ordinate decomposition products in the ^{31}P spectra it became apparent that yet another equilibrium was operating:



$$2\left[\mathrm{X{-}\underset{PEt_3}{\overset{PEt_3}{Pt}}{-}SeH}\right] \rightleftharpoons \left[\mathrm{X{-}\underset{PEt_3}{\overset{PEt_3}{Pt}}{-}X}\right] + \left[\mathrm{HSe{-}\underset{PEt_3}{\overset{PEt_3}{Pt}}{-}SeH}\right]$$

The platinum(II) species equilibrated to give relative proportions of the three complexes which depended markedly on the halide. The mixed species again predominated when X = I whereas in the chloride system no resonance could be assigned with any confidence to [$\mathrm{PtCl(SeH)(PEt_3)_2}$]. The situation when X = Br was again intermediate. The n.m.r. parameters of the [$\mathrm{Pt(SeH)X(PEt_3)_2}$] species are given in Table 4. Only the iodide was fully characterised. The phenomenon of ligand scrambling has been observed in the reaction of HX with *trans*-[$\mathrm{PtH(Y)(PEt_3)_2}$] (X,Y = Cl, Br, or I; X ≠ Y).[3] The major product at 183 K was the mixed dihydride, but weak resonances due to the two possible symmetrical dihydrides were also present at this temperature and increased in intensity with increasing temperature.

TABLE 4

N.m.r. parameters of *trans*-[$\mathrm{Pt(EH)X(PEt_3)_2}$] in $\mathrm{CH_2Cl_2}$ at 300 K

Complex	δ(EH)	δ(^{31}P)	δ(^{195}Pt)	^1J(PtP)	^2J(PtH)	^3J(PH)
[$\mathrm{PtBr(SeH)(PEt_3)_2}$]	n.o.	7.8	n.o.	2 411	n.o.	n.o.
[$\mathrm{PtI(SeH)(PEt_3)_2}$]	−3.5	3.4	−286	2 374	−71	12
[$\mathrm{Pt(CN)(SeH)(PEt_3)_2}$]	−4.0	9.8	47	2 350	−53	15
[$\mathrm{PtI(SH)(PEt_3)_2}$]	−0.8	5.5	−68	2 395	−68	11

n.o. = Not observed.

(*d*) *With trans*-[$\mathrm{Pt(CN)H(PEt_3)_2}$]. The ^{1}H n.m.r. spectrum of an equimolar mixture of *trans*-[$\mathrm{Pt(CN)H(PEt_3)_2}$] and $\mathrm{H_2Se}$ in $\mathrm{CH_2Cl_2}$ at 213 K showed three resonances in the low-frequency region, at δ −13.6, −13.3, and −5.1 p.p.m. Two of these are clearly due to PtH protons in a platinum(IV) complex and showed the usual triplet pattern with ^{195}Pt satellites, while one of them displayed an additional small doublet splitting. The third resonance had the position and shape expected for an SeH proton in a six-co-ordinate platinum species. All the three peaks were shown by heteronuclear double resonance to arise from the same species, which was assigned as *cis,cis,trans*-[$\mathrm{Pt(CN)H_2(SeH)(PEt_3)_2}$]. No evidence for any ligand scrambling was observed: neither the presence of [$\mathrm{PtH_2(SeH)_2(PEt_3)_2}$] nor of any resonance which could have been attributed to [$\mathrm{Pt(CN)_2H_2(PEt_3)_2}$] {which has defied synthesis[8] from [$\mathrm{Pt(CN)H(PEt_3)_2}$] and HCN} was detected. The n.m.r. data for the mixed dihydride are included in Table 3. When the solution was warmed to room temperature decomposition occurred with evolution of dihydrogen and the formation of a new four-co-ordinate species, whose n.m.r. parameters indicated it to be *trans*-[$\mathrm{Pt(CN)(SeH)(PEt_3)_2}$]. These parameters are included in Table 4.

The lack of ligand scrambling in this case can be rationalised by postulating that elimination of HCN from the mixed dihydride product is not favourable presumably due to a kinetic barrier. Since the initial $\mathrm{H_2Se}$ addition appears to occur rapidly and irreversibly, the only route to decomposition open to the dihydride is loss of dihydrogen which occurs on warming.

(*e*) *With trans*-[$\mathrm{PtH(SH)(PEt_3)_2}$]. The course of the reaction between equimolar amounts of $\mathrm{H_2Se}$ and *trans*-[$\mathrm{PtH(SH)(PEt_3)_2}$] in $\mathrm{CH_2Cl_2}$ was followed, over a range of temperature, by recording the proton-decoupled ^{31}P spectra. At low temperatures the spectra were dominated by unchanged starting material but a small quantity of a six-co-ordinate species was also present with δ(^{31}P) 0.7 p.p.m. and ^1J(PtP) 1 770 Hz. At 213 K the signal of *trans*-[$\mathrm{PtH(SeH)(PEt_3)_2}$] was detected and this increased in intensity and then diminished as the reson-

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[8] I M. Blacklaws, L. C. Brown, E. A. V. Ebsworth, and F. J. S. Reed, in preparation.

ance of another six-co-ordinate species, identified as *cis,cis,trans*-$[PtH_2(SeH)_2(PEt_3)_2]$ appeared. The complex *trans*-$[Pt(SeH)_2(PEt_3)_2]$ was also identified in the reaction mixture as it warmed to room temperature. Some $[PtH(SH)(PEt_3)_2]$ remained at the end of the reaction and no other species containing the hydrogensulphide ligand were observed. These results can be quite satisfactorily explained by assuming that the reaction follows the same general pattern seen in the $[PtH(X)(PEt_3)_2]$ (X = Cl, Br, or I) and H_2Se systems, with the crucial difference that loss of H_2S occurs very readily and seemingly irreversibly from the initial product *cis,cis,trans*-$[PtH_2(SH)(SeH)(PEt_3)_2]$ and that the free H_2S appears not to react with the starting material $[PtH(SH)(PEt_3)_2]$. Thus only very small quantities of the mixed dihydride (to which the resonance at 0.7 p.p.m. is assigned) are observed. The loss of H_2S from this initial product gives *trans*-$[PtH(SeH)(PEt_3)_2]$ which reacts with free H_2Se to yield the dihydridobis(hydrogenselenido)-species. This eliminates dihydrogen on warming, to form *trans*-$[Pt(SeH)_2(PEt_3)_2]$.

(2) *Reactions of* H_2S. Since the addition of H_2Se to platinum monohydrides had provided a ready route to six-co-ordinate platinum hydrogenselenides, this type of reaction was investigated using H_2S to see whether the analogous platinum(IV) hydrogensulphides could be obtained.

(*a*) *With trans*-$[PtH(I)(PEt_3)_2]$. When equal proportions of H_2S and *trans*-$[PtH(I)(PEt_3)_2]$ were mixed in CH_2Cl_2 at low temperatures the ^1H n.m.r. spectrum gave no indication of any reaction having occurred. No new low-frequency hydride resonances were detected and the signals of the starting materials appeared unchanged. The reagents were then allowed to react at ambient temperature for several hours, whereupon the colour of the solution deepened to yellow and sporadic bubbling was observed. The ^1H spectrum at this stage showed that a small quantity of a four-co-ordinate platinum hydrogensulphide had been formed. After further reaction the intensity of this signal increased sufficiently to enable heteronuclear-decoupling measurements to be made. The n.m.r. parameters found were quite different from those obtained for *trans*-$[Pt(SH)_2(PEt_3)_2]$ and *trans*-$[PtH(SH)(PEt_3)_2]$ and the product of this reaction was therefore identified as *trans*-$[PtI(SH)(PEt_3)_2]$, being the only other platinum(II) hydrogensulphido-complex likely to have been formed. These results appear to indicate a reaction scheme simpler than those encountered in the H_2Se additions. It seems that the reaction of H_2S and $[PtH(I)(PEt_3)_2]$ involves a slow addition and an equilibrium, the position of which lies far to the left, *i.e.* favouring H_2S and the monohydride. Only when the reaction mixture is allowed to reach room temperature is the position of equilibrium changed since the mixed dihydride product can then decompose with loss of dihydrogen to give the new platinum(II) complex *trans*-$[PtI(SH)(PEt_3)_2]$. The absence of any resonances which can be assigned to $[PtH_2I_2(PEt_3)_2]$ or *trans*-$[PtI_2(PEt_3)_2]$ implies that the lifetime of the mixed dihydride at low temperatures is too short to allow dissociation of HI and that at higher temperatures loss of H_2 is the major decomposition route.

(3) *Reactions of trans*-$[PtH(SH)(PEt_3)_2]$. Since we were unable to prepare platinum(IV) hydrogensulphido-complexes by oxidative addition of H_2S, the alternative route was attempted, *viz.* addition of HX to *trans*-$[PtH(SH)(PEt_3)_2]$ (X = Cl, I, or SeH). Since HX is known to add readily to platinum(II) hydrides this route was expected to be more fruitful.

(*a*) *With* H_2Se. See above.

(*b*) *With* HCl. The reaction between equimolar quantities of HCl and *trans*-$[PtH(SH)(PEt_3)_2]$ in CH_2Cl_2 was followed over a range of temperature by ^{31}P spectroscopy employing proton decoupling. The ^{31}P spectrum recorded at 183 K revealed that most of the starting material was unchanged but that a significant quantity of *cis,cis,trans*-$[PtCl_2H_2(PEt_3)_2]$ had formed. No other resonances were detected. At 203 K two more resonances, both arising from platinum(II) complexes, were observed. The n.m.r. parameters of one of these concurred very closely with those obtained for the SH-bridged binuclear cation *trans*-$[\{PtH(PEt_3)_2\}_2SH]^+$ which we have recently synthesised.[9] The other resonance was assigned to *trans*-$[PtCl(H)(PEt_3)_2]$. It seems that the sulphur atom in $[PtH(SH)(PEt_3)_2]$ is sufficiently nucleophilic to attack the metal atom in a molecule of $[PtCl(H)(PEt_3)_2]$ thereby forming a bridged species and displacing a chloride ion. The signals due to the bridged cation increased in intensity and then diminished until at 223 K only a trace amount remained. Likewise the $[PtH(SH)(PEt_3)_2]$ resonance had declined and disappeared at 223 K. Only $[PtCl(H)(PEt_3)_2]$ and $[PtCl_2H_2(PEt_3)_2]$ remained and as the solution was warmed further the signal of the monohydride decreased, apparently due to its conversion into the dihydride, for at room temperature the only complex present containing phosphorus was $[PtCl_2H_2(PEt_3)_2]$. This implies that the ratio of starting materials had not been 1 : 1 since an equimolar mixture should have contained only one chloride per platinum.

These observations suggest that there is an initial rapid addition of HCl to $[PtH(SH)(PEt_3)_2]$ to give a dihydride intermediate which is not detected and is therefore assumed to eliminate H_2S immediately. The $[PtCl(H)(PEt_3)_2]$ thus formed is oxidatively attacked at once by HCl to yield the dichlorodihydride which is observed even at 183 K.

(*c*) *With* HI. Treatment of $[PtH(SH)(PEt_3)_2]$ with a slight excess of HI in CH_2Cl_2 at 183 K produced *cis,cis,trans*-$[PtH_2I_2(PEt_3)_2]$ as the major product and a significant quantity of *trans*-$[PtH(I)(PEt_3)_2]$, as shown by ^{31}P spectroscopy. The ^{31}P spectrum also showed unchanged starting material and a very small amount of an unknown platinum(IV) complex at 1.7 p.p.m. [^1J(PtP) 1 760 Hz].

As the temperature was gradually increased the

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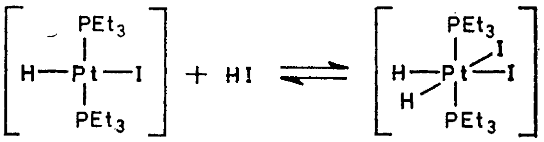
[9] E. A. V. Ebsworth, H. M. Ferrier, B. J. L. Henner, F. J. S. Reed, D. W. H. Rankin, H. E. Robertson, and J. D. Whitelock, *Angew. Chem. Internat. Edn.*, 1977, **16**, 482.

resonance due to $[PtH(SH)(PEt_3)_2]$ declined and that of $[PtH(I)(PEt_3)_2]$ increased, whereas the quantities of both platinum(IV) species remained essentially unchanged. The spectra recorded between 213 K and ambient temperature showed that $[PtH(I)(PEt_3)_2]$ and $[PtH_2I_2(PEt_3)_2]$ were the only complexes present. Moreover, these complexes seemed to be in equilibrium:



The equilibrium was upset at room temperature by decomposition of the dihydridodi-iodide with loss of dihydrogen to give *trans*-$[PtI_2(PEt_3)_2]$. This new resonance and that of *trans*-$[PtI(SH)(PEt_3)_2]$ appeared after 2-h reaction at 303 K; the latter resonance was identified as arising from $[PtI(SH)(PEt_3)_2]$ by comparison of the directly observed ^{31}P chemical shift and that obtained for this complex by heteronuclear double resonance in the reaction of $[PtH(I)(PEt_3)_2]$ and H_2S. After 2 d at 303 K the ^{31}P spectrum revealed that the ultimate products of the reaction were *trans*-$[PtI_2(PEt_3)_2]$ and *trans*-$[PtI(SH)(PEt_3)_2]$, both present in approximately the same concentration. Only a small quantity of $[PtH(I)(PEt_3)_2]$ remained and none of the dihydride. The observations made in this experiment are consistent with a reaction scheme similar to that proposed for the reaction of $[PtH(SH)(PEt_3)_2]$ and HCl. There is again a fast oxidative addition of HX to give a six-co-ordinate intermediate which in this case can be detected, albeit in low concentrations. The chemical shift of 1.7 p.p.m. and associated value for $^1J(PtP)$ of 1 760 Hz can very reasonably be assigned to *cis,cis,trans*-$[PtH_2I(SH)(PEt_3)_2]$. It is also very reasonable, in view of what was found in the analogous SeH systems, that this mixed dihydride should be more stable with respect to loss of HX or H_2S than the corresponding chloride species, and therefore be detectable. Loss of H_2S, however, again occurs readily, affording *trans*-$[PtH(I)(PEt_3)_2]$. The monohydride and unchanged HI exist in equilibrium with the dihydridodi-iodide until the position of the equilibrium is shifted by elimination of dihydrogen from the dihydride.

The appearance of *trans*-$[PtI(SH)(PEt_3)_2]$ as a reaction product only after several hours reaction at room temperature is very reminiscent of the result of the reaction between $[PtH(I)(PEt_3)_2]$ and H_2S. This reaction would therefore logically seem to be the origin of $[PtI(SH)(PEt_3)_2]$ in this system since both $[PtH(I)(PEt_3)_2]$ and H_2S are present from the early stages of the reaction. Although the same general reaction scheme can be applied to both systems, there appear to be two differences between the reactions of HCl and HI with *trans*-$[PtH(SH)(PEt_3)_2]$. The first lies in the positions of equilibria for the reaction $[PtH(X)(PEt_3)_2] + HX \rightleftharpoons [PtH_2X_2(PEt_3)_2]$. When X = Cl the position lies further to the right than when X = I. The second difference is that the dihalogenodihydride formed is stable at room temperature when X = Cl but decomposes on warming to room temperature when X = I under these reaction conditions.

The failure to obtain any well characterised platinum(IV) complexes that contain SH ligands contrasts sharply with the success achieved in synthesising the hydrogenselenido-complexes. Elimination of H_2S seems to be the main driving force in the rapid decomposition of the small quantities of platinum(IV) hydrogensulphides which are formed. That H_2Se is not also readily eliminated points to the significance of bond energies in these systems. The thermal stabilities and bond strengths of the chalcogen hydrides are known to decrease considerably from sulphur to selenium. This would also account for the reluctance of H_2S to add oxidatively to platinum(II) monohydrides.

EXPERIMENTAL

Infrared spectra were recorded on a Beckman-RIIC FS720 interferometer (low-frequency spectra) and on a Grubb–Parsons Spectromajor. Hydrogen-1 n.m.r. data were obtained using a Varian Associates HA100 spectrometer operating at 100 MHz. This instrument was double tuned to accept a second radiofrequency, provided by a Schlumberger FS30 frequency synthesiser. Phosphorus-31, ^{77}Se, and ^{195}Pt spectra were recorded on a Varian Associates XL100 spectrometer in the Fourier-transform mode. The complexes *trans*-$[PtH(X)(PEt_3)_2]$ (X = Cl, Br, I, or CN) were prepared by standard methods.[10] All the reactions were carried out in sealed n.m.r. tubes with 0.2-mmol quantities of reagents dissolved in methylene chloride; volatile compounds were manipulated using standard vacuum apparatus.

Preparation of trans-$[PtH(EH)(PEt_3)_2]$ (E = S *or* Se).—The complex *trans*-$[PtCl(H)(PEt_3)_2]$ (0.47 g, 1 mmol) was treated *in vacuo* with an excess of Na[EH] (E = S [11] or Se [12]) in ethanol. The ethanol was removed by distillation *in vacuo* and the creamy residue was extracted with methylene chloride. Filtration *in vacuo* to remove NaCl and excess of Na[EH] resulted in a clear solution from which the product was obtained after solvent removal.

[7/1550 *Received*, 31*st August*, 1977]

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