The Co-ordination of Small Molecules by Bistriphenylphosphineplatinum(0): The Reaction with H_2S, H_2Se, and H_2Te

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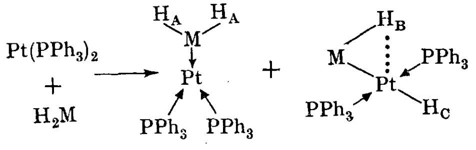
BISTRIPHENYLPHOSPHINEPLATINUM(0), recently characterised in this laboratory,[1] can be roughly compared to an active centre on the surface of a heterogeneous platinum catalyst.[2] Molecules such as H_2S, H_2Se, and H_2Te poison platinum surfaces, so it was thought of interest to study the co-ordination of these molecules with $Pt(PPh_3)_2$ in order to find a model for the poison mechanism.

Hydrogen sulphide co-ordinates on to iridium[3] and manganese[4] complexes. When H_2S and H_2Se were bubbled into degassed benzene solution of $Pt(PPh_3)_2$ or $Pt(PPh_3)_3$, the colour changed after some minutes and white–cream stable compounds were recovered by evaporation of the solvent. These compounds of formula $Pt(PPh_3)_2MH_2$ (M = S, Se) are stable in air and very soluble in organic solvents in which they are monomeric, $Pt(PPh_3)_2SH_2$ [$M_{obs}(CHCl_3) = 696$, $M_{calc} = 753$] and $Pt(PPh_3)_2SeH_2$ [M_{obs} $(CHCl_3) = 740$, $M_{calc} = 798$]. In Nujol mull, these compounds show strong i.r. absorption bands ν(Pt–H) at 2116 cm.$^{-1}$ (M = S) and at 2140 cm.$^{-1}$ (M = Se). In polar solvents, like ethanol, they slowly lose H_2S or H_2Se or H_2 at room temperature but in other solvents, heat is required.

With H_2Te the reaction rate, at room temperature, seems to be very slow; by evaporating the solvent, a pale yellow compound, which does not show any ν(Pt–H) stretchings, was obtained.

The n.m.r. spectra of H_2S and H_2Se compounds in saturated $CDCl_3$ or CH_2Cl_2 solution were run on a 100 Mc./sec. Varian Spectrometer at different temperatures (Table 1 and 2). Both compounds have very similar spectra, each with three principal absorptions. The low-field peak can be assigned to the proton H_A of the structure (a). It lies at a lower field than the peaks of pure H_2M (τ 9·218, M = S in $CDCl_3$; τ 11.610, M = Se in C_6D_6 R.T.) and shows a linear variation with temperature, typical of intermolecular hydrogen bonds.[5]



(a) (b)

The high-field peaks can be attributed to the H_B and H_C of the structure (b). The H_C peak is about at the same position for both M = S or Se and slightly changes with the temperature. The chemical shift of H_B does not vary with temperature and depends on the nature of M. Its value seems to indicate that H_B is not a σ-bonded hydridic hydrogen.

Besides, the coupling constant $J(^{195}Pt–H_C)$ has a normal high value typical for σ-hydrido-compounds,[6] while the coupling constant $J(^{195}Pt–H\ )$

TABLE 1

N.m.r. spectra of $Pt(PPh_3)_2SeH_2$ *at different temperatures (chemical shifts are in* τ *values)*

Temperature	Solvent	Absorptions[a]		
		H_A	H_B	H_C
+50°	$CDCl_3$	8·367	14·229	18·828
+27	$CDCl_3$	8·400	14·221	18·807
0	$CDCl_3$	—	14·212	18·732
—30	$CDCl_3$	—	14·185	18·673
−20	CH_2Cl_2	—	14·372	18·668
−40	CH_2Cl_2	—	14·377	18·633
−60	CH_2Cl_2	—	14·365	18·580
−90	CH_2Cl_2	—	14·337	18·487

[a] All spectra show absorptions due to phenyl rings of phosphines at nearly τ 3; intensities of protons B and C are in ratio 1 : 1; absorptions due to protons B and C are doublet [$J(H_B–H_C)$ = 2·9 c./sec.] and show satellites due to ^{195}Pt–H coupling. [$J(Pt–H_B)$ = 44·6 c./sec.; $J(Pt–H_C)$ = 992·9 c./sec]. These absorptions broaden by lowering temperature, absorptions due to proton A are always rather broad.

TABLE 2

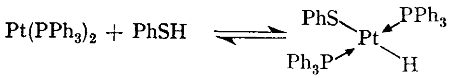
N.m.r. spectra of $Pt(PPh_3)_2SH_2$ *at different temperatures (chemical shifts are in* τ *values)*

Temperature	Solvent	Absorptions[b]		
		H_A	H_B	H_C
+40°	$CDCl_3$	8·249	11·445	19·220
+20	$CDCl_3$	8·057	11·438	19·187
0	$CDCl_3$	7·895	11·433	19·140
−20	$CDCl_3$	7·652	11·446	19·110
−40	$CDCl_3$	7·325	11·451	19·052
+27	CH_2Cl_2	8·092	11·641	19·195
−40	CH_2Cl_2	7·336	11·590	19·057
−60	CH_2Cl_2	—	11·569	19·032
−80	CH_2Cl_2	—	11·567	18·995

[b] All spectra show absorptions due to phenyl rings of phosphines at nearly τ 3; intensities of protons B and C are in ratio 1 : 1; absorptions due to protons B and C are singlet (half an amplitude about 2 c./sec., so, if present, J_{AB} must be less than 2 c./sec.) and show satellites due to ^{195}Pt–H coupling [$J(Pt–H_B)$ = 43·8 c./sec.; $J(Pt–H_C)$ 932 c./sec.]. These absorptions broaden by lowering the temperature and at −80° they split into triplets due to ^{31}P–H coupling [$J(P–H_B)$ = 10 c./sec., $J(P–H_C)$ = 11 c./sec.].

is unusually low showing that platinum to hydrogen interaction is of a different type. Possibly H_C is bonded through a platinum orbital with a normal *s* character, while H_B interacts weakly with the d_{z^2} orbital of platinum.

However, the coupling $^{195}Pt–H_B$ could be transmitted through the S or Se atoms,[7] though structure (a) does not show any such coupling. Strangely enough there is no observable coupling of H_B and H_C with ^{31}P at room temperature; the coupling, which appears at lower temperature, shows the presence of two *trans*-phosphorous atoms and cannot be easily explained. In fact this behaviour is not due to a rapid exchange between H_B and H_C. By adding D_2O, the H_B peak disappears suddenly, the H_A peak after a few minutes, but that of H_C only after 24 hours. In order to explain this effect we have investigated the yellow compound obtained by interaction of $Pt(PPh_3)_2$ with PhSH [ν(Pt–H) 2130 cm.$^{-1}$ in Nujol, M_{obs} (in $CHCl_3$) = 610, M_{calc} = 892]; at 25° it shows two n.m.r. peaks ($CDCl_3$), one weak at τ 6·65 (singlet) and the other one at τ 19·926 (singlet), J_{Pt-H} = 960 c./sec. This spectrum and the low molecular weight can be explained by the equilibrium:



In CH_2Cl_2 solution, at −60° the τ 19·926 peak splits into a triplet [J(P–H) = 12 c./sec.]. The behaviour shows again that a rapid exchange hypothesis for structure (b) is not acceptable.

On the other side it is clear, from the exchange with D_2O that structures (a) and (b) do not interconvert quickly at room temperature. Though the mechanism of interchange of structures (a) and (b) is not yet clear and needs a more detailed investigation in solution, which is in progress; it is clear that possibly the mechanism of poisoning of platinum surface goes *via* hydrogen abstraction of H_2M species bonded to the surface. Preliminary studies show a similar behaviour with palladium(0), nickel(0), and rhodium(I) phosphine compounds.

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