Linkage Isomerism in Hydride Complexes of Platinum(II)

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Complexes of the type *trans*-[L_2PtHX] (L = Ph_3P, Ph_2EtP, $Bu^n{}_3P$, Et_3P, Et_3As and X = NCO, NCS, CN, NCSe) have been prepared. It was found that linkage isomerism was exhibited only by the thiocyanate complexes. The assignment of spectral parameters was not based on the nuclear quadrupole broadening effect of the nitrogen atom since phosphine ligand exchange is known to occur in these complexes. The effects of temperature, solvent, concentration, and the nature of L on the linkage isomer ratio have been studied.

COMPLEX hydrides of platinum(II) of the type *trans*-$(R_3P)_2PtHX$ were first prepared by Chatt *et al.*[1,2] From the ^1H n.m.r. spectra, Powell and Shaw[3] deduced that linkage isomerism occurred in both cyanato- and thiocyanato-complex hydrides containing triethyl-phosphine or -arsine. In each case, two sets of hydride resonance patterns were observed and in each case the broader set was assigned to the N-bound isomer, since the broadening was attributed to quadrupole relaxation by the ^{14}N nucleus. These assignments have been accepted by

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[1] J. Chatt, L. A. Duncanson, and B. L. Shaw, *Proc. Chem. Soc.*, 1957, 343.

[2] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1962, 5075.

[3] J. Powell and B. L. Shaw, *J. Chem. Soc.*, 1965, 3879.

several authors.[4-9] All other studies [10-23] of linkage isomerism in complexes of platinum(II) and also of

chloro-complexes with the appropriate potassium salts. The chloro-complexes were prepared by the methods linkage isomers. The assignment of the spectral parameters to N- and S-bound forms is given in the Discussion.

Table 2

N.m.r. data for *trans*-[L_2PtHX] in chloroform solution

L	X	$\tau \pm 0{\cdot}04$ p.p.m.	${}^1J_{\text{Pt–H}}$ Hz (± 3 Hz)	${}^2J_{\text{P–Pt–H}}$ Hz ($\pm 0{\cdot}4$ Hz)
PhP	–NCO	26·64	989	13·7

DISCUSSION

Assignment of Thiocyanate Linkage Isomers.—It is well known that tertiary phosphine ligand exchange occurs in solutions of several transition-metal complexes.[26-28] This type of ligand exchange has been observed in the study of platinum(II) complex hydrides.[29] In some cases, the exchange rate caused line broadening is in agreement with that found for thiocyanato-complexes of palladium and cobalt.[13,19] It would appear that the S-bonded complex is favoured by polar solvents and this is possibly due to its high dipole moment in the H–Pt–X direction. However, solvation may also occur at the axial site of the complex, in which case this would suggest that there is a higher d_{z^2} electron density in the S-bound isomer. This is to be expected since sulphur is a stronger σ-donor than nitrogen and is also capable of synergically increasing its σ-donation to the metal atom by $d \longrightarrow d$ π-acceptance, using the metal d_{x^2}, d_{y^2}, and d_{xy} orbitals.

At concentrations below 50% w/w, there appear to be no significant changes in the isomer ratio for all the complexes studied. The –NCS to –SCN ratio was found to be always greater than unity and dependent on the nature of the tertiary phosphine in the complex, increasing in the order $Et_3P \sim Bu_3P < Et_3As < Ph_2EtP < Ph_3P$. Steric crowding in the complexes would favour the N-bound isomer [33] which contains the linear isothiocyanate ligand rather than the bent thiocyanato-group. This would explain the invariable predominance of the N-bound isomers and the above phosphine dependence.

A temperature n.m.r. study of *trans*-[$(Ph_2EtP)_2$-PtHSCN] and the triethylphosphine and tri-n-butylphosphine analogues in 20% w/w deuteriochloroform solution showed that the –NCS to –SCN ratio is little influenced on decreasing the temperature from 36 to –40 °C. A comparable study of the analogous triphenylphosphine complex was prohibited by its poor solubility.

Cyanate, Cyanide, and Selenocyanate Complex Hydrides.—The hydridic proton resonance of *trans*-[$(Et_3P)_2$-PtHNCO] has been reported [3] to consist of three broad triplets which were assigned to the isocyanate complex and a weak sharp triplet which was attributed to the oxygen-bonded isomer. In the present study, similar spectra were observed for analogous complexes. However, on careful purification of the complexes or their preparation from the bromo-derivative, only the broad triplets could be detected. On addition of a trace of hydrochloric acid to a solution of pure cyanato-complex, the sharp triplet appeared in the ^1H n.m.r. spectrum and could be made to disappear by metathesis. Furthermore, the chemical shifts of all sharp triplet resonances coincided with those of the corresponding chloro-complexes, chloro-hydride impurity not being detected by C and H analysis. All this evidence indicates that the cyanato-complex hydrides are mono-isomeric, and since only isocyanato-complexes are known for both platinum and palladium,[10,11,14,15] the hydride complexes must also be N-bonded. This is supported by the i.r. data which are discussed below.

The i.r. spectra of the isocyanate complex hydrides showed two intense, partly-overlapping bands in the region of 2200 cm^{-1}. By means of deuteriation the band at 2196 cm^{-1} was assigned to the Pt–H stretching vibration and that at 2232 cm^{-1} to the N≡C stretching mode (ν_{Pt-D} 1580 cm^{-1}). The mono-isomeric nature of the isocyanato-complexes was confirmed by the observation of only one ν_{Pt-D} band in each case.

The selenocyanate complex hydrides were prepared by metathesis. Complete purification of the complexes was impossible due to their low thermal and solvolytic stability. The ^1H n.m.r. spectra of these complexes showed only one set of hydridic resonances and the corresponding i.r. spectra only a single Pt–H (or Pt–D) stretching frequency. By a comparison of the spectroscopic data for the selenocyanato-hydrides with that of the corresponding thiocyanate complexes, it was deduced that the isomer was Se-bound. Other studies confirm that the selenocyanato-group prefers to co-ordinate to platinum through the selenium atom.[11] No linkage isomerism is exhibited by *trans*-[L_2PtHCN]. However, in common with the isocyanate and isothiocyanate complexes, the cyanide hydrides show broad hydridic proton resonances at room temperature. As previously mentioned, this does not indicate the presence of a nitrogen-bound group in the *trans*-position to the hydride ligand.

CONCLUSIONS

For complexes of the general type *trans*-[L_2PtHX], linkage isomerism is only exhibited when X is the thiocyanate ligand. Contrary to these observations, Roundhill, Tripathy, and Renoe [34] have reported recently that the complex in which L = Ph_3P and X = NCS exists solely in the isothiocyanato-form both in the solid phase and in chloroform solution. This was concluded on the basis of a single Pt–H stretching frequency in the Nujol mull i.r. spectrum and a single central hydridic resonance in the ^1H n.m.r. spectrum. In the present study, all the thiocyanate hydrides normally exhibited single high-frequency ν_{Pt-H} bands in their Nujol mull i.r. spectra and were presumably isothiocyanato-complexes. However, in solution i.r. spectra, two Pt–H stretching frequencies were invariably observed. Roundhill *et al.* were unable to rationalise the relatively high frequency of the Pt–H stretching absorption in terms of the *trans*-influence of the isothiocyanato-group. We suggest that when both Pt–H and C–N stretching vibrations occur in a complex, the frequencies of these vibrations are modified by resonance coupling in the solid phase. This has been observed for [$(Ph_3P)_2$PtHCN].[35] Therefore, the ν_{Pt-H} value would not be expected accurately to reflect a relative ground-state bond-weakening effect.

Wagner [36] calculated that of the possible ambidentate ligands SCN, NCO, SeCN, and CN the thiocyanate ion has the smallest charge difference between terminal atoms and is therefore the most likely to form linkage isomers. The thiocyanate ion is also unique in that it

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[33] F. Basolo, W. H. Baddley, and J. L. Burmeister, *Inorg. Chem.*, 1964, **3**, 1202.

[34] D. M. Roundhill, P. B. Tripathy, and B. W. Renoe, *Inorg. Chem.*, 1971, **10**, 727.

[35] W. H. Baddley and P. Ugualgliati, *J. Chem. Soc.* (*A*), 1969, 2772.

[36] E. L. Wagner, *J. Chem. Phys.*, 1965, **43**, 2728.

has relatively large negative charge densities on its terminal atoms, which again facilitates ambidentate co-ordination. For the selenocyanate ion, the charge difference between terminal atoms is double that in the thiocyanate ion. Indeed, the negative charge density on the selenium atom is so large that bonding through the nitrogen atom would be precluded except under extreme steric provocation.[37]

If it is assumed that the strong bonding of phosphines and arsines to class (b) metals, such as platinum, is at least partly due to the presence of ligand-to-metal $d\pi$–$d\pi$ acceptor bonds (the extent and significance of which is in doubt [38]), then the order of the ligands L which reflect an increasing -NCS: -SCN isomer ratio is also one of increasing π acidity.[39] This sequence is in accord with the theoretical predictions of Norbury.[40] The effect of solvents on the bonding mode of the thiocyanate group was investigated by Norbury whose prediction that polar solvents would favour the S-bound isomer is confirmed by our experimental results. However, this solvent dependence may be explained more simply in terms of the differing degrees of solvation of the two isomers.

Norbury's calculations did not take steric effects into consideration. However, the observed dependence of the isomer ratio on the nature of L may be rationalised in terms of the different steric requirements of the isothiocyanato- and thiocyanato-ligands which are linear and angular respectively.

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[39] D. I. Nichols, *J. Chem. Soc.* (*A*), 1970, 1216.

[40] A. H. Norbury, *J. Chem. Soc.* (*A*), 1971, 1089.