Inorganica Chimica Acta, 20 (1976) L13 - L14

Cyanoalkyl Complexes of Transition Metals.
V. Geometry and Phosphorus–Proton Coupling of Platinum Complexes Containing a Benzylmercapto Group

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(Received August 10, 1976)

In a previous paper [1] we showed that geometry of $PtX(CH_2CN)(PPh_3)_2$ (X = an anionic ligand) could be deduced from (1) the methylene resonance (2) the phenyl resonance [2] (*cis*: one multiplet, *trans*: two multiplets) and (3) a band at 550 ± 5 cm^{-1} (i.r.) [3] (*cis*: strong, *trans*: weak). The cyanomethyl protons of the *trans* isomers appeared as a triplet at higher field (*ca.* 0.6 ppm) than that of the corresponding *cis* isomers without exception. For the *cis* isomers, the same resonance generally appeared as a doublet of doublets, but in some cases, especially when the group X is bulky (like I^-), the methylene protons gave a signal different from the expected pattern, although they still resonated at lower field than that of the corresponding *trans* isomer. In this paper, we show that $|^4J(PH)|$ in a system L–Pt–S–C–H (L = a phosphorus ligand) is useful to identify a relative configuration of L to –SCH and the structure of $Pt(NMe_2CH_2CH_2S)(CH_2CN)(PPh_3)$ can be deduced from the $|^4J(PH)|$.

cis-$Pt(CH_2CN)(SCH_2Ph)(PPh_3)_2$ (I) and *trans*-$Pt(CH_2CN)(SCH_2Ph)(PPh_3)_2$ (II) were prepared from a corresponding chloride and benzylmercaptane in methanol respectively (*Anal.* Found: C, 61.17; H, 4.60. N, 1.67. Required for (I): C, 61,19; H, 4.46; N, 1.59. Found: C, 60.64; H, 4.50; N, 1.66. Required for (II): C, 16.19. H, 4.46; N, 1.59%). $Pt(CH_2CN)(SCH_2Ph)(PC{=}CP)$ (PC=CP: *cis*$Ph_2PCH{=}CHPPh_2$) (III) was prepared from (II) by a ligand exchange reaction in benzene (*Anal.* Found: C, 55.87; H, 4.15; N, 1.62. Required for (III): C, 56.05; H, 3.50; N, 1.87%).

The methyl resonances ($-CH_2CN$ and $-SCH_2-$) of these three complexes are shown in the Figure. The phenyl resonance of (I) showed a multiplet centered at τ 2.6, while that of (II) gave two multiplets at τ 2.3 and 2.5. Far infrared spectrum of (I) showed a strong absorption at 544 cm^{-1}, but for (II) only a weak absorption was observed at 548 cm^{-1}. Thus except the methylene resonance of (I), all spectroscopic evidences indicate that (I) is *cis* and (II) is *trans*. The *cis* configuration of (I) is also supported by the similar $\tau(CH_2CN)$ found in (I) and (III).

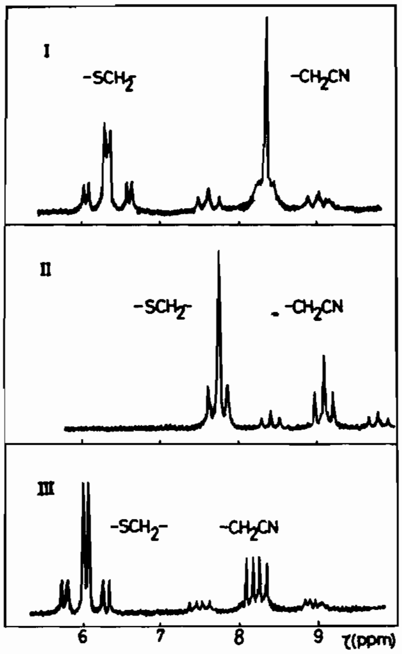
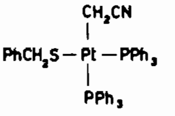
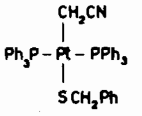


Figure. ^1H nmr spectra of *cis*-$Pt(CH_2CN)(SCH_2Ph)(PPh_3)_2$ (I), *trans*-$Pt(CH_2CN)(SCH_2Ph)(PPh_3)_2$ (II) and $Pt(CH_2CN)(SCH_2Ph)(PC{=}CP)$ (III).



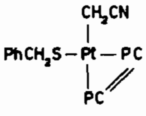
$$\begin{array}{c} CH_2CN \\ | \\ PhCH_2S-Pt-PPh_3 \\ | \\ PPh_3 \end{array}$$

(I)



$$\begin{array}{c} CH_2CN \\ | \\ Ph_3P-Pt-PPh_3 \\ | \\ SCH_2Ph \end{array}$$

(II)

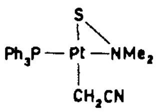


(III)

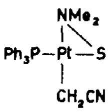
An unusual methylene resonance of (I) is probably due to bulkyness of the benzylmercapto group as found in the bromo and iodo analogues [1].

It should be emphasized that the $-SCH_2-$ protons showed a different spectral pattern in (I) and (II). The resonance appeared as a doublet in (I), while that of (II) showed a singlet. The difference between (I) and (II) is that (I) has a phosphorus atom *trans* to the benzylmercapto group. Therefore, this result indicates that $|^4J(PH)|$ of *trans*-P–Pt–S–C–H is large enough to detect, but that of *cis*-P–Pt–S–C–H is too small to observe. This is also supported by the fact that the same resonance of (III) where only one configuration (*cis*) is possible, appeared as a doublet.

We prepared $Pt(CH_2CN)(PPh_3)(NMe_2CH_2CH_2S)$ (IV) from *cis*-$PtCl(CH_2CN)(PPh_3)_2$ and $NMe_2CH_2CH_2SH$ HCl in EtOH (*Anal.* Found: C, 48.49; H, 4.58; N, 4.37. Required for (IV): C, 47.89; H, 4.53; N, 4.66%). For this complex there are two possible structures, (IVa) and (IVb).



(IVa)



(IVb)

$\widehat{S\text{-}NMe_2}$; $SCH_2CH_2NMe_2$

Since the methyl protons appeared as a doublet (τ(Me) = 7.00d, J(PH) = 3.0 Hz, J(PtH) = 27.5 Hz), we assigned structure (IVa) to the complex because it has a *trans*-P–Pt–N–C–H group. This configuration is sterically preferred since the interaction between the phenyl and methyl group is smaller for (IVa) than for (IVb). These results suggest that $|^4J(PH)|$ provides a useful mean to distinguish between the *cis*- and *trans*-P–M–A–C–H (M = a metal, A = a coordinating atom) group in square planar complexes.

References

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