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Preliminary communication

trans-CHELATION OF 1,12-BIS(DIMETHYLARSINO)DODECANE TO PALLADIUM(II)

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Summary

The diarsine ligand, 1,12-bis(dimethylarsino)dodecane, reacts with tetrachloropalladate(II) in ethanol/dichloromethane to form in high yield the monomeric [Pd(ligand)Cl_2] complex containing the *trans*-chelating diarsine.

Recently [1-5] there has been considerable interest in the ability of bidentate ligands of suitable geometry to chelate *trans* to a metal ion, a phenomenon that was felt to be unlikely only a few years ago. Shaw [1,2] and co-workers have prepared *trans*-[$PtLCl_2$] and *trans*-[Ir(CO)LCl] with the ligand $t\text{-}Bu_2P(CH_2)_{10}PBu\text{-}t_2$ and argue that the bulky t-butyl groups produce favourable conformational effects and internal entropy changes which favour the formation of these complexes. We found [5] that the potentially tetradentate diarsine dithioether, 1,3-bis(dimethylarsinopropylthio)propane, $Me_2As(CH_2)_3S(CH_2)_3S(CH_2)_3AsMe_2$ (L′), formed $ML'X_2$ (M = Pd, Pt; X = Cl, Br, I) which exist as *trans*-planar complexes with As_2X_2 donor sets in dichloromethane solution. Since this ligand did not contain bulky terminal groups, we were prompted to examine the related diarsine 1,12-bis(dimethylarsino)dodecane, $Me_2As(CH_2)_{12}AsMe_2$ (ligand).

This ligand reacts with $PdCl_4{}^{2-}$ in dilute solution in $EtOH/CH_2Cl_2$ to yield [Pd(ligand)Cl_2] (70% yield) which separates as a yellow powder from a saturated CH_2Cl_2 solution on long standing at 0°C. Elemental analyses are in excellent agreement with this formulation, and the molecular weight in 10^{-3} *M* chloroform (found 547, calcd. 555), along with its non-electrolytic character, indicate the presence of a monomeric complex. The electronic spectrum in chloroform solution, $\epsilon_{max} = 29.8 \times 10^3$ cm^{-1}, confirms the presence of planar palladium(II), whilst the ^1H NMR spectrum in $CDCl_3$ exhibits a single methyl signal at τ 8.2 ppm (compared with τ 9.1 ppm in the free ligand). The

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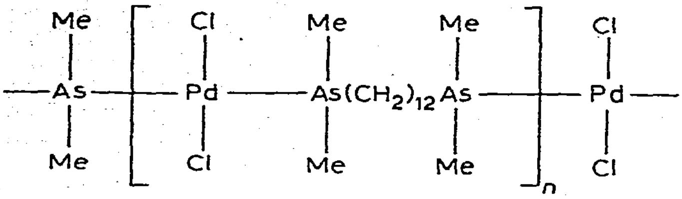
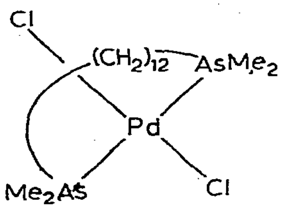
infrared spectrum in Nujol mull and in chloroform shows a single ν(Pd—Cl) at 348 cm^{-1} (cf. 353 cm^{-1} in *trans*-$Pd(AsEt_3)_2Cl_2$ [6]).

These data are consistent with the assignment of a *trans* geometry to $[Pd\{Me_2As(CH_2)_{12}AsMe_2\}Cl_2]$. One might have expected that with a very flexible ligand such as $Me_2As(CH_2)_{12}AsMe_2$, polymeric structures of type I would be produced. *cis*-Chelation is not expected for a ligand which would produce a fifteen-membered ring; the surprising result, and the significance of this work, is that *trans*-chelation II is produced rather than bridging bidentate behaviour. This result suggests that with ligands containing a suitably long backbone *trans* complexes can be obtained without the presence of bulky t-Bu terminal groups.



(I)



(II)

We are currently investigating other palladium(II) and platinum(II) complexes of this and related bidentate ligands, and preliminary results suggest that the principle reason why this type of complex was not recognised earlier is most probably the very slow rate at which the complexes crystallise (sometimes several months) which frequently makes purification difficult; this has so far prevented us from obtaining crystals suitable for X-ray analysis.

References

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