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Stability of 3,5-Dimethylpyrazole Complexes of Organotin Halides

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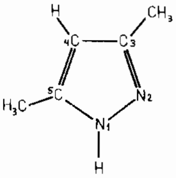
Complexes of 3,5-dimethylpyrazole (DMP) with $(CH_3)_2SnX_2$ (X = Cl or Br) and $(CH_3)_3SnCl$ have been characterized by means of i.r. and n.m.r. spectroscopy. The stability constants of the adducts $(CH_3)_2SnCl_2 \cdot DMP$, $(CH_3)_2SnBr_2 \cdot DMP$ and $(CH_3)_3SnCl \cdot DMP$ in carbon tetrachloride at 19° C have been determined by i.r. measurement of the free monomer DMP concentration.

Introduction

This paper describes a study on complex formation between some organotin halides, *i.e.* $(CH_3)_2SnCl_2$, $(CH_3)_2SnBr_2$, $(CH_3)_3SnCl$ and 3,5-dimethylpyrazole (DMP).



Pyrazole and substituted pyrazoles coordinate to metal ions generally through the N(2) atom[1], but equilibria between N(1) and N(2) bonded pyrazole complexes in solution have also been observed[2]. Intramolecular hydrogen bonding, N(1)—H · · · X, has been established for several octahedral and tetrahedral complexes of these ligands with transition metals, of the type M $(pyrazole)_nX_m$ (where X^- is a univalent anion)[1]. Recently we have reported that in complexes of palladium(II) and platinum(II), of formula $M(DMP)_2X_2$ and $[M(DMP)_4]X_2$, the hydrogen bond is also an important structural element[3].

Results and Discussion

I.r. Spectra

The i.r. spectrum of 3,5-dimethylpyrazole in carbon tetrachloride shows a fundamental N–H stretching mode at 3483 cm^{-1}, with a half band width of 20 cm^{-1}, together with a broad N–H band from *ca.* 3400 to *ca.* 2000 cm^{-1}. The 3483 cm^{-1} mode is assigned to free monomer and the 3400–2000 cm^{-1} band to cyclic hydrogen bonded dimer and trimer[4]. The broad band, showing several sharp peaks, is apparent also in the spectra of Nujol mulls of DMP, whereas the free end N–H stretching mode is not observed.

In the i.r. spectra of the complexes $(CH_3)_2SnCl_2 \cdot DMP$, $(CH_3)_2SnCl_2 \cdot 2DMP$ and $(CH_3)_2SnBr_2 \cdot 2DMP$ as Nujol mulls a band at 3375 cm^{-1}, 3303 cm^{-1} (br., asym.), and 3309 cm^{-1} (br., asym.), respectively, is assigned to the N–H stretch. These frequencies are lower than the free end N–H stretching frequency of DMP. Shift to lower frequencies could be taken as an indication of intramolecular hydrogen bonding between the pyrazole ligand and the counteranion, N(1)—H · · · X[5]. We suggest this is the case for the hexacoordinate complexes, $(CH_3)_2SnX_2 \cdot 2DMP$, where a remarkable decrease of N–H stretching frequency is accompanied by broadening of the band (half-height width of 50 cm^{-1}), as expected for hydrogen bond formation[6]. In these systems, however, the presence of intermolecular hydrogen bonds cannot be ruled out.

On the other hand, a rather small N–H stretching frequency shift is observed for the complex $(CH_3)_2SnCl_2 \cdot DMP$, compared with shifts observed for other pyrazole complexes of metal halides. This observation together with the narrow nature of the N–H stretching band (halfheight width of 20 cm^{-1}, Nujol mull) indicates a small extent of hydrogen bonding, if any, in the complex.

The spectra of solutions of $(CH_3)_2SnCl_2 \cdot DMP$ in carbon tetrachloride show in the N–H region a sharp band assigned to the coordinated ligand (see Table I) superimposed to the spectral pattern of uncomplexed DMP (monomer plus cyclic polimers), indicating partial dissociation. Also the spectra of mixtures of $(CH_3)_2SnBr_2$ and DMP and of $(CH_3)_3SnCl$ and DMP in carbon tetrachloride show the typical pattern of uncomplexed DMP together with a narrow band assigned to the N–H stretch of the adducts $(CH_3)_2SnBr_2 \cdot DMP$ and $(CH_3)_3SnCl \cdot DMP$, respectively. The observed frequencies are close to that of $(CH_3)_2SnCl_2 \cdot DMP$ (see Table I) and suggest also for these pentacoordinate adducts small extent of internal hydrogen bonding, if any. No N–H stretching bands assignable

TABLE I. I.r. and N.m.r. Data.

Complex	N–H Stretch cm^{-1}	Coupling Constants ^2J(Sn–CH$_3$), Hz[a]	
		$J(^{119}Sn–^1H)$	$J(^{117}Sn–^1H)$
$(CH_3)_2SnCl_2 \cdot DMP$	3375(Nujol) 3396(CCl_4)	83.4	79.8
$(CH_3)_2SnCl_2 \cdot 2DMP$	3303(Nujol)	94.5	90.3
$(CH_3)_2SnBr_2 \cdot DMP$	3387(CCl_4)	77.7	74.2
$(CH_3)_2SnBr_2 \cdot 2DMP$	3309(Nujol)	88.2	84.0
$(CH_3)_3SnCl \cdot DMP$	3395(CCl_4)	59.4	56.8

[a] Data for 0.36 *M* solutions in $CDCl_3$ at 28° C.

to hexacoordinate adducts are observed in the spectra of mixtures of DMP and organotin halide in CCl_4 in the concentration range studied (see Experimental).

N.m.r. Spectra

The spectra of the complexes $(CH_3)_2SnCl_2 \cdot DMP$, $(CH_3)_2SnCl_2 \cdot 2DMP$, $(CH_3)_2SnBr_2 \cdot 2DMP$ and the spectrum of an equimolar mixture of DMP and $(CH_3)_2SnBr_2$ in deuteriochloroform have been measured. Resonances in the ranges $-2.19 \div -2.47\ \tau$ (NH), $4.07 \div 4.12\ \tau$ (CH), $7.66 \div 7.67\ \tau$ (CH_3) and $8.44 \div 8.72\ \tau$ (Sn–CH_3) are observed for 0.36*M* solutions at 28° C. The Sn–CH_3 resonances are flanked by doublet-satellites, which arise from the coupling of methyl protons with ^{119}Sn and ^{117}Sn. The observed coupling constants are presented in Table I.

The increase of *J* values for the complex $(CH_3)_2SnCl_2 \cdot DMP$ with respect to $(CH_3)_2SnCl_2$ ($J(^{119}Sn–^1H) = 68.9$ Hz; $J(^{117}Sn–^1H) = 65.7$ Hz) is in agreement with a trigonal bypyramidal structure of the adduct, where the two methyl groups are located in the trigonal plane[7]; the degree of dissociation of this adduct under the n.m.r. experimental conditions should be negligible on the basis of the molecular weight measurement in $CHCl_3$. In the case of the other dimethyltin halide–DMP adducts complete complexation in the n.m.r. experimental conditions is possibly not attained, judging from molecular weight measurements carried out on 0.1*M* solutions in chloroform (37° C). For these cases, *J* data must be in principle regarded to as average values for equilibrium mixtures in conditions of rapid exchange. Even if the limiting *J* values of $(CH_3)_2SnBr_2 \cdot DMP$ are not known, the increase of the observed coupling constants of this complex with respect to $(CH_3)_2SnBr_2$ ($J(^{119}Sn–^1H) = 66.2$ Hz; $J(^{117}Sn–^1H) = 63.4$ Hz) is also in agreement with the formation of a trigonal bipyramidal adduct, where the methyl groups are in the trigonal plane. An increase of the observed ^2J(Sn–CH_3) values with respect to $(CH_3)_2SnCl_2 \cdot DMP$ is found for the complex $(CH_3)_2SnCl_2 \cdot 2DMP$. This result is consistent with the formation of an octahedral adduct involving a linear C–Sn–C arrangement[7]. Likely, the limiting *J* values for this complex are much closer than the observed values to the highest coupling constants reported for methyltin(IV) derivatives, where a linear C–Sn–C arrangement is present (for the aqueous $(CH_3)_2Sn^{2+}$ cation a value of $J(^{119}Sn–^1H) = 108.7$ Hz is found[8]). Similar conclusions could be drawn for the complex $(CH_3)_2SnBr_2 \cdot 2DMP$, but in this case the limiting ^2J(Sn–CH_3) values of the pentacoordinate adduct are not available for comparison.

The spectrum of an equimolar mixture of trimethyltin chloride (0.36*M*) and DMP is slightly different from the sum of the separate spectra of the components, indicating small association in $CDCl_3$. This is shown, for example, by comparison of the observed $J(^{119}Sn–^1H)$ value with the corresponding values of $(CH_3)_3SnCl$ (58.0 Hz) and $(CH_3)_3SnCl \cdot$Pyridine (67.0 Hz[9]).

All the complexes studied show a single methyl resonance for the DMP ligand, which appears as a doublet due to coupling with 4-H. No Sn–H spin–spin couplings are observed for any ligand proton. These observations are in agreement with the presence of dissociation equilibria of the complexes fast on the n.m.r. time scale; averaging of the 3-CH_3 and 5-CH_3 protons is ascribed to rapid proton exchange associated to hydrogen-bonding equilibria of uncomplexed DMP. It is pertinent to note that separate resonances are observed for 3-CH_3 and 5-CH_3 protons in the complexes of the type $M(DMP)_2X_2$ and $[M(DMP)_4]X_2$ (where M = Pd or Pt) and that $^{195}Pt–^1H$ couplings are apparent in the spectra of the platinum complexes[3].

Equilibrium Constant Studies

The stability constants of the complexes $(CH_3)_2SnCl_2 \cdot DMP$, $(CH_3)_2SnBr_2 \cdot DMP$ and $(CH_3)_3SnCl \cdot DMP$ in carbon tetrachloride at 19 ± 1° C have been determined by means of i.r. measurement of the concentration of free monomer DMP (3483 cm^{-1} band). Self-association constants of 3,5-dimethylpyrazole in CCl_4 at 19 ± 1° C have been reported: values of $\log\beta_2$ and $\log\beta_3$ are 2.453 and 4.660, respectively, where $\beta_2 = [(DMP)_2]/[DMP]^2$ and $\beta_3 = [(DMP)_3]/[DMP]^3$ [4]. The equilibrium concentrations of uncomplexed methyltin halide, [Sn], and of the adduct, [Sn–

DMP], have been calculated from the concentration of free monomeric ligand, [DMP], by means of the following equations:

$$[\mathrm{DMP}] + 2\beta_2[\mathrm{DMP}]^2 + 3\beta_3[\mathrm{DMP}]^3 + [\mathrm{Sn{-}DMP}] = [\mathrm{DMP}]_o \quad (1)$$

$$[\mathrm{Sn}] + [\mathrm{Sn{-}DMP}] = [\mathrm{Sn}]_o \quad (2)$$

(where $[\mathrm{DMP}]_o$ and $[\mathrm{Sn}]_o$ represent the total concentration of ligand and organotin halide, respectively). The stability constants, *K*, for the complexes studied are reported in Table II, together with the standard errors of the mean. The *K* values probably carry much greater errors than the stated uncertainty intervals would imply, mainly because of the indirect evaluation of concentration terms, which involve self-association constants of DMP being used two times for each determination (see also Experimental).

The stability of $(CH_3)_3SnCl\cdot DMP$ is found to be greater than that of $(CH_3)_3SnCl\cdot$Pyridine in the same solvent ($K = 1.9M^{-1}$, at 26° C[9]). This is a rather unexpected result in view of the greater steric hindrance and the lower basicity of 3,5-dimethylpyrazole with respect to pyridine; pK_a values (4.1[10] and 5.2, respectively) indicate greater proton affinity for pyridine, even if allowance is made for statistical factors. The relative stability of the dimethyltin halide adducts, *i.e.* $(CH_3)_2SnCl_2\cdot DMP > (CH_3)_2SnBr_2\cdot DMP$, can be accounted for by decreased N–Sn bond strength as well as by increased non-bonding interactions on going from chloride to less electronegative and bulkier bromide. On the basis of *i.r.* evidence, hydrogen bonding should not be relevant to the stability of these pentacoordinate adducts.

It is worth noting that the Lewis acid strengths of corresponding organotin halides are not always in the same order. Thus, for example, an opposite stability order, *i.e.* Cl < Br, is observed for complexes of the type $(CH_3)_2SnX_2\cdot$Bipy in acetonitrile[11]. These different behaviours can be rationalised in terms of different dominant contributions of factors involved in complex formation, such as donor–acceptor bond making, weakening of metal–halide bonds, rehybridization at the tin atom and changes of solvation.

Experimental

Preparation of Compounds

The complexes were prepared by mixing the organotin compound and DMP in the stoichiometric ratio in methylene dichloride at room temperature and then removing the solvent under reduced pressure. The products were recrystallized from cyclohexane. Reactions and purifications were carried out under a nitrogen atmosphere to avoid moisture. The preparation of the complexes $(CH_3)_2SnBr_2\cdot DMP$, $(CH_3)_3SnCl\cdot DMP$ and $(CH_3)_3SnBr\cdot DMP$ were attempted. In the first case mixtures of products were obtained, from which a pure compound could not be obtained. In the case of trimethyltin halides the separate components were always recovered from the reacting mixtures.

TABLE II. Stability Constants of DMP Complexes in Carbon Tetrachloride, at 19° C.

Complex	K, M^{-1}
$(CH_3)_2SnCl_2\cdot DMP$	1660 ± 85
$(CH_3)_2SnBr_2\cdot DMP$	365 ± 14
$(CH_3)_3SnCl\cdot DMP$	49 ± 3

Analytical Data

Calcd. for $(CH_3)_2SnCl_2\cdot DMP$: C, 26.62; H, 4.47; N, 8.87; Mol.Wt., 316. Found: C, 26.84; H, 4.58; N, 8.94; Mol.Wt., 311; M.P., 104–105° C.

Calcd. for $(CH_3)_2SnCl_2\cdot 2DMP$: C, 34.99; H, 5.38; N, 13.60; Mol.Wt., 412. Found: C, 35.11; H, 5.59; N, 13.62; Mol.Wt., 294; M.P., 124–125° C.

Calcd. for $(CH_3)_2SnBr_2\cdot 2DMP$: C, 28.78; H, 4.43; N, 11.19; Mol.Wt., 501. Found: C, 28.90; H, 4.55; N, 11.30; Mol.Wt., 323 M.P., 110–111° C.

Physical Measurements

All handling of the organotin derivatives was done in a nitrogen atmosphere. Solvents were dried over 4-Å molecular sieves and used without any further purification. Molecular weights were determined for 0.1*M* solutions in chloroform at 37° C using a Mechrolab 301 A Osmometer. I.r. spectra were recorded on a Perkin–Elmer 457 spectrometer. The uncertainty in the reported figures is ±5 cm^{-1}. N.m.r. spectra for $CDCl_3$ solutions, with tetramethylsilane as internal reference, were recorded on a 90 MHz HFX Bruker spectrometer.

Equilibrium Constant Determinations.

I.r. measurements of the solutions were done using a 2 mm cell with NaCl windows fitted in a thermostatted cell compartment. The temperature was controlled by means of a pre-calibrated thermistor set in a hole of a cell window; the temperature uncertainty was less than ± 1° C. The instrument was operated with pure solvent in the reference beam. The linear dependence of measured optical densities upon optical path lengths was checked by means of a variable pathlength cell filled with standard solutions. The concentrations of free monomer DMP in the equilibrium mixtures were measured from the intensity of the 3483 cm^{-1} band. Optical densities for solutions of the ligand alone were plotted previously as a function of free monomer concentration, [DMP], calculated by the following equation:

$$[\mathrm{DMP}] + 2\beta_2[\mathrm{DMP}]^2 + 3\beta_3[\mathrm{DMP}]^3 = [\mathrm{DMP}]_o$$

It was shown that the intensity of the free end N–H band adhered to Lambert's law in a concentration range of $[\mathrm{DMP}]_o = 9.7 \times 10^{-4} \div 1.06 \times 10^{-1} M$. Equilibrium studies of the system $(CH_3)_3SnBr$–DMP could not be carried out because of too low degree of association.

The concentration ranges for the three systems studied were:

$[(CH_3)_2SnCl_2] = 4.3 \times 10^{-3} \div 5.47 \times 10^{-2} M$, $[\mathrm{DMP}] = 4 \times 10^{-3} \div 1.96 \times 10^{-2} M$ (10 runs); $[(CH_3)_2SnBr_2] = 5.4 \times 10^{-3} \div 6.6 \times 10^{-2} M$, $[\mathrm{DMP}] = 3.8 \times 10^{-3} \div 2.09 \times 10^{-2} M$ (11 runs); $[(CH_3)_3SnCl] = 2.04 \times 10^{-2} \div 1.89 \times 10^{-1} M$, $[\mathrm{DMP}] = 2.1 \times 10^{-3} \div 4 \times 10^{-2} M$ (9 runs).

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