### **ORIGINAL PAPER**



# <sup>31</sup>P NMR study of the stoichiometry, stability, and thermodynamic data for the complexation of several HgX<sub>2</sub>: acetylemethylene tripara tolyl phosphorane complexes in various tetrahydrofuran–dimethyl sulfoxide mixtures

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### Abstract

Hg(II) halides are shown to react with the unsymmetrical phosphorus ylide,  $CH_3COCHP(p-tolyl)_3$  (Y) to be shaped binuclear products with the composition {HgX\_2[CH\_3COCHP(p-tolyl)\_3(Y)]}<sub>2</sub>, where X=I, Br, and Cl. <sup>31</sup>P NMR measurements were occupied to monitor the stability and stoichiometry of phosphorus ylide complexes with HgX<sub>2</sub> in binary tetrahydro-furan-dimethyl sulfoxide mixtures of changing composition. In all instance studied, the change of <sup>31</sup>P chemical shift with the [HgX<sub>2</sub>]/[Y] mole ratio showed the formation of 1:1 complexes. The stable constants of the arising from complexes were appraised from computer fitting of the mole ratio information to an equation that relates the monitored chemical shifts to the stable constant. In all solvent mixtures studied, the stabilities of the consequence 1:1 complexes varied in the order HgI<sub>2</sub> < HgBr<sub>2</sub> < HgCl<sub>2</sub>. It was found that, in the instance of all complexes, an addition in the percentage of tetrahydrofuran in the solvent mixtures, consequentially increased the stability of the complexes. The temperature relation formation constants were used for the appraisal of the entropy and enthalpy values for the complexation reaction. It was deduced that in all complexes, the resulting complex enthalpy is made stable and entropy destabilized.

**Keywords** Acetylemethylene tripara tolyl phosphorane  $\cdot$  Phosphorus ylide  $\cdot$  Binuclear products  $\cdot$  Stable constant  $\cdot$  Tetrahydrofuran-dimethyl sulfoxide mixtures

# Introduction

The organometallic chemistry of phosphorus ylides  $R_3P=C$ (R') (R'') (R, R', R" = alkyl or aryl groups) has undergone great growth over the last few years, mainly due to their interesting application as reactants in organometallic and metal-mediated organic synthesis [1, 2]. Adjacence of carbanion and the keto group in the phosphorus ylide APPY allows for resonance delocalization of the ylidic electron density, providing additional stabilization to the ylide class (Scheme 1). This so-called  $\alpha$ -stabilization provides APPY with the potential to act as an ambidentate phosphorus ylide and thus bond to a metal center through either carbanion (b) or the enolate oxygen (c). The enolate from (c) may assume either a cis or trans arrangement, the geometry of which will be retained upon bonding to the metal [3, 4].

In the compounds informed to date, coordination through carbon is more primary and is monitored with soft metal ions, e.g., Hg(II), Pd(II), Pt(II), Ag(I), Au(I), and Au(III) [5–9] and only very few examples of O-coordinated ylides are known [10, 11]. Cretain of these examples contain the vlide O-coordinated to a hard, very oxophilic metal center, such as Sn(IV) [10, 12] or group 4 metals with a high oxidation number, e.g., Ti(IV), Zr(IV), and Hf(IV) [12]. Solely W(0) complexes of the type  $W(CO)_5L$  (L = ylide) [13] and Pd(II) complexes of the stoichiometry  $[Pd(C_6F_5)]$  $L_2$ (APPY)](ClO<sub>4</sub>) [14] [APPY = Ph3CCOMe; L = PPh<sub>3</sub>, PBu<sub>3</sub>;  $L_2 = bipy$ ] contain stable ylides O-linked to a soft metal center. We have lately centered on the stability and formation of a number of binuclear complexes extracted from mercury(II) salts and phosphorus ylides [15–19]. This inclusive definition comprises nearly all kind of possible

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Scheme 1 Canonical formats of APPY (R=CH<sub>3</sub>)

di- or poly-dentate phosphorus ylides but in this paper our intention is to center our point of view on the coordination chemistry of the acetylemethylentriparatolylphosphorane (L) (scheme 2) [16].

Our benefit in the physico-chemical properties of the phosphorus vlide encouraged us to study (in recent years, we have introduced) some of spectrophotometric methods for the evaluation of the formation constants of some transition metal cations with new synthetic phosphorus ylide, formation, and stability of a number of mercuric salts phosphorus ylide complexes in different solvents [17, 18]. In this research, we utilized <sup>31</sup>P NMR as a very exquisite probe to study the complexation of HgI<sub>2</sub>, HgBr<sub>2</sub> and HgCl<sub>2</sub> with acetylemethylene tripara tolyl phosphorane (Y) in binary tetrahydrofuran-dimethyl sulfoxide mixtures of changing composition. We experienced to use Hg(NO<sub>3</sub>)<sub>2</sub> salt for collation in this proses, but this salt does not solve in utilized solvents. It should be sizeable that mercuric ions used have unsuitable NMR properties such as insensitive chemical shift, low receptivity [20], high quadrupole moment, etc.

### Experimental

Mercury salts were obtained from the Aldrich. Tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO) were commercially available from the Merck and used as received. acetylemethylene tripara tolyl phosphorane (Y) was do as previously delineated [15, 16] by the reaction of connected phosphine with 2-bromo-4'-chloroacetophenone and attendant elimination of HBr by NaOH. The characteristic of the solvents used in these research is given in Table 1 [21–25].

All NMR studies were made on a FX90Q JEOL NMR spectrometer with a field power of 2.35T supplied with a temperature controller, ( $\pm 0.1$  °C). At this system, <sup>31</sup>P resonates at 36.26 MHz characteristic acquisition parameters were 5000 Hz sweep width, 500 scans, 2 s relaxation delay, 2 s acquisition time, 24  $\mu$ s pulsewidth (45° pulse), and 64 k = 65,536 words with proton decoupling in 89.90 MHz. In <sup>31</sup>P NMR studies, the standard was 85%  $H_3PO_4$ . Stock solutions of the acetylemethylene tripara tolyl phosphorene (Y) were rigged by weighting a suitable amount of the phosphorus ylide at concentrations of 0.01 M in binary tetrahydrofuran-dimethyl sulfoxide mixtures of changing composition. Allot quantities of metal salts at concentrations of 0.10 M dissolved in the referred to solvents were added up to the [HgX<sub>2</sub>]/[Y] mole ratio of 4, using a micro-syringe. After blending of the solutions beneath ultrasonic for 10 min, their <sup>31</sup>P NMR spectra were registered at 20.0, 35.0, 50.0, and  $60.0 (\pm 0.1)$  °C.

Scheme 2 X=Cl<sup>-</sup>, Br<sup>-,</sup> and I<sup>-</sup>



Table 1         Properties of the solvents	Solvent	Viscosity	Had	μ	D	DN	AN	bp (°C)	mp (°C)
	THF	0.48	1.407	1.63	7.5	20.0	8.0	66	- 108.4
	DMSO	2.00	1.479	3.96	47.2	29.8	20.4	189	18.5

 $\mu$  dipole moment in Deby units, *D* dielectric constant (25 °C), *DN* Gutmann donor number(kcal mol<sup>-1</sup>), *AN* acceptor number(kcal mol<sup>-1</sup>), *Bp* boiling point, *Mp* melting point

## **Results and discussion**

NMR spectroscopy has been greatly used to the stability and stoichiometry studies [26–29]. The chemical shifts are measurable factor used for these researches. The <sup>31</sup>P chemical shifts of 0.01 M phosphorus ylide solutions in different tetrahydrofuran and dimethyl sulfoxide mixtures were observed as a function of  $[HgX_2]/[Y]$  ratio up to a molar ratio of 4. Sample spectra are demonstrated in Fig. 1. In all cases, only one population averaged resonance was monitored and one signal form arises from a fast interchange between complexed and free phosphorus ylide [Y] on the NMR time scale [30–34].

The arise from <sup>31</sup>P chemical shift—mole ratio plots for different Phosphorus ylide—HgX<sub>2</sub> systems in various tetrahydrofuran–dimethyl sulfoxide mixtures in 20 and 35 °C are shown in Figs. 2 and 3. As can be seen from Figs. 2 and 3, increasing the concentration of the ylide to the HgX<sub>2</sub> solution gently shifts the comparable <sup>31</sup>P resonance of phosphorus ylide downfield, to the [HgX<sub>2</sub>]/[Y] mole ratios abreast about 1. This behavior clearly shows the formation of 1:1 (MY) complexes in solution under total studied conditions.

The same conclusion was acquired for this reaction in X-ray crystal structure and theoretically the gas phase of complexes of  $[HgBr_2-Y]_2$  [16]. In total instances, addition of the ylide solution to  $HgX_2$  causes a nearly linear paramagnetic shift that commences to level off at mole ratios > 1. The slant of the analogous mole ratio plots changes meaningfully at the point where the phosphorus

ylide-mercuric ion is equal to 1, indicating the formation of a relatively stable complex. Usually, the behavior of the <sup>31</sup>P chemical shift as a function of  $[HgX_2]/[Y]$  mole ratio shown in Figs. 2 and 3 can be nearly divided into two groups: (1) the downfield shift changes linearly with the  $[HgX_2]/[Y]$  mole ratio until a mole ratio of about 1 is reached; more increase of the phosphorus ylide does not alter the resonance frequency. Similar behavior, which is clearly monitored for total mercuric salts in pure THF (Fig. 3e), binary %75 THF and %50 THF mixtures (Fig. 3d, c) are showing of normal stable 1:1 complex in solution. (2) A progressive paramagnetic chemical shift of the <sup>31</sup>P resonance with raising phosphorus ylide concentration that does not display any tendency to level off become even at a mole ratio of four. Such behavior, which is monitored for total mercuric salts in binary 25% THF (Fig. 3b) and pure DMSO (Fig. 3a), emphasizes the formation of a weaker than 1:1 complex between (Y) and HgX<sub>2</sub>. The now study depicts the stability and formation of a series of dimeric mercury(II) complexes extracted from phosphorus ylides and mercuric halides. On the basis of the spectroscopic NMR data and physico-chemical, we suggest that the phosphorus ylides here show monodentate C-coordination toward the metal central, what was antecedently approved by the X-ray crystal structure of the complexes. Theoretical studies in the gas phase indicate that the observed the possible cis-like structures for the present complexes are always less stable than trans-like structures [16].

The stable constants of 1:1 complexes were computed from the variation of the  $^{31}$ P chemical shift [HgX<sub>2</sub>]/[Y] mole



Fig. 1 <sup>31</sup>P spectra of a 0.01 M solution of phosphorus ylide in  $20.0 \pm ^{\circ}C$  at various a [HgI<sub>2</sub>]/[Y] mole ratios in dimethyl sulfoxide and b [HgCl<sub>2</sub>]/[Y] mole ratios in tetrahydrofuran



Fig. 2 <sup>31</sup>P chemical shifts as a function of the **a** [HgCl<sub>2</sub>]/[Y], **b** [HgBr<sub>2</sub>]/[Y], and **c** [HgI<sub>2</sub>]/[Y] mole ratio in various tetrahydrofuran–dimethyl sulfoxide mixtures in 20 °C

ratio. It has been shown antecedently [25] that the monitored chemical shift is given by

KINFIT schedule results from the high degree of confidence in this program [37].

$$\begin{split} \delta_{\rm obs} &= \left\{ \left[ (K_f C_{\rm HgY_2} - K_f - K_f C_Y - 1) + (K_f^2 C_Y^2 + K_f^2 C_{\rm HgX_2}^2 - 2K_f^2 C_Y C_{\rm HgX_2} + 2K_f C_Y + 2K_f C_{\rm HgX_2} + 1)^{1/2} \right] \\ &\times (\delta_Y - \delta_{\rm HgX_2 - Y}) / 2K_{\rm HgX_2} C_{\rm HgX_2} \right\} + \delta_{\rm HgX_2 - Y}, \end{split}$$
(1)

where  $K_f$  is the stable constant for the 1:1 complex,  $C_{HgX_2}$  and  $C_Y$  are the analytical concentrations of the mercuric salt and Y, respectively, and  $\delta_{HgX_2-Y}$  and  $\delta_Y$  are the respective chemical shifts of the complexed and free phosphorus ylide. Stable constants of the resulting 1:1 complexes were computed by fitting the resulting chemical shift—mole ratio plots, with the KINFIT schedule [35, 36]. A specimen computer fit of the <sup>31</sup>P chemical shift—mole ratio data is displayed in Fig. 4, and acquired Log K<sub>f</sub> for complexation of HgX<sub>2</sub> with Y under total the conditions are displayed in Table 2. An equitably agreement between the calculated and monitored chemical shifts shown in Fig. 4 that are more supports for the forming of a complex with 1:1 stoichiometry between Y and HgX<sub>2</sub>.

Therefore, from the data exhibited in Table 2, it is immediately apparent that for a given phosphorus ylide the stability of the resulting complex is related on the solvent mixture composition. In total instances, the stability increases consequently with increasing amount of THF in the solvent mixture. It has been well substantiated that the solvating capability of the solvent, as explicated by the Gutmann donor number [25] and dielectric constant, acts a key function in different complexation reactions [37–49]. It should too be noted that an intensify in the dielectric constant causes an increase in the bond formation. It is well known that DMSO as a solvent of high solvating capability (DN=29.8, D=47.2) competes with the phosphorus ylide for the mercuric salts much more than THF as a low density solvent (DN=20.0, D=7.5). Therefore, it is



**Fig. 3** <sup>31</sup>P chemical shifts as a function of the  $[HgX_2]/[Y]$  mole ratio in various 100% DMSO **a**, 75% DMSO—25% THF **b**, 50% DMSO—THF **c**, 25% DMSO—75% THF **d**, and 100% THF **e** solutions in 35 °C

**Fig. 4** Computer fit of <sup>31</sup>P chemical shift vs.  $[HgCl_2]/[Y]$  mole ratio in tetrahydrofuran in 20 °C, (x) experimental point; (o) calculated point; (=) experimental and calculated points are the same within the resolution of the plot



olvent	$HgX_2$	$\log K_{\rm f}$				$\Delta H^{o}$	$\Delta S^{o}$	$\Delta G^{\mathrm{o}}$
Composition (wt MSO in THF)	%	20 °C	35 °C	50 °C	60 °C	$(kjmol^{-1}K^{-1})$	$(jmol^{-1}K^{-1})$	(kjmol <sup>-1</sup> )
% DMSO								
	$HgCl_2$	$3.01 \pm 0.09$	$2.83 \pm 0.06$	$2.67 \pm 0.01$	$2.53 \pm 0.05$	$-25.0\pm1.0$	$-18\pm4$	$-19.6\pm1.3^{a}$
	$HgBr_2$	$2.47 \pm 0.04$	$2.35 \pm 0.05$	$2.21 \pm 0.02$	$2.16 \pm 0.04$	$-21.4\pm0.3$	$-21 \pm 1$	$-15.1 \pm 0.4^{a}$
	$HgI_2$	$2.04 \pm 0.02$	$1.88 \pm 0.03$	$1.65 \pm 0.02$	$1.51\pm0.06$	$-18.9\pm0.2$	$-29 \pm 1$	$-10.3\pm0.4^{a}$
5% DMSO								
	$HgCl_2$	$2.46 \pm 0.04$	$2.29 \pm 0.03$	$2.12 \pm 0.05$	$2.03 \pm 0.02$	$-22.3 \pm 1.0$	$-19\pm4$	$-16.6\pm1.3^{a}$
	$HgBr_2$	$2.08 \pm 0.02$	$1.94 \pm 0.02$	$1.83 \pm 0.04$	$1.69 \pm 0.03$	$-19.5\pm0.7$	$-23 \pm 1$	$-12.7 \pm 1.1^{a}$
	$HgI_2$	$1.73 \pm 0.02$	$1.58 \pm 0.05$	$1.43 \pm 0.07$	$1.31 \pm 0.06$	$-17.4\pm0.3$	$-31 \pm 1$	$-8.2\pm0.6^{a}$
0% DMSO								
	$HgCl_2$	$2.28 \pm 0.03$	$2.12 \pm 0.02$	$2.01 \pm 0.05$	$1.93 \pm 0.04$	$-20.2 \pm 1.0$	$-21 \pm 3$	$-13.9\pm1.4^{a}$
	$HgBr_2$	$1.83 \pm 0.02$	$1.66 \pm 0.04$	$1.53 \pm 0.03$	$1.41 \pm 0.05$	$-18.2\pm0.3$	$-23 \pm 1$	$-11.3\pm0.5$
	$HgI_2$	$1.46 \pm 0.06$	$1.32 \pm 0.03$	$1.20 \pm 0.03$	$1.15 \pm 0.02$	$-16.7\pm0.2$	$-33 \pm 1$	$-6.9\pm0.5^{a}$
'5% DMSO								
	$HgCl_2$	$1.94 \pm 0.03$	$1.78 \pm 0.05$	$1.64 \pm 0.04$	$1.55 \pm 0.07$	$-18.3 \pm 1.0$	$-25\pm4$	$-10.8\pm1.7^{a}$
	$HgBr_2$	$1.52 \pm 0.02$	$1.39 \pm 0.04$	$1.25 \pm 0.03$	$1.16 \pm 0.02$	$-17.9\pm0.7$	$-28\pm1$	$-9.6\pm1.3^{a}$
	$HgI_2$	$1.22 \pm 0.02$	$1.10 \pm 0.03$	$0.97 \pm 0.05$	$0.82 \pm 0.06$	$-16.1 \pm 0.3$	$-39\pm1$	$-4.5\pm1.1^{a}$
00% DMSO								
	$HgCl_2$	$1.46 \pm 0.02$	$1.27 \pm 0.05$	$1.15 \pm 0.03$	$1.03 \pm 0.04$	$-17.5 \pm 1.0$	$-28\pm 4$	$-9.3 \pm 1.2^{a}$
	$HgBr_2$	$1.24 \pm 0.04$	$1.09 \pm 0.03$	$1.00 \pm 0.02$	$0.91 \pm 0.05$	$-16.00\pm0.7$	$-35 \pm 1$	$-5.6\pm1.0^{a}$
	$HgI_2$	$0.98 \pm 0.03$	$0.83 \pm 0.02$	$0.71 \pm 0.04$	$0.64 \pm 0.03$	$-14.9\pm0.3$	$-41 \pm 1$	$-2.7 \pm 1.6^{a}$

not unexpected that addition of DMSO to THF will reduce the stability of the  $[HgX_2-Y]_2$  complexes.

The information given in Table 2 clearly shows that, in a given THF–DMSO mixture, the stability of HgX<sub>2</sub> complexes increases in the command HgI<sub>2</sub>–Y < HgBr<sub>2</sub>–Y < HgCl<sub>2</sub>–Y. In reality, where the frame remainders the same, the stable constants on the resulting complexes increase in the order THF to DMSO solvents. The presence of I<sup>-</sup> ion would cause an important decrease in the formation of the resulting complex, compared with Br<sup>-</sup> and Cl<sup>-</sup> ions–phosphorus ylide. These consequences clearly illustrate the fundamental role of the different counter ions on complex formation constant [50, 51]. It is useful to regard the enthalpy and entropic contributions of the reaction in command to have a more than comprehending of the thermodynamic of the complexation. Hence, the  $\Delta H$  and  $\Delta S$  values were calculated from the slope and take of the van't Hoff plot, separately (Eq. 2):

$$2.303R\log K_f = -\Delta H\left(\frac{1}{T}\right) + \Delta S.$$
(2)

The van't Hoff plots of log  $K_f$  against 1/T for the complexes in THF–DMSO mixture solution are explained in Fig. 5. The obtained  $\Delta H$  and  $\Delta S$  values are recorded in Table 2. These results display that the HgX<sub>2</sub>–Y complexes

are enthalpy stabilized. In addition, the  $\Delta G$  values demonstrate that complexation reactions are totally spontaneous. It was admitted that stability of the resulting complexes powerfully depends on the quantity of DMSO in the solution. The formation constant of the complexes was reduced by increasing DMSO amount. Total complexes in THF solutions were determined to be more stable than those in THF-DMSO mixture solutions and pure DMSO solvent. Since the thermodynamic data summarized in Table 2, it is deduced that against the Gibbs free energy and enthalpy, the entropy of total complexes acted as a factor uncomfortable in all solvents. In addition, the resulting complex is mainly enthalpy stabilized in THF, 75% THF - 25% DMSO, while in the 50% THF-DMSO, the enthalpy is nearly the singular contributor in the Gibbs free energy of the reaction [31]. Although in this matter, the solvating ability of the solvent increased and the dielectric constant are decreased, lower energy will need to be disconnected the cation and anion. Thus, lower enthalpy and Gibbs free energy were obtained in THF and %75 THF-25% DMSO as a result of the solvating ability of the solvent and the lower dielectric constant for THF [52, 53]. However, the different entropy and enthalpy of the reaction in two solvents would be explained in terms of different solvent-complex interactions, in these media. THF with



Fig. 5 Van't Hoff plot for the complexation reaction between Y with  $HgX_2$  in (a) THF, (b) 75% THF—25% DMSO, (c) 50% THF—DMSO, (d) 25% THF—75% DMSO, and (e) DMSO

larger the solvating ability perhaps react high powerfully with the complexes to shape further stable solvated complex [54].

# Conclusion

The complexation reaction betwixt the HgI<sub>2</sub>, HgBr<sub>2</sub> and HgCl<sub>2</sub> salts with the unsymmetrical phosphorus ylide, CH<sub>3</sub>COCHP(p-tolyl)<sub>3</sub> (Y), in binary THF–DMSO were inspected by <sup>31</sup>P NMR spectroscopy. In total instances examined, the variation of <sup>31</sup>P chemical shift with the the  $[HgX_2]/[Y]$  mole ratios indicated the formation of 1:1 complexes in all solvents. It was discovered that formation of the resulting complexes is powerfully dependent upon the amount of DMSO in the solution. In total instances, the stability reduces significantly with increasing quantity of DMSO in the solvent mixture. In total solutions, the stability of total complexes increases in the order the  $HgI_2-Y < HgBr_2-Y < HgCl_2-Y$ . The stability constant of complex results by the superposition of several factors containing the extent of interaction of Hg(II) halides with donor groups of the Y. The consonance between the phosphorus ylide and kind the counter anion depends to metal ion. Hard-soft acid-base characters of the metal ion and the donating groups of the phosphorus ylide. Solvation of the resulting complex and desolvation of the Y and Mercuric cation. The two later factors causes being powerfully dependent on the nature of solvents used. The enthalpy and entropic values for the complexation reaction were acquired from the temperature dependence of the stable constants. It is obviously that, in total complexes, the resulting complex is totally enthalpy stabilized nevertheless the  $T\Delta S$  unfair contribution.

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