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# Solubility of halide-containing organometallics is dramatically enhanced in diiodomethane: can the solvent•••complex halogen bonding be held responsible?

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**Abstract:** In the current study, we evaluated a solubility of a number of organometallics and showed that it is noticeably improved in diiodomethane when compared to other haloalkane solvents. Better solvation properties of  $CH_{2l_2}$  were associated with a dramatic growth of the  $\sigma$ -hole donating ability of this solvent, and that results in the formation of the uniquely strong solvent-(metal complex) halogen bonding. The strength of halogen bonding is attenuated by the introduction of additional halogens to the organometallic species due to the competitive formation of more favourable intermolecular complex-complex halogen bonding. Exceptional solvation properties of diiodomethane and its inertness towards organometallics make this solvent a good candidate for NMR solvent-of-choice, in particular, for the acquisition of insensitive spins.

Insufficient solubility is one of the major problems limiting structural characterization of compounds in solution, e.g. by NMR spectroscopy and also their application in synthesis. In particular, frequently higher reactivity and intrinsic instability of organometallic species preclude the use of many common solvents for their dissolution. Application of more inert, but often less solubilizing solvents, limits the concentration of compound resulting in significantly longer accumulation time upon NMR acquisition of insensitive nuclei (13C, 15N, etc). Solvation, as a process leading to a dissolution of compounds, encompasses several different types of intermolecular interactions between a solute and a solvent. These include van der Waals forces, iondipole interactions, hydrogen bonding (HB), as well as halogen bonding (XB) for halogen-containing species.<sup>[1]</sup> Although the contribution of different interactions in solvation is recognized, their interplay is rather complex and an empirical matching of the solvent polarity to that of the solute continues to be the main approach to improving solubility.<sup>[2]</sup> Among weak interactions, contribution of HB is frequently taken into account, while impact

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of XB is rarely considered and clearly needs an in-depth study.

In this study, we examined the solvation properties of a number of different haloalkane solvents using palladium- and platinum-isocyanide species as solvation probes. Haloalkanes are one of the most inert solvents used to solubilize organometallics; they, and their deuterated versions, are widely applied as media for solution NMR studies. Metal-isocyanides are commonly used precursors to the metal-(acyclic diaminocarbenes) that are of broad significance in catalysis.<sup>[3]</sup>

A series of new and known palladium- and platinumisocyanide complexes (1-16, Table 1) were prepared and characterized by CHN elemental analyses, high-resolution mass spectrometry (ESI+/--HRMS), FT-IR, and <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy (see Supplementary Information (SI) for more details). The structures of complexes 10.2CH<sub>2</sub>I<sub>2</sub>, 11, 11.2CH<sub>2</sub>I<sub>2</sub>, and 12 were established by single-crystal X-ray diffraction. The geometry of all the complexes in solid state and in solution were assigned on the basis of far-IR spectroscopy and X-ray diffraction (see SI). All palladium complexes 1-12 are isomerically pure in the solid state (cis for chloro, and trans for bromo and iodo derivatives). In solution, chloro-complexes 1-4 were found to be a mixture of the *cis* and *trans* isomers (60–65% of *cis* isomer at RT), whereas both the bromo and iodo species 5-12 contain more than 95% of the *trans* isomer. Platinum complexes (13–16) are not subject to isomerization and are pure cis in both solution and solid state.

 
 Table 1. The numbering scheme of prepared metal-isocyanide complexes used as probes for solvation properties of haloalkanes.

	Complex					
x		x T we Br	x C vie C en C x			
Н	M = Pd 1, Pt 13	5	9			
CI	M = Pd <b>2</b> , Pt <b>14</b>	6	10			
Br	M = Pd 3, Pt 15	7	11			
I	M = Pd <b>4</b> , Pt <b>16</b>	8	12			

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**Table 2.** Solubility for **4**, **7**, **11**, and **12** in liquid haloalkanes, maximum ESPs ( $V_S(r)_{max}$ , kcal·mol<sup>-1</sup>) on the Hal and H atoms in solvents, their dipole moment (µ), and dielectric constant.

Solvent	Solubility, mg/mL			V <sub>s</sub> (r) <sub>max</sub> , <sup>[b]</sup> kcal⋅mol <sup>-1</sup>		Dipole moment,	Dielectric constant,		
	4	7	11	12	Hal	н	μ	(T, °C)	
C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	1	9	11	1	-0.3	24.6	1.48	10.42(20)	
CH <sub>2</sub> Cl <sub>2</sub>	1	16	20	3	2.6	32.9	1.6	8.93(20)	
CHCl₃	1	26	32	5	10.4	39.5	1.04	4.81(25)	
CDCI <sub>3</sub>	1	26	32	5	10.4	39.5	1.04	4.81(25)	
CDCI3 <sup>[a]</sup>	1	30	35	5	10.4	39.5	1.04	4.81(25)	
CH <sub>2</sub> Br <sub>2</sub>	3	37	37	18	13.7	29.9	1.43	7.77(10)	
CCI <sub>4</sub>	2	7	4	2	16.0	-	0	2.24(20)	
CH <sub>2</sub> I <sub>2</sub>	10	46	77	79	23.1	27.4	1.08	5.316(25)	

[a] For all experiments except this, 5 vol.% of acetone- $d_6$  were added for the NMR lock purpose; [b]  $V_s(r)_{max}$  for all solvents, except for  $C_2H_4Cl_2$  and CDCl<sub>3</sub>, were calculated in our previous work.<sup>[4]</sup>

Solvation properties of various haloalkanes were initially tested by measuring the solubility of representative complexes **4**, **7**, **11**, and **12** (Table 2, SI: Figures S1–3). An approach based on quantitative <sup>1</sup>H NMR spectroscopy measurements<sup>[5]</sup> in the presence of hexamethyldisiloxane as an internal standard was preferred.

Amongst all haloalkane solvents studied, diiodomethane, CH<sub>2</sub>I<sub>2</sub>, demonstrated the best solvation properties determined by the highest solubility of all model compounds. Thus, the solubility of **4**, **7**, **11**, and **12** in CH<sub>2</sub>I<sub>2</sub> was up to an order of magnitude larger when compared to that in commonly used CHCI<sub>3</sub>. In addition, similar trends were established for isomerically pure **7**, **11**, and **12** and complex **4** that exists as an isomeric mixture allowing exclusion of the influence of *cis/trans* isomerization on solubility.

Given CH<sub>2</sub>I<sub>2</sub> demonstrated the greatest solvation properties, it was chosen for further experiments on the comparative solubility of all isocyanide complexes 1-16 (Table 3); results were compared to CDCI<sub>3</sub>, a commonly used organic solvent for NMR spectroscopy. In addition, CDCl<sub>3</sub> has comparable polarity to that of  $CH_2I_2$  (dipole moment,  $\mu$ : 1.04 for  $CDCI_3$  vs 1.08 for CH<sub>2</sub>I<sub>2</sub>), matching the contribution of solvent polarity to solubility of organometallics studied. For all complexes 1-16 excluding 10, CH<sub>2</sub>I<sub>2</sub> remains the solvent with superior solvating properties towards both platinum (14-16) and palladium (1-4) derivatives. The solubility of complexes increases upon the transition from cis-chloro complexes (1-4) to trans-bromo (5-8) and, to a greater degree, trans-iodo derivatives (9-12). Although transcomplexes have a symmetric ligand arrangement at metal, it is known that those in solutions are significantly distorted when compared to the solid state.<sup>[6]</sup> Isocyanide ligands, i.e. those in 5-12 are not monoatomic; they can easily bend and that will lead to the appearance of the dipolar moment.

Placement of the secondary halogen atom into the structure of the isocyanide ligands alters the solubility of 1-16 (Table 3). For both palladium (1-4) and platinum (13-16) *dichloride* complexes, upon going from unsubstituted phenyl- to a *p*-chlorophenyl isocyanide, the solubility is significantly increased. For palladium *dibromide* (5-8) and *diiodide* (9-12) complexes, an opposite effect was observed: the solubility is significantly

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dropped on going from unsubstituted phenyl- to a *p*-chlorophenyl isocyanide. We have also noted the variation in solubility in the row of complexes containing different halogen-substituted isocyanides (*p*-chloro- vs *p*-bromo- vs *p*-iodophenyl isocyanides, e.g. **2–4**, **6–8** or **10–12**) although the exact effect was not clear. For instance, in complexes **10–12** solubility decreases in CHCl<sub>3</sub>, while it grows in CH<sub>2</sub>I<sub>2</sub>.

Table 3. The solubility and isomeric ratios of 1-16 in CHCl3 and CH2l2.

Complex			Solubility, mg/mL	
Hal	x	Complex	CDCI3	CH <sub>2</sub> I <sub>2</sub>
	н	1	8	9
CI	СІ	2	15	31
(M = Pd)	Br	3	6	29
	1	4	1	10
	н	13	7	7
CI	CI	14	13	61
(M = Pt)	Br	15	20	72
	1	16	2	20
	н	5	65	94
Pr	CI	6	72	73
ы	Br	7	30	46
	1	8	2	12
	н	9	157	215
	CI	10	82	19
	Br	11	35	77
	I	12	5	79

To further attest the scope of this approach and usefulness of CH<sub>2</sub>I<sub>2</sub> as solvent for NMR studies, we evaluated solubilities in CDCl3 - taken for comparison as the most common NMR solvent - and in CH2l2 of various kinetically inert metal complexes including square-planar cis and trans non-electrolyte species bearing halide ligands and also halide-free complexes of different configuration (see Table S3). For the vast majority of platinum- and palladium halide species (entries 1-16), the solubility in CH<sub>2</sub>I<sub>2</sub> was found to be notably higher than that in CDCI<sub>3</sub>. Halide complexes of other metals (entries 19-21) as well as those without halide- but with acetylacetonate ligands (entries 17-18) demonstrate a similar trend. It is noteworthy that lone pairs of metal-bound acac ligands exhibit a pronounced tendency to form XB with suitable XB donors.<sup>[7]</sup> So far we found only one exception from the observed solubility trend when we tested metal species with aromatic ring ligands exhibiting rotational freedom (entries 24-31). We assume that the known<sup>[8]</sup> X–H/ $\pi$  (X = C, N, O) interactions with the acidic H atom of chloroform<sup>[9]</sup> contribute towards a better solubility of those species in this solvent.

Intrigued by our findings on different solvation properties of structurally and chemically related haloalkanes, we attempted to rationalize them. Insofar as one can reasonably exclude the effect of different polarity of haloalkanes studied on the solubility

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of model compounds, we focused our attention on weak interactions such as halogen bonding.  $^{\left[ 10\right] }$ 

The phenomenon of halogen bonding has recently attracted great attention due to relevance of XBs to pharmaceutical chemistry and drug design,<sup>[11]</sup> polymer and materials science,<sup>[12]</sup> organocatalysis<sup>[13]</sup> and crystal engineering.<sup>[14]</sup> XB is defined as a non-covalent interaction between a localized positive region on a halogen atom in the extension of the covalent bonds ( $\sigma$ -hole) and electron donor species serving as XB acceptors. From this perspective, an emergence of XB between halogen-containing organometallics (as a solute) and solvent or *vice versa* can have an impact on solvation. However, a quantitative effect of XBs on solubility of organometallics has never been verified.

Haloalkanes, apart from positive H centers responsible for HBs, feature an alternative type of partially positive charge centers, *viz.* the  $\sigma$ -holes<sup>[15]</sup> of covalently bound halogen atoms capable of non-covalent interactions. We have previously showed<sup>[4, 16]</sup> that the values of the electrostatic potential of the  $\sigma$ -holes (Vs(r)<sub>max</sub>), and subsequently the ability to form XBs, depend on the nature and number of halogen atoms in the structure of haloalkanes. The value of Vs(r)<sub>max</sub> on halogen atom grows in the row Cl < Br < I and with increase in electron-withdrawing ability of the substituent by a halogen atom, viz. a number of halogen atoms at the C atom for haloalkanes. Note that DFT calculations of electrostatic potentials (ESPs) at M06-2X/CEP-121G theory level revealed that CH<sub>2</sub>I<sub>2</sub> exhibits the largest positive potential on the halogen  $\sigma$ -holes (23.1 kcal-mol<sup>-1</sup>) among all studied haloalkanes (Table 2).

For all the complexes, the relationship between the positive potential on the halogen atom (Vs(r)max) and solubility as a rule increases symbiotically with  $\sigma$ -hole donating ability of a solvent (Figure S1, SI), except for CCl<sub>4</sub>. Tetrachloromethane possesses a high positive potential on the chlorine atom, but a null dipolar moment being the only non-polar solvent among those studied. Highest solubility of model compounds was observed for CH<sub>2</sub>I<sub>2</sub> as a solvent with the largest maximum positive potential on the halogen  $\sigma$ -holes, *i.e.* it is 10 times higher (10 mg/mL) for 4 and ca. 79 times (79 mg/mL) for 12 when compared against C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> as solvent with the lowest halogen  $\sigma$ -hole donating properties  $(V_s(r)_{max} = -0.3 \text{ kcal} \cdot \text{mol}^{-1})$ . Generally, when the quantity of halogen atoms present is increased and their polarizability (greater  $\sigma$ -hole) is increased (Cl < Br < I), better solubility of complexes is more likely due to the formation of solventcomplex XBs in solution. Apparently, the acidity of H atoms (represented by the maximum positive potential on the H, Table 1, Figure S2) does not play a significant role in the solvation process. At this point, one can reasonably suggest that the emergence of XBs between molecules of complex and solvent plays the key role in the dissolution process.

Since non-covalent interactions can hardly be studied in solution, we examined those in the XRD structures of some of our complexes. This canonical approximation is widely used to evaluate the XB situation and properties of solvates for different compounds. Halogen—halogen interactions can be assigned to one of two types on basis of their geometry.<sup>[17]</sup> Contacts of the type 1 are mainly of dispersion nature, whereas those of the type 2 are driven by electrostatic interactions between the polar and equatorial regions. In all contacts described below, the Hal—Hal distances are less than the sum of their Bondi vdW radii,<sup>[18]</sup> while the corresponding angles C–Hal—Hal and Hal—Hal–Pd are in the range 160–180° and 90–120°, respectively (Tables S7–9). In accord with the IUPAC criteria, these interactions are recognised as the type 2.<sup>[10]</sup> Two solvates

with  $CH_2I_2$  (10.2 $CH_2I_2$  and 11.2 $CH_2I_2$ , Figure 1) and two individual iodo complexes (11 and 12, Figure 2) were evaluated; ESP distribution for complexes 10-12 (Figure 3, Table 4) was also calculated. According to the computations, the iodides ligated to palladium have negative ESP on the whole of their surface and can act only as XB acceptors. At the same time, the halogen atoms in isocyanide ligands have areas with positive ESP corresponding to  $\sigma$ -hole position which makes these halogens potential XB donors. Complexes 10 and 11 form the CH<sub>2</sub>I<sub>2</sub> isomorphic solvates upon crystallization from their CH<sub>2</sub>I<sub>2</sub> solutions. In 10.2CH2l2 (Figure 1, left) and 11.2CH2l2 (Figure 1, right), the H<sub>2</sub>C(I)-I•••I-Pd XBs between each molecule of complex and four molecules of CH<sub>2</sub>I<sub>2</sub> were found. The calculated energy of each solvent-complex XB was 2.2-2.5 kcal/mol, and their contribution to the lattice energy in each case appears to be the most significant.

In both **10** and **11**,  $V_s(r)_{max}$  value on the halogen atom in the isocyanide ligand is lower than that for iodine in  $CH_2I_2$  making it a better XB donor for Pd-bound iodide.



Figure 1. The H<sub>2</sub>C(I)–I•••I–Pd XBs in 10·2CH<sub>2</sub>I<sub>2</sub> (left) and 11·2CH<sub>2</sub>I<sub>2</sub> (right).



Figure 2. The C-X<sup>2</sup>•••-Pd (X<sup>2</sup> = Br, I) XBs between two complex molecules in 11 (top) and 12 (bottom).

Crystals of **11** grown from the less  $\sigma$ -hole donating solvent, CHCl<sub>3</sub> (V<sub>s</sub>(r)<sub>max</sub> = 10.4 kcal·mol<sup>-1</sup>) contain only individual molecules of the complex with the intermolecular C–Br•••I–Pd XBs (Figure 2, top structure). Energy of C–Br•••I–Pd XBs interaction in this crystal is lower and such non-covalent contacts are less numerous when compared to the H<sub>2</sub>C(I)–I•••I–Pd XBs in solvate **11**·2CH<sub>2</sub>I<sub>2</sub>. This leads to an assumption that in the presence of CH<sub>2</sub>I<sub>2</sub> the system prefers to form solvate. However, in less  $\sigma$ -hole donating solvents a competition between complexcomplex and solvent–complex XBs could occur during dissolution process. Using a more  $\sigma$ -hole donating solvent (CH<sub>2</sub>I<sub>2</sub>, V<sub>s</sub>(r)<sub>max</sub> = 23.1 kcal·mol<sup>-1</sup>) leads to an increase in the number of solventcomplex XBs and good solubility, whereas in CDCI<sub>3</sub> (V<sub>s</sub>(r)<sub>max</sub> = 10.4 kcal·mol<sup>-1</sup>) the complex–complex interactions (C–Br•••I–Pd XBs, V<sub>s</sub>(r)<sub>max</sub>(CNC<sub>6</sub>H<sub>4</sub>–**Br**) = 19.8 kcal·mol<sup>-1</sup>) is more preferable

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and works towards a precipitation of complex. These results agree with the changes in solubility of **11**, vis. from 35 mg/mL in CDCl<sub>3</sub> to 70 mg/mL in CH<sub>2</sub>l<sub>2</sub>.

For **12**, crystallization from even the strongest *o*-hole donating solvent as CH<sub>2</sub>I<sub>2</sub> does not lead to any solvates and the crystals contain only individual molecules of the complex. They are isomorphic to **11** (Figure 2, bottom) and possess a similar pattern of intermolecular XBs C-I•••I-Pd (energy 2.2–2.5 kcal/mol). In this case, emergence of complex-complex XBs C-I•••I-Pd presumably due to higher positive ESP on *p*-iodide substituents in isocyanide ligands of **12** than on iodine in CH<sub>2</sub>I<sub>2</sub>, viz. 28.7 kcal·mol<sup>-1</sup> vs. 23.1 kcal·mol<sup>-1</sup> (Figure 3). This tendency of palladium complexes with *p*-iodo substituted isocyanides to form strong intermolecular complex-complex interactions could explain why they have the poorest solubility of the isocyanide derivatives studied.

Table 4. The solubility of  $10{-}12$  in CDCl<sub>3</sub> and CH<sub>2</sub>l<sub>2</sub> and maximums electrostatic potentials (V\_S(r)\_{max}, kcal  $\cdot$  mol^-1) on the X in  $10{-}12$  and halogen in haloalkanes.

<b>a</b> 1	Solubility, mg/mL		Vs(r) <sub>max</sub> , kcal⋅mol <sup>-1</sup>			
Complex	CDCI <sub>3</sub>	$CH_2I_2$	$\rm XC_6H_4$	CDCl <sub>3</sub>	$CH_2I_2$	
10	82	19	8.4			
11	35	79	19.8	10.4	23.1	
12	5	77	28.7			



**Figure 3**. ESP distribution in **12** (X = I, Hal = I) (M06-2X/CEP-121G level of theory). Blue color – negative ESP, red color – positive ESP.

To conclude, we scrutinized the solvation properties of a solvents against a series number of haloalkane of organometallic species. Using NMR measurements, we established that CH<sub>2</sub>I<sub>2</sub> demonstrated the best solvation properties among all haloalkanes studied; solubility values for organometallics were improved by up to an order of magnitude when compared to the commonly used CHCl<sub>3</sub>. Since no correlation between the polarity of haloalkanes and the solubility of all model complexes was observed, we looked for an alternative explanation. We anticipated that better solvation properties of  $CH_2I_2$  are related to a dramatic growth of the  $\sigma$ -hole donating ability of this solvent when compared to others, and that results in the formation of strong solvent-(metal complex) halogen bonding. The emergence of these uniquely strong XBs in diiodomethane and its inertness towards organometallics make this solvent a good candidate for NMR solvent-of-choice, in particular, for the acquisition of insensitive spins, where the concentration of an analyte is crucial. Whereas a number of methods to suppress an undesired solvent signal in <sup>1</sup>H NMR are available,<sup>[19]</sup> a deuterated version of CH<sub>2</sub>I<sub>2</sub> might be prepared,<sup>[20]</sup> if necessary. The strength of XBs is influenced by the introduction of additional halogens to the organometallic species. Herein, we demonstrated that strength of XBs and subsequently the solubility decreases with the rise of the positive potential on halogen moieties placed on isocyanide ligands due to the formation of more favourable *intermolecular* complex-complex XBs. Further studies on understanding the role of XBs and their application in organometallic chemistry, are currently underway in our group.

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**Keywords**: halogen bonding • solvation• organometallics • haloalkanes • isocyanide complexes

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#### Entry for the Table of Contents

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Unique solvation properties of diiodomethane towards halidecontaining organometallics are associated with its enhanced  $\sigma$ -hole donating ability leading to stronger solvent-(metal complex) halogen bonding.



M. A. Kinzhalov,\* M. V. Kashina, A. S. Mikherdov, E. A. Mozheeva, A. S. Novikov, A. S. Smirnov, D. M. Ivanov, M. A. Kryukova, A. Yu. Ivanov, S. N. Smirnov, V. Yu. Kukushkin, K. V. Luzyanin\*

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Solubility of halide-containing organometallics is dramatically enhanced in diiodomethane: can the solvent\*\*\*complex halogen bonding be held responsible?

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