Model for the Initial Stage in the Oxidative Addition of I_2 to Organoplatinum(II) Compounds. X-ray Structure of Square-Pyramidal $[Pt^{II}I\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}(\eta^1\text{-}I_2)]$ Containing a Linear Pt-I-I Arrangement

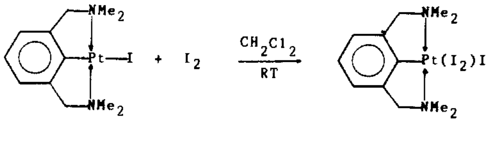
Johannus A. M. van Beek,[1a] Gerard van Koten,*[1a]
Wilberth J. J. Smeets,[1b] and Anthony L. Spek[1b]

Anorganisch Chemisch Laboratorium
University of Amsterdam
1018 WV Amsterdam, The Netherlands
Vakgroep Algemene Chemie, Afdeling Kristal- en
Structuurchemie, University of Utrecht
3508 TB Utrecht, The Netherlands

Received March 28, 1986

Much interest exists in the coordination of halocarbons (e.g., MeI) and halogens (e.g., I_2) to transition metals because halo-metal complexes may serve as models for probable intermediates formed during early stages of oxidative addition reactions. The fact that these electrophiles are weak ligands and at the same time prone to decompose via oxidative addition adds to the problems encountered in obtaining stable complexes. Recently, a few halocarbon-metal complexes have been isolated, i.e., *cis,trans*-$[IrH_2(o\text{-}C_6H_4I_2)(PPh_3)_2]BF_4$[2] and $[Ir(COD)(\eta^2\text{-}o\text{-}BrC_6H_4PPh_2)]SbF_6$,[3] while the existence of $[RhICl(Me)(PPh_3)_2(IMe)]$ had been proposed already in 1966.[4] We now report the first example of a complex in which the highly reactive halogen I_2 is coordinated to a transition metal.

The reaction of $[PtI\{C_6H_3(CH_2NMe_2)_2\text{-}o,o\}]$,[5,6] PtI(NCN), with I_2 in a 1:1 molar ratio (in CH_2Cl_2 at room temperature) affords the iodine-platinum(II) complex **2**[7] in 40% yield (eq 1). The



(1)

1, PtI(NCN) 2

^1H NMR spectrum of the starting compound **1** shows $^3J(^{195}Pt\text{-}^1H)$ couplings of 40 Hz on the *N*-methyl protons and of 46 Hz on the benzylic protons, values which are in the expected region for platinum(II) compounds containing trans N-donor ligands.[5] The fact that for **2** these couplings are smaller (28 and 30 Hz, respectively) suggested that an oxidative addition product had been obtained. The platinum(IV) compound $PtCl_3(NCN)$,[8] which was obtained from the reaction of PtCl(NCN) with Cl_2, showed reduced $^3J(^{195}Pt\text{-}^1H)$ couplings of 29 and 30 Hz indeed. However, the striking color (deep violet) and the UV spectra of **2**[9] prompted us to carry out an X-ray structure determination[10] to verify the nature of **2**.

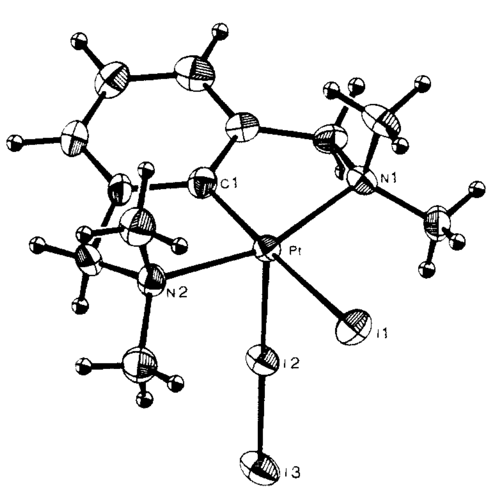


Figure 1. ORTEP drawing of **2**. Selected bond distances (Å) and angles (deg): Pt-C(1), 1.937 (9); Pt-N(1), 2.116 (7); Pt-I(1), 2.727 (1); Pt-N(2), 2.106 (8); Pt-I(2), 2.895 (1); I(2)-I(3), 2.822 (1); Pt-I(2)-I(3), 179.43 (4); N(1)-Pt-N(2), 160.7 (3); C(1)-Pt-I(1), 172.4 (3).

The molecular structure of **2**, see Figure 1, reveals that a fascinating molecule has been obtained with the iodine molecule interacting with the platinum(II) center in the η^1-coordination mode. Characteristic structural features are the following:

1. The distorted square-pyramidal geometry is observed, with I_2 occupying the apical and C(ipso), N(1), N(2), and I(1) occupying the basal positions. The platinum center is lifted by 0.18 (2) Å out of the least-squares plane calculated for the basal ligands.

2. The η^1-coordination of the neutral iodine molecule to platinum(II) has an almost linear Pt-I(2)-I(3) arrangement and a long Pt-I(2) distance of 2.895 (1) Å[11] (cf. the Pt-I(1) bond length of 2.727 (1) Å involving the iodide anion). The platinum-iodine bonding results in an elongation of the I-I bond distance from 2.715 (6) Å in "free" iodine[12] to 2.822 (1) Å in complex **2**. A similar elongation of the covalent I-I bond has been found in donor-acceptor complexes of organic molecules and I_2, e.g., $Me_3N\text{---}I_2$[13] has an I-I bond length of 2.83 (1) Å and a N-I-I bond angle of 179°.

3. In the crystal structure each molecule is linked via two short intermolecular I---I contacts (I(1)---I(3)* = 3.595 (2) Å) into an infinite chain running along the *b*-directed screw axis.[14]

The η^1-bonding in **2** can be described by donation of electron density from platinum to I_2 by overlap of the filled d_{z^2} platinum orbital with the empty σ^* orbital of I_2. The enhanced basicity of the platinum center in **1** arises from the presence of the hard N- and C-donor ligands and has earlier been demonstrated by isolation of, for example, the stable η^1-SO_2 complex $[PtBr(NCN)(\eta^1\text{-}SO_2)]$.[15]

Halogen complexes like **2** have been proposed as intermediates

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* To whom correspondence should be addressed.

[1] (a) University of Amsterdam. (b) University of Utrecht.

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[6] Crystal structure of **1**: Smeets, W. J. J.; Spek, A. L.; van Beek, J. A. M.; van Koten, G., unpublished results.

[7] ^1H NMR (CD_2Cl_2, 100 MHz, room temperature) of **2**: δ 3.26 (s, 12 H, $^3J(^{195}Pt\text{-}^1H) = 28$ Hz), 4.18 (s, 4 H, $^3J(^{195}Pt\text{-}^1H) = 30$ Hz), 7.10 (m, 3 H). Correct elemental analyses were obtained.

[8] Terheijden, J.; van Koten, G.; de Booys, J. L.; Ubbels, H. J. C.; Stam, C. H. *Organometallics* **1983**, *2*, 1882. $PtCl_3(NCN)$ has a *mer*-Cl_3 arrangement. In light of the present results, the earlier conclusion that the reaction of **1** with I_2 gave a similar $PtI_3(NCN)$ complex proves to be not correct.

[9] The UV, IR, and Raman data of $PtCl_3(NCN)$ and **2** show marked differences. The spectra are currently studied and full interpretation will be presented in the full paper.

[10] Crystal data for **2**: $C_{12}H_{19}I_3N_2Pt$, orthorhombic, space group $P2_12_12_1$, with $a = 7.976$ (2) Å, $b = 9.532$ (2) Å, $c = 23.577$ (7) Å, $V = 1792.5$ (8) Å^3, $Z = 4$, $D_c = 2.842$ g cm^{-3}, $F(000) = 1368$, $\mu(\text{Mo } K\alpha) = 130.1$ cm^{-1}, 2392 independent reflections with $0.87° < \theta < 27.5°$ were measured on an Enraf-Nonius CAD 4F diffractometer using Zr filtered Mo Kα radiation ($\lambda = 0.71073$ Å). Data were corrected for Lorentz-polarization effects, absorption (Gaussian integration), and a small linear decay (~4%). The structure was solved by Patterson (SHELX 84) and difference Fourier techniques and refined by blocked full-matrix least squares (SHELX 76) to an R value of 0.0256, wR $(\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2} = 0.0317$, $w^{-1} = \sigma^2(F_o)$ for 2148 reflections with $I > 2\sigma(I)$. In the final stages of refinement, hydrogen atoms were introduced on calculated positions; all non-hydrogen atoms were refined with anisotropic thermal parameters.

[11] The sum of the van der Waals radii of Pt and I $\geq$3.65 Å: Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

[12] The I-I distance of I_2 in the solid at 110 K is 2.715 (6) Å: van Bolhuis, F.; Koster, P. B.; Migchelsen, T. *Acta Crystallogr.* **1967**, *23*, 90.

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[14] The distance of 3.595 (2) Å is comparable to reported $I_2\text{---}I^-$ distances: Millan, A.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1982**, 73 and references cited there.

[15] Terheijden, J.; van Koten, G.; Mul, W. P.; Stufkens, D. J.; Muller, F.; Stam, C. H. *Organometallics* **1986**, *5*, 519.

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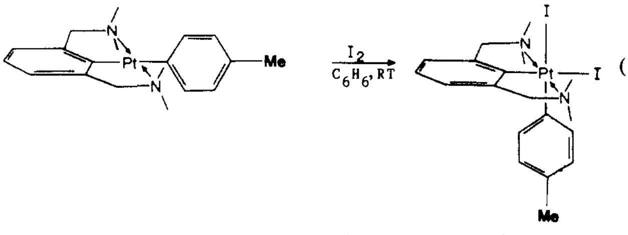
in oxidative addition reactions of X_2 to platinum(II) complexes.[16] The fact that **2** is stable and does not react further either to $PtI_3(NCN)$ or to Pt–C bond cleavage products is therefore surprising and may be partly brought about by steric factors. This seems to be substantiated by the observation that Pt(*p*-tolyl)(NCN) reacts with I_2 cleanly to the oxidative addition product PtI_2(*p*-tolyl)(NCN)[17] (see eq 2).



(2)

In the latter, octahedral Pt(IV) complex the formerly trans orientation of the carbon ligands has changed to a cis arrangement. ^1H NMR studies have revealed that the flat *p*-tolyl group is fixed in a position perpendicularly to the N–Pt–N axis.

The mechanistic aspects of oxidative addition reactions of X_2 and alkyl and aryl iodides to PtX(NCN) complexes are currently investigated.

Acknowledgment. The Netherland Foundation for Chemical Research (SON) and the Netherland Organization for Pure Research (ZWO) are thanked for financial support. Thanks are due to Prof. K. Vrieze for his stimulating interest.

Registry No. 1, 82112-97-8; **2**, 103148-37-4; I_2, 7553-56-2.

Supplementary Material Available: Fractional atomic coordinates, anisotropic thermal parameters, all bond distances and angles, and observed and calculated structure factors of **2** (16 pages). Ordering information is given on any current masthead page.

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[17] (a) This was confirmed by an X-ray structure determination of PtI_2(*p*-tolyl)(NCN): Terheijden, J. Ph.D. Thesis, 1986, University of Amsterdam, the Netherlands. (b) van Beek, J. A. M.; van Koten, G.; Dekker, G. P. C. M.; Terheijden, J.; Muller, F.; Stam, C. H., unpublished results.

Slow Complexation Rates of Crown Ethers: What Is Taking So Long?

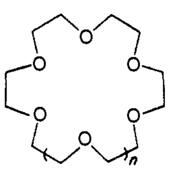
J. Rebek, Jr.,* S. V. Luis, and L. R. Marshall

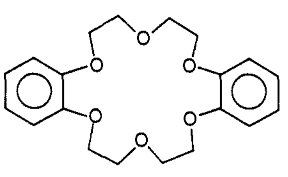
Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260

Received March 10, 1986

Cation complexation by simple crown ethers is a fast process. Association rates are typically in the megahertz range and can be determined by ultrasonic techniques,[1] while exchange rates between ions and their complexes are generally fast on the NMR time scale.[2] We have recently determined that complexation rates for crown ethers and certain organomercurials are slow on the *human time scale*; here we report our methods and suggest a probable cause for the sluggishness of the reactions.

In organic solvents, the binding of 18-crown-6 **2** to $Hg(CN)_2$ can be conveniently measured by ^1H NMR through the disappearance of the singlet for the free crown (3.54 ppm) or the appearance of the singlet for the 1:1 complex[3] (3.40 ppm). The


1, n = 0
2, n = 1
3, n = 2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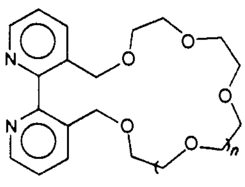
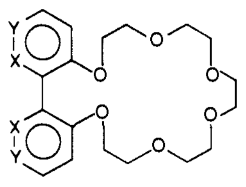
reaction is second order and the rate constant (Table I) corresponds to half-life of nearly 1 h at ambient temperature and 0.01 M reactants. In the range 273–313 K, the Arrhenius parameters E_{act} = 11.4 kcal/mol and log A = 6.9 were determined. No binding between $Hg(CN)_2$ and the smaller **1** could be detected, but very fast complexation ($t_{1/2}$ < 1 s at these concentrations) was observed with the larger **3**, or even the 20-membered **7**.


5, n = 1
6, n = 2



7, X = Y = CH
8, X = N, Y = CCH_3

Conformational mobility of the crown further affects the rate. The dibenzo derivative **4** showed a rate (Table I) some 60 times slower than **2** with $Hg(CN)_2$. Exchange of this Hg derivative between **2** and **4** was very slow; gradual changes were observed in the NMR spectra of either complex in the presence of the other crown over a period of months.

With $Hg(CF_3)_2$ rates can be even slower. Earlier[4] we described how the 2,2′-bipyridyl function of **6** can act as an on–off switch for the uptake and release of $Hg(CF_3)_2$ by the ethereal cavity. Rapid exchange occurs with the 22-membered ring of **6**, but metals which are chelated by the bipyridyl, i.e., $PdCl_2$, cause a conformational change (allosteric effect) that reduces the effective size of the macrocycle. With the 21-membered ring of **3**, uptake of $Hg(CF_3)_2$ is also rapid but its release is slow. Since $Hg(CN)_2$ binds even more tightly to this ether, the release of $Hg(CF_3)_2$ by **3** could be measured by the substitution reaction of eq 1. The

$$\mathbf{3}\cdot Hg(CF_3)_2 \underset{\text{slow}}{\overset{k_1}{\rightleftharpoons}} Hg(CF_3)_2 + \mathbf{3} \xrightarrow[\text{fast}]{Hg(CN)_2} \mathbf{3}\cdot Hg(CN)_2 \qquad (1)$$

reaction rate (Table I) was independent of the concentration of $Hg(CN)_2$ and corresponds to a dissociation barrier $\Delta G^{\ddagger}$ of 21.7 kcal/mol.

No binding of $Hg(CF_3)_2$ to **2** or the 19-membered **5** was observed, but the slow complexation with 20-membered rings[5] **7** and **8** could be measured. With **7** the association rate was determined over a period of days by ^{19}F NMR in $CDCl_3$ (free, −36.6 ppm; complex, −38.6 ppm from internal $CFCl_3$). The release rate was measured by using the substitution reaction of eq 2; this corre-

$$\mathbf{7}\cdot Hg(CF_3)_2 + Hg(CN)_2 \rightarrow \mathbf{7}\cdot Hg(CN)_2 + Hg(CF_3)_2 \qquad (2)$$

$$\mathbf{8}\cdot Hg(CF_3)_2 + Hg(CN)_2 \rightarrow \mathbf{8}\cdot Hg(CN)_2 + Hg(CF_3)_2 \qquad (3)$$

sponds to a half-life of about 1 month and $K_{eq} \approx 1700\ M^{-1}$. The rates and equilibrium for the bipyridyl **8** were measured in a similar manner (eq 3). The lower K_{eq} for **8** (K_{eq} αpp 200 M^{-1}) reflects a 20-fold slower uptake rate and 2.5-fold slower release rate in the reactions of **8** vs **7**.

Why are these reactions so slow? For complexation of *ions* in polar solvents,[6] *desolvation* generally contributes to the rate-determining step (the Eigen–Winkler mechanism[7]) rather than

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