Kinetico-Mechanistic Studies on Intramolecular C−X Bond Activation (X = Br, Cl) of Amino-Imino Ligands on Pt(II) Compounds. Prevalence of a Concerted Mechanism in Nonpolar, Polar, and Ionic Liquid Media

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Abstract

The C−Br and C−Cl oxidative addition reactions of molecules containing a set of {N-amino,N-imino} chelating donor groups (2-X,6-$YC_6H_4CHNCH_2CH_2NMe_2$, X = Br, Cl; Y = Cl, H) attached to a $\{Pt^{II}(Ar)_2\}$ (Ar = Ph, 4-MeC_6H_4) have been studied. The Pt(IV) complexes formed, [$PtAr_2X\{2\text{-}YCC_5H_3CH{=}NCH_2CH_2NMe_2\}$], containing a metalated tridentate [C,N,N′] ligand have been fully characterized by the usual techniques, and the X-ray crystal structure of the complex with Ar = 4-MeC_6H_4 and X =Y = Cl has been determined. Monitoring of the reactions at varying temperatures and pressures and in different solvents agrees with a mechanism that involves the preliminary decoordination of the N-amino donor from the ligand to produce a threecoordinated intermediate. This evolves, via a concerted C−X bond activation, to form a second pentacoordinated intermediate species that, on coordination of the N-amino donor, produces the final complex. The kinetico-mechanistic parameters measured indicate that the concerted character of the process is maintained from nonpolar (xylene and toluene) to polar (acetone) and ionic liquid (($Bmin(NTf_2)$)) media. Furthermore, the $\Delta V^{\ddagger}$ values measured indicate that, for the (2,6-Cl)$C_6H_3CH{=}NCH_2CH_2NMe_2$ ligand, the existence of hydrogen bonding within the metalating molecule is a determinant for the acceleration observed.

1. INTRODUCTION

The oxidative addition of carbon−halogen bonds is a key step in many stoichiometric and catalytic reactions mediated by transition-metal complexes.[1] In particular, there is an increasing evidence of the involvement of palladium(IV) compounds in palladium-catalyzed processes.[2,3] Due to the comparatively easier access to platinum(IV) species, mechanistic studies of oxidative addition are often based on organoplatinum chemistry,[4] and these reactions are well-established.[5] Some studies carried out on intermolecular systems involving oxidative addition of $R_{alkyl}X$ have been conducted for some time and the classical SN2 mechanism fully established from a kinetico-mechanistic perspective.[6−9] Even ionic liquid solvent systems have been recently used in order to reveal the importance of polarity in the reaction medium.[10] For processes involving $R_{aryl}X$ oxidative addition reactions, such a mechanism is prohibitive for an sp^2 carbon center, and a concerted alternative should be operative.[11] Furthermore, if this process occurs on a previously coordinated organic ligand (i.e., directing group), a formal intramolecular cyclometallation process will be occurring, which is expected to require lower energetic demands and produce higher yields.

In this respect, intramolecular C_{aryl}−X bond activation (X = H, F, Cl, Br) at dimethylplatinum(II) centers takes place under rather mild conditions for adequately designed ligands having N donors as directing groups.[12−16] The corresponding kineticomechanistic study has been also conducted for both ligands containing either one (imino) or two (amino-imino) nitrogendonor directing groups.[17−20] In recent years, renewed interest for analogous reactions at diarylplatinum(II) relies on the fact that the resulting platinum(IV) species are involved in C−C coupling reactions, leading to biphenyl systems along with formation of several types of platinum(II) compounds containing five-, six-, or seven-membered platinacycles.[20−24] However, mechanistic studies carried out for this type of systems are scarce.[25]

In this paper, we present a detailed kinetico-mechanistic study on the C−Br and C−Cl oxidative addition reactions of molecules containing a set of {N-amino, N-imino} chelating

donor groups (2-X,6-YC$_6$H$_4$CHNCH$_2$CH$_2$NMe$_2$, X = Br, Cl; Y = Cl, H) attached to a {Pt^{II}(Ar)$_2$} (Ar = Ph, 4-MeC$_6$H$_4$) unit.

The Pt(IV) complexes formed, [PtAr$_2$X{2-YCC$_5$H$_3$CH=NCH$_2$CH$_2$NMe$_2$}], containing a metalated tridentate [C,N,N′] ligand, have been fully characterized by the usual techniques, indicating the existence of the fac-[C,N,N′] arrangement together with the usual mer-[C,N,N′] isomer in some cases. The X-ray crystal structure of the complex with Ar = 4-MeC$_6$H$_4$ and X =Y = Cl has also been determined, agreeing with the characterization data in solution. The kineticomechanistic results agree with the concerted mechanism established for previous studies on monodentate N-imino directing group systems. The absence of any polar component in the concerted transition state proposed is made clear by the independence of the parameters measured for ortho-xylene, toluene, acetone, or (Bmin)(NTf$_2$) (1-butyl-3-methylimidazolium bis{trifluoromethanesulfonyl}imide) solvents. Furthermore, the continuity of the mechanism proposed is made clear by a very good alignment with the $\Delta H^{\ddagger}/\Delta S^{\ddagger}$ compensation plot for all the systems available in the literature.[19] The more positive values found for the systems studied agree with the need of the N-amino decoordination as a preliminary steady-state step to the proper C−X bond activation, as already found for equivalent {N-amino,N-imino} chelating systems with {Pt^{II}(Me)$_2$} units.[12] The existence of hydrogen-bonding interactions involved in the reactivity of the 2,6-Cl$_2$C$_6$H$_4$CHNCH$_2$CH$_2$NMe$_2$ ligand is also made evident by the usual lack of parallelism in the $\Delta V^{\ddagger}/\Delta S^{\ddagger}$ trend.[19,26]

2. RESULTS AND DISCUSSION

Compounds. The syntheses of Pt(IV) compounds [PtAr$_2$X {2-YCC$_5$H$_3$CH $=$ NCH$_2$CH$_2$NMe$_2$}] (Ar = Ph or 4-MeC$_6$H$_4$; X = Br or Cl; Y = Cl or H) have been previously reported.[20,24] These compounds are formed via the intramolecular oxidative addition of C−X bonds from the corresponding Pt(II) coordination compounds [PtAr$_2${2-X,6-YC$_6$H$_3$CH $=$ NCH$_2$CH$_2$NMe$_2$}]. Compound [Pt{4-MeC$_6$H$_4$} 2Cl {2-ClCC$_5$H$_3$CH $=$ NCH$_2$CH$_2$NMe$_2$}] (**3-Cl,Cl**) was characterized crystallographically in this work. The structure depicted in Figure 1 shows the three carbon donors in the usual *fac*-PtC$_3$ geometry and the tridentate ligand adopting a *mer*-[C,N,N′] disposition, in agreement with the arrangement reported for [PtMe$_2$Cl {2-ClCC$_5$H$_3$CH $=$ NCH$_2$CH$_2$NMe$_2$}].[12] The Pt−NMe$_2$ distance, 2.298(4) Å, is significantly longer than that for the Pt−NCH bond, 2.059(3) Å, which is consistent with the relatively weak ligand character of tertiary amines for platinum.[27] All bond distances are in the expected range, and the bond angles at the platinum center deviate slightly from the ideal 90°. The smallest, N1−Pt−N2 = 79.72 (12)° and C1−Pt1−N2 = 81.03 (14)°, involve the tridentate [C,N,N′] ligand. The ^{1}H NMR spectra of compounds [Pt{4-MeC$_6$H$_4$ } 2Cl {2-ClCC$_5$H$_3$CH $=$ NCH$_2$CH$_2$NMe$_2$}] (**3-Cl,Cl**) and [Pt{4-MeC$_6$ H$_4$} 2Cl - {CC$_5$H$_4$CH $=$ NCH$_2$CH$_2$NMe$_2$}] (**3-Cl,H**) in CDCl$_3$ or acetone-d6 indicate the presence of a single isomer, and the structure determined in the X-ray study of **3-Cl,Cl** is assumed. As previously reported,[24] these compounds react in solution to give seven-membered metallacycles and toluene, which prevents further studies.

In this respect, the higher inertness of compound [Pt {4- MeC$_6$H$_4$} 2Br {CC$_5$H$_4$CH $=$ NCH$_2$CH$_2$NMe$_2$}] (**3-Br,H**) allows for a more detailed study of its behavior in different deuterated solvents. Analysis of the signals in the − N $=$ CH − region indicates the presence of a single isomer in deuterated toluene, while two isomers are observed in CDCl$_3$ and CD$_3$COCD$_3$ (relative ratios of 91:9 and 89:11, respectively); in dmso-d$_6$, three resonances are apparent with relative ratios of 3:94:3. Considering that the three Pt−C bonds of the **3-Br,H** compound have to be mutually *fac*, due to the donor character of the ligands around

120 the platinum center,[28,29] two different isomers with the [C,N,N′] ligand either in *mer* or *fac*

121 arrangements can exist in solution (Scheme 1).

122 Calculations carried out for analogous [PtMe2X (C,N,N′)] compounds indicated a

123 slightly higher stability for the *mer*-versus *fac*-[C,N,N′] ligand arrangement (ca. 8−9

124 kcal/mol), as expected due to the preference of the metalated imine ligand to be

125 approximately planar.[12] The *mer*-[C,N,N′] structure is thus assigned to the major isomer of

126 **3-Br,H** observed in CDCl3 based on the NOESY cross-peaks between the tolyl groups and

127 both methyl substituents from the amino group. Although the trend in chemical shifts, in

128 particular, for the iminic hydrogen, observed for the major isomer (Table 1) can be fitted to

129 the different polarity parameters of the different solvents used in a reasonable way, NOESY

130 spectra indicated that a different arrangement of the [C,N,N′] unit might occur in some of

131 the media. In this respect, the NOESY contact between the ortho proton signals of the

132 metalated ring and both dimethylamino groups, observed for the major isomer in dmso,

133 points to the alternative facial arrangement of the [C,N,N′] ligand in this solvent.

134 Nevertheless, an easy isomerization between the mer and the fac arrangement of the [C,N,N′]

135 ligand is expected from the quasi-labile character of these compounds, as already established

136 for the substitution of the SMe2 ligand in similar [C,N] cyclometalated Pt(IV) complexes.[30]

137 Furthermore, the coexistence of the two isomers indicated in Scheme 1 has already been

138 established in other systems of the same family, as well as their interconversion on changing

139 the size of the ancillary neutral ligand from SMe2 to PPh3.[31] Finally, decoordination of the

140 dimethylamino moiety in dmso might account for the observation of a third imine resonance

141 in this solvent. Because of the small intensity of the signal observed, any further assignment

142 to a specific isomer has not been conducted.

143 Interestingly, the signals corresponding to the ethylene bridge protons ($=N-C\underline{H}_2$ -

144 $C\underline{H}_2-N(CH_3)_2$) of the [C,N,N′] metalated ligand show diverse patterns appearing at very

145 different chemical shifts, depending on the solvents used. Even in dmso and toluene solution,

146 the four protons appear as nonequivalent. In the latter solvent, they appear in the widest

147 range (4.12, 3.35, 3.17, and 1.87 ppm) with a marked upfield chemical shift for one of the

148 $-CH_2-C\underline{H2}-N(CH_3)_2$ nuclei. These data cannot be rationalized on the exclusive basis of the

149 different polarities of the solvents and can be related to different conformations of the [N,N′]

150 chelate as well as different preferred orientations of the tolyl ligands.

151   **Kinetico-Mechanistic Studies.** The oxidative addition reaction of the C−X bond

152 occurring on **1 - Cl, H**, **2 – Cl , H, 1 - Br, H**, and **1 – Cl, Cl** Pt (II) complexes (Scheme 2),

153 producing the corresponding Pt(IV) derivatives (eq 1), has been timeresolved by monitoring

154 the changes in the UV−vis and proton NMR spectra of the samples in different solvents.

155   Proton NMR spectra monitoring of the reactions carried out in toluene, after reduced

156 pressure evaporation of the solvent, indicated that, effectively, the process followed

157 corresponds to the reaction shown in eq 1 on the time scale used. Thus, the validity of the

158 UV−vis monitoring of the reaction under the same conditions has been proved. In all cases,

159 a very wellbehaved first-order behavior has been observed with a large decrease of the

160 absorbance in the electronic spectrum at ca. 400 nm, which corresponds to the disappearance

161 of the Pt(II) complex.[17,32] When the compounds were left for longer times in the reaction

162 medium, a new increase of the response of the electronic spectra at this wavelength was

163 observed, corresponding to the formation of new Pt(II) species.[22,25] These reductive

164 elimination processes are currently under study. Specifically, the isolation of neat 1-Br,H

165 has not been achieved; nevertheless, as stated above, NMR monitoring indicates that the

166 kinetic profiles measured effectively correspond to the C−Br bond activation on compound

167 **1-Br,H**.

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1-X,Y (R = Me)
or 2-X,Y (R = H)   3-X,Y (R = Me)
                                    or 4-X,Y (R = H)   (1)
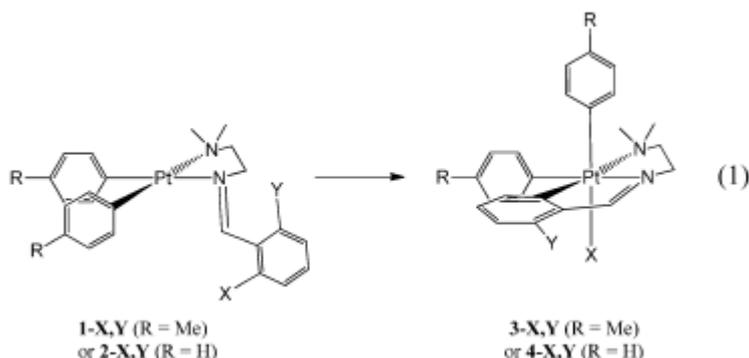
169   The reactions were followed in toluene, ortho-xylene, (Bmin)(NTf$_2$), and acetone

170 solutions at different concentrations, temperatures, and pressures via conventional electronic

171 spectroscopy and using the convenient instrumentation indicated in the Experimental

172 Section. Changes in the concentration of the platinum complex within the $(0.5−5) \times 10^{-4}$ M

margin produced no changes in the measured rate constants, as expected for reactions as those indicated in eq 1. Similarly, the use of the diversity of solvents indicated in the processes does not produce significant changes in the reaction rates, as already found for the concerted oxidative addition occurring on very similar complexes (Figure 2).[17,18] This is specially relevant for the use of (Bmin)(NTf$_2$) ionic liquid as the solvent, given the fact that the use of such a solvent has been found having determinant effects when changes in the polarity on going to the transition state are involved.[10,33,34]

Table 2 collects the relevant kinetic and activation parameters measured for the reactions monitored. From the data, it is clear that rather different values have been determined for the two sets of compounds studied: (i) those having a monodentate {N-imino} metalating and an ancillary dimethylsulfide ligand and (ii) those with an {N-imino,N-amino} bidentate unit. For the former, the reaction occurs in a facile way at room temperature with little enthalpic requirements and a high degree of ordering and compression on going to the transition state. In this case, the reaction sequence had been established as one that involves the sulfide ligand dissociation, formation of an undetected 14-electron intermediate, and a subsequent facile concerted C−X bond activation.[17,35,36] Accordingly, if, for the {N-imino,N-amino} bidentate systems, such a 14-electron intermediate is responsible for the C−X bond activation, its energetic demands should be much higher,[37] which is effectively seen in the activation parameters. Furthermore, in this case, the dangling arrangement of the Namino moiety should also produce a definite increase of the volume and entropy of activation, despite keeping the concerted nature of the C−X bond oxidative addition. Figure 3 shows a very good $\Delta H^{\ddagger}/\Delta S^{\ddagger}$ compensation plot for all the systems indicated in Table 2, which corroborates the uniformity of the C−X bond activation processes being studied, independent of the nature of the directing groups of the metalating ligand.[38,39] From the data collected, it is also clear that the changes introduced by changing a 4-MeC$_6$H$_4$ for a phenyl spectator ligand do not have any significant effect on the process.

From the data collected in Table 2, it is also clear that the compounds having two methyl ancillary ligands have smaller $\Delta H^{\ddagger}$ values, while the $\Delta S^{\ddagger}$ values are more negative than for the equivalent bis-aryl analogues (1-Cl,H/*v*, 1-Br,H/*vi*, 1 - Cl,Cl/*vii, xiii/xiv*).[22] The

202 effect is specially pronounced for entries *xii* and *xiv*, which are related to monodentate

203 dimethylsulfide complexes. The trend can be associated with the lower donor character of

204 the phenyl ligands, when compared with the equivalent complex with methyl groups, that

205 hampers the relative dissociation of the nonorganometallic ligands and the formation of the

206 14-electron intermediate, especially for monodentate dimethylsulfide systems (eq 2).
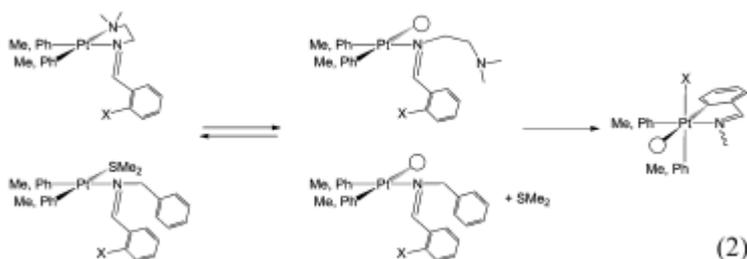
207   (2)

208   A close examination of the data in Table 2 shows, nevertheless, two sets of values

209 that fall out of the expected $\Delta S^{\ddagger}/\Delta V^{\ddagger}$ correlation plot indicated in Figure 4 (provided no

210 hydrogen bonding is involved in the activation process). [19,22,26,40] For compound

211 [PtMe$_2$\{CC$_5$F$_5$CHNCH$_2$C$_6$H$_5$\}- (SMe$_2$)], *ix*, the possible hydrogen bonding has been found

212 to favor an earlier transition state for the C−F bond activation and produce such a deviation

213 (low enthalpy, very negative entropy, and small contraction). [19] In the present case for

214 compound 1 - **Cl,Cl**, this explanation is rather difficult to come to terms with, unless a

215 hydrogen bond between the nonmetalating chloride *ortho* substituent in the ring and the =

216 CH − hydrogen is claimed, as already established in other similar systems. [37,41] If this is the

217 case, a much more ordered transition state can be expected (Scheme 3), thus explaining the

218 anomalous $\Delta S^{\ddagger}/\Delta V^{\ddagger}$ correlation point.

219   In this respect, the existence of the hydrogen-bonding interaction indicated in

220 Scheme 3, involving a nonmetalating chloride group, can also explain the much less

221 favorable enthalpy found for the activation of the C−Cl bond in **1-Cl,H** when compared with

222 **1-Cl,Cl**. Furthermore, time-resolved proton NMR monitoring of the reaction from **1-Cl,H**

223 to 3- **Cl,H** indicated the presence in very small quantities (5−10%) of free toluene and a five-

224 membered Pt(II) compound. [42] The latter has been putatively associated with that obtained

225 by an *ortho* C−H bond activation of the ligand, from a species, such as that indicated in

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226   Scheme 3, involving a three-centered H− Pt−C interaction, followed by tolyl−H reductive

227   elimination from a hydride Pt(IV) intermediate compound.[22]

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3. CONCLUSIONS

The oxidative addition reaction of the (2-X,6-Y) $C_6H_3CH=NCH_2CH_2NMe_2$ (X = Br or Cl; Y = H, or Cl) ligands on Pt(II) organometallic compounds has been studied from a kineticomechanistic perspective. In all cases, the process from [PtAr$_2${(2-X,6-Y)$C_6H_3CH=NCH_2CH_2NMe_2$}] (Ar = Ph or 4-MeC$_6$H$_4$) produces the corresponding Pt(IV) species [PtAr$_2$X{2-YCC$_5$H$_2$CH=NCH$_2$CH$_2$NMe$_2$}]. The monitoring of the reactions at varying temperatures and pressures and in different solvents indicates a mechanism that involves the preliminary decoordination of the N-amino donor from the ligand to produce a three-coordinated intermediate. This evolves, via a concerted C−X bond activation, to form a second pentacoordinated intermediate species that, on coordination of the N-amino donor, produces the final complex. The kinetic and activation parameters measured indicate that the concerted character of the process is maintained from nonpolar (xylene and toluene) to polar (acetone) and ionic liquid ((Bmin) (NTf$_2$)) media and that an excellent thermal activation parameter compensation plot exists for all studied systems of the same family, which include reported monodentate imine and ancillary SMe$_2$ ligands. The expected $\Delta V^{\ddagger}/\Delta S^{\ddagger}$ compensation plot indicates that, for the (2,6-Cl) $C_6H_3CH=NCH_2CH_2NMe_2$ ligand, the existence of hydrogen bonding within the molecule is a determinant for the acceleration observed, as well as for the unexpected large expansion on going to the transition state. The same effects had already been observed for other concerted reaction systems prone to internal hydrogen bonding.

4. EXPERIMENTAL SECTION

General. Microanalyses were performed at the Serveis Cientifico-Tècnics (Universitat de Barcelona). Electrospray mass spectra were performed at the Servei d'Espectrometria de Masses (Universitat de Barcelona) in a LC/MSD-TOF spectrometer using H_2O-CH_3CN (1:1) to introduce the sample. NMR spectra were performed at the Unitat de RMN d'Alt Camp de la Universitat de Barcelona using Mercury-400 or Varian-500 spectrometers and referenced to $SiMe_4$. Δ values are given in parts per million and J values in hertz. The following abbreviations are used: s = singlet; d = doublet; t = triplet; m = multiplet; br = broad. The (Bmim)(NTf$_2$) ionic liquid (99.5%) was purchased from Solvionic and was used without further purification.

Preparation of Compounds. Compounds *cis*-[Pt{4-MeC$_6$H$_4$})2{μ-SEt$_2$}]$_2$,[43] 1-Cl,Cl,[24] 2-Cl,H,[20] 3-Br,H,[24] 3-Cl,Cl[24] and 4-Cl,H,[20] as well as the corresponding ligands,[12] were prepared as reported elsewhere. The detailed preparative procedures and characterization data are collected in the Supporting Information.

X-ray Structure Analysis. A prismatic crystal ($0.1 \times 0.1 \times 0.2$ mm) was selected and mounted on a MAR345 diffractometer with an image plate detector. Intensities were collected with graphite monochromatized Mo Kα radiation. The structure was solved by direct methods using the SHELXS computer program and refined by the full-matrix least-squares method, with the method, with the SHELXL97 computer program using 27 210 reflections (very negative intensities were not assumed).[44] The function minimized was $\Sigma w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0397\ P)^2 + 3.1962\ P]^{-1}$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. *f*, *f* ', and *f* '' were taken from the *International Tables of Xray Crystallography*.[45] All hydrogen atoms were computed and refined using a riding model with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atom to which they are linked. Further details are given in Table 3.

Kinetics. The kinetic profiles for the reactions were followed by UV$-$vis spectroscopy in the 700$-$300 nm range. Atmospheric pressure runs were recorded on HP8453 or Cary50 instruments equipped with thermostatted multicell transports. Observed

288 rate constants were derived from absorbance versus time traces at the wavelengths where a

289 maximum increase and/or decrease of absorbance was observed. For runs at variable

290 pressure, a previously described pressurizing system and pill-box cell were used;[46,47] the

291 system was connected to a J&M TIDAS spectrophotometer that was used for the absorbance

292 measurements. The calculation of the observed rate constants from the absorbance versus

293 time monitoring of reactions, studied under second- or first-order concentration conditions,

294 were carried out using the SPECFIT software.[32] The general kinetic technique is that

295 previously described.[19,21,48] Table S1 (Supporting Information) collects the obtained k_{obs}

296 values for all the systems studied as a function of the starting complex, process studied,

297 platinum and imine concentrations, pressure, and temperature. All post-run fittings were

298 carried out by the standard available commercial programs.

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5. ACKNOWLEDGEMENTS

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Notes

325   The authors declare no competing financial interest.

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427 **Table 1** Selected NMR Data in Several Deuterated Solvents[a]

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solvent	$\delta\ (-N{=}C\underline{H}-)$	$\delta\ (-N(C\underline{H}_3)_2)$	$\delta\ (4{-}C\underline{H}_3{-}C_6H_4{-})$
dmso[b]	8.91 (45)	2.74 (−)	2.25
		2.48 (−)	2.04
acetone[b]	8.87 (47)	2.88 (11)	2.29
		2.59 (17)	2.07
CDCl₃[b]	8.58 (45)	2.97 (10)	2.34
		2.46 (15)	2.14
toluene	7.28 (45)	2.64 (10)	2.34
		1.95 (15)	2.00

[a]Chemical shifts in ppm and coupling constants J(Pt−H) in Hz in parentheses. [b]Data for the major isomer.

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Table 2. Kinetic and Activation Parameters for the Oxidative Addition of C−X Bonds on the Platinum(II) Complexes Indicated in Scheme 2 in Toluene Solution. Relevant Values in Acetone Solution for Similar Compounds Are Also Included

Entry	Complex	Reference	$10^5 \times ^{298}k$ /s^{-1}	$\Delta H^{\ddagger}$ /kJ mol^{-1}	$\Delta S^{\ddagger}$ /J K^{-1}mol^{-1}	$\Delta V^{\ddagger}$ /cm^{3}mol^{-1}
i	**1-Cl,H**	This work	0.13 [a]	127±6	66±17	9±2
ii	**2-Cl,H**	This work	0.065 [a]	124±5	50±15	Not determined
iii	**1-Br,H**	This work	31 [a]	100±4	21±13	10±1
iv	**1-Cl,Cl**	This work	13 [a]	87±2	−30±7	16±1
v	[structure]	12	5.5	101±5	10±17	Not determined
vi	[structure]	12	31	97±2	11±10	Not determined
vii	[structure]	12	65	71±7	−70±25	Not determined
viii	[structure]	17,19	340	60±5	−100±10	−17±1
ix	[structure]	18,19	340	30+5	−195±15	−14±1
x	[structure]	17,19	210	60±9	−93±28	−20±1
xi	[structure]	19	540	70±5	−70±5	−12±1
xii	[structure]	17,19	590	48±7	−125±23	−22±1
xiii	[structure]	17,19	260	23±1	−218±2	−31±1
xiv	[structure]	22	140	87±4	−11±13	−4±1
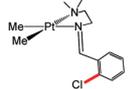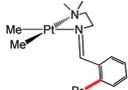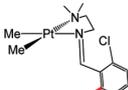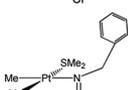
[a] Extrapolated from the thermal parameters indicated.

458   **Table 3** Crystallographic and Refinement Data

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formula	$C_{25}H_{28}Cl_2N_2Pt \cdot CH_2Cl_2$
fw	707.41
temp, K	293(2)
wavelength, Å	0.71073
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	13.277(4)
b, Å	13.065(3)
c, Å	20.035(5)
α, deg	90
β, deg	128.322(17)
γ, deg	90
V, Å^3; Z	2726.5(12); 4
d (calcd), Mg/m^3	1.723
abs coeff, mm^{-1}	5.556
$F(000)$	1384
rflns coll./unique	27210/8164 [R(int) = 0.0645]
data/restraint/parameters	8164/8/330
GOF on F^2	1.068
final R_1($I > 2\sigma(I)$); wR_2	0.0330; 0.0903
R (all data); wR_2	0.0359; 0.0939
peak and hole, e·Å^{-3}	1.987 and -1.315

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Figures Captions

Figure 1. Molecular structure of compound 3-Cl,Cl. Selected bond lengths (Å) and angles
(deg) with estimated standard deviations: Pt1−C1= 2.004(4), Pt1−C12 = 2.036(4), Pt1−C19
= 2.026(4), Pt1−N1 = 2.298(4), Pt1−N2 = 2.059(3), Pt1−Cl1 = 2.4681(10); C1−Pt1−Cl1 =
89.72(11), C1−Pt1−C12 = 84.30(15), C1−Pt1−C19 = 98.63(16), C1−Pt1−N2 = 81.03(14),
C12−Pt1−N1 = 98.84(14), C12−Pt1−N2 = 93.93(15), C19−Pt1−Cl1 = 89.83(12),
C19−Pt1−C12 = 90.83(16), C19−Pt1−N1 = 100.39(15), N1−Pt1−Cl1 = 86.89(9),
N2−Pt1−Cl1 = 85.35(9), N2−Pt1−N1 = 79.72(12).

Figure 2. Eyring plot for the oxidative addition reaction of complex 1-Cl,Cl in the full set
of solvents used in the study.

Figure 3. Activation enthalpy/entropy compensation plot for the full series of concerted
oxidative addition C−X activation reactions indicated in Table 2. Numbering indicates the
table entries of the data from the literature.

Figure 4. $\Delta V^{\ddagger}/\Delta S^{\ddagger}$ correlation plot for the full series of concerted oxidative addition C−X
activation reactions indicated in Table 2. Numbering indicates the table entries of the data
from the literature.

485   **Figure 1**

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491 **Scheme 1.**

mer-[C,N,N']   *fac*-[C,N,N']

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Scheme 2.

1-Cl,H   **2-Cl,H**   **1-Br,H**   **1-Cl,Cl**
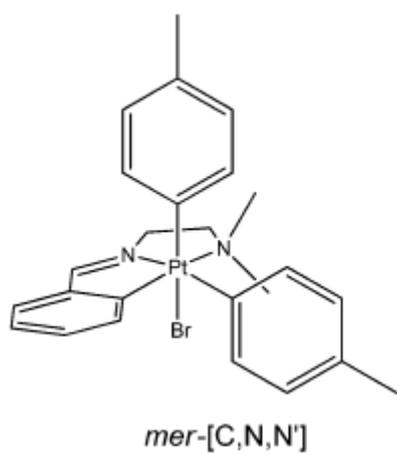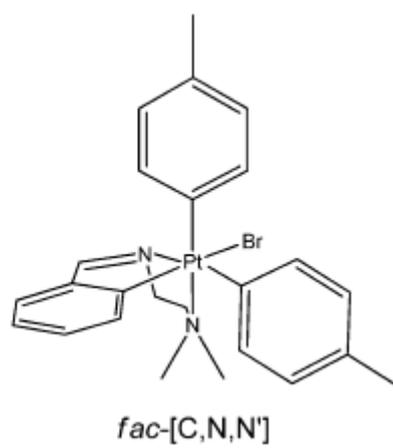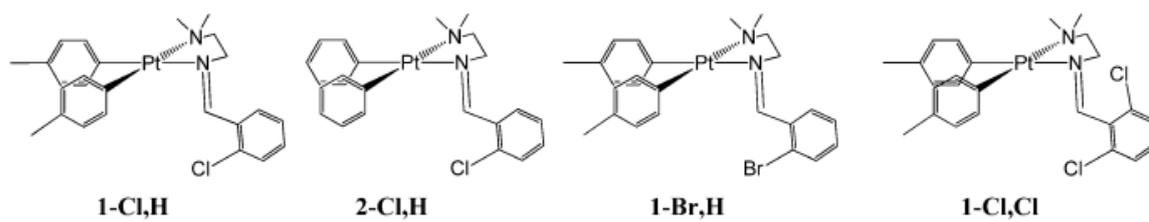
499   **Figure 2**

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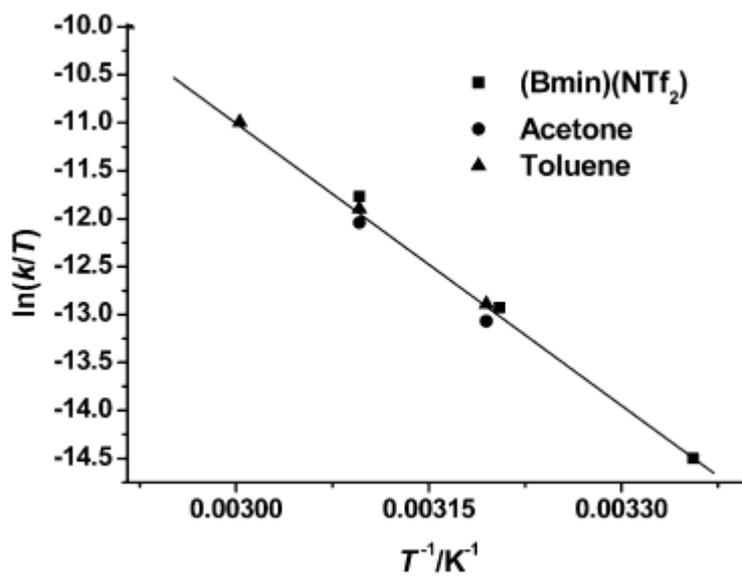
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504 **Figure 3**

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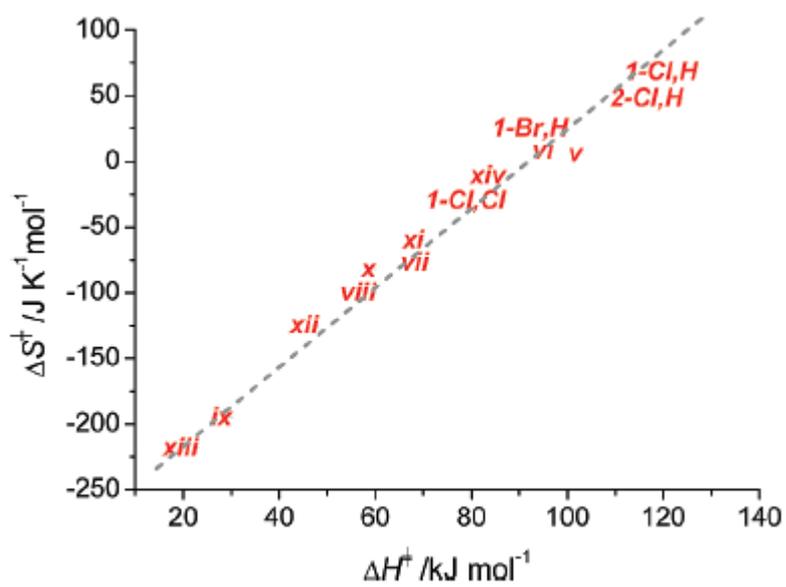
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514   **Figure 4**
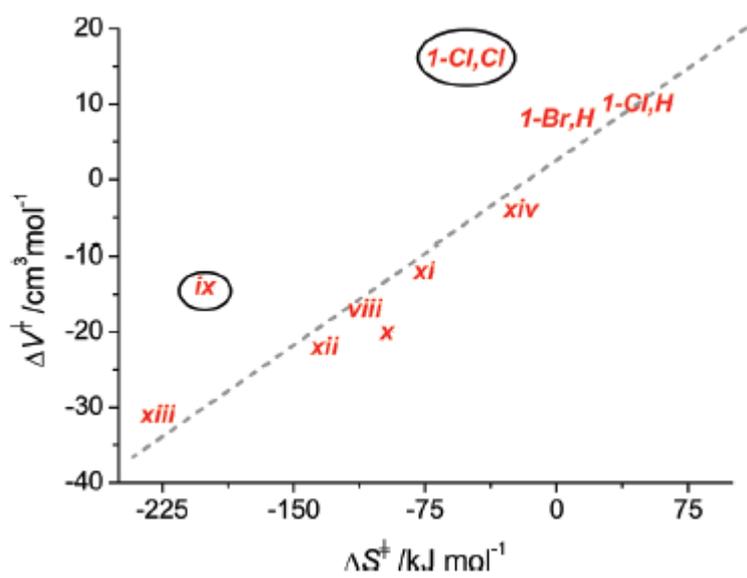
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518 **Scheme 3**
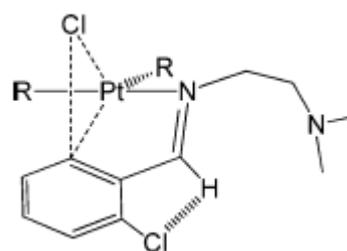
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