Iodine Oxidative Addition to Isomeric Platinum(II) Phosphine Complexes

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The reaction between cis and trans isomers of $(Et_3P)_2PtAr_2$ (Ar = 4-FC_6H_4) (**1a** and **1b**, respectively) with I_2 was studied in detail. At low temperatures, the clean formation of an intermediate was observed for each of the isomers. Upon warming, both intermediates provided the single thermodynamic product *trans*-$(Et_3P)_2PtAr_2(I)_2$ (**2**), where each of the iodo ligands is located trans to the aryl group in the equatorial plane. The reactions followed first-order kinetics with the intermediate formed from **1b** converting into **2** at a faster rate than that from **1a**. The conversion was significantly faster in toluene than in acetone, with the reaction in toluene giving a very large negative activation entropy (ca. −40 cal/mol· K^{-1}). On the basis of the NMR analysis and kinetic data, both intermediates are proposed to be the corresponding products of the trans oxidative addition. Subsequent iodide dissociation and rearrangement of the resulting pentacoordinate Pt(IV) complex provides complex **2**.

Introduction

Two-electron oxidative addition to a square planar d^8 late transition metal center represents the key step in a variety of catalytic processes and has been extensively studied for several decades.[1,2] It is generally accepted that while the C−H, H−H, and X−H bonds are cleaved in a concerted three-center fashion to give the cis-oxidative addition product,[3,4] C−X and X−X bonds (X = halogen) are activated heterolytically in an S_N2-like process, giving the trans isomer.[5] In the latter case, the initial formation of an η^1-coordinated X_2 adduct was proposed.[6] Such a complex was reported in an amine-based pincer Pt(II) system; however, it did not lead to the oxidative addition product (Scheme 1a).[7] A more electron rich Pt-aryl complex of the same pincer ligand underwent a smooth oxidative addition reaction, giving

Scheme 1
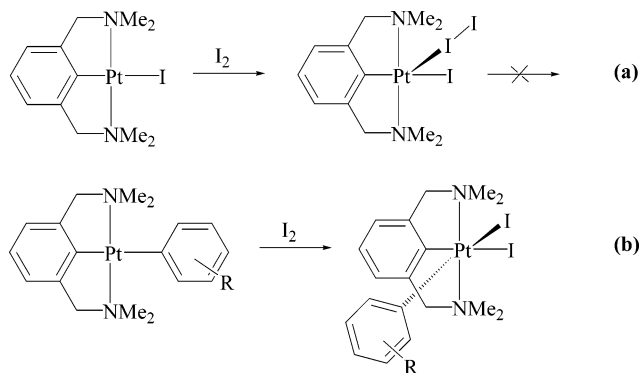
the formal cis-addition product (Scheme 1b). While extensive studies on the S_N2-type oxidative addition to Pt(II) have been performed on complexes bearing the chelating nitrogen ligands, most notably by the groups of van Koten, Puddephatt, and Hughes,[8] very little mechanistic information regarding the corresponding

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Scheme 2

Scheme 3
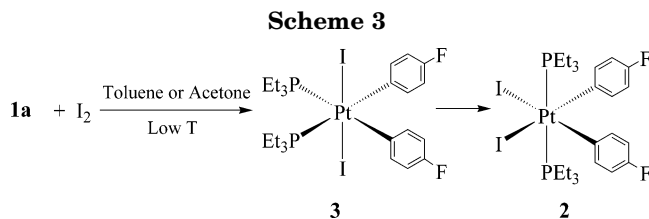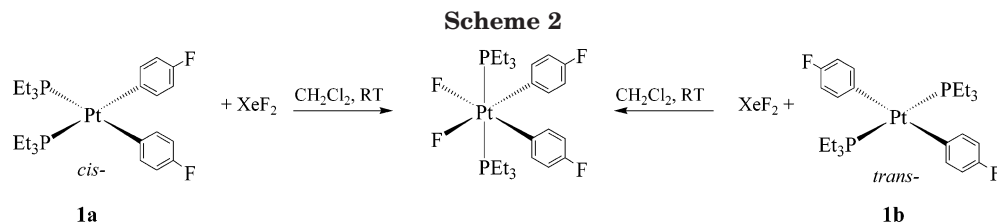
phosphine complexes is available.[9] Since tertiary phosphines are present in a large number of catalytically active d^8 metal complexes, mechanistic studies of the oxidative addition processes in metal-phosphine complexes are an important area of research.

We recently found that addition of XeF₂ to the cis phosphine complex **1a** gives the Pt(IV) oxidative addition product where both phosphine atoms occupy the axial position of an octahedron and each of the fluoro ligands sits trans to the aryl group.[10] Although the resulting product is the thermodynamic one for the Pt(IV) complex bearing two phosphines, halides, and aryl groups,[11] it cannot be formed in a single step. While studying the reaction in detail, we found that the addition of XeF₂ to the trans complex **1b** gave the same (thermodynamic) Pt(IV) product (Scheme 2). Attempts to directly investigate the mechanism of this oxidative addition reaction were encumbered by low solubility and high reactivity of XeF₂. Thus, we were interested in investigating a model reaction where two halogen ligands are added to a square planar d^8 metal center bearing two monodentate phosphines and aryl groups. Herein, we present our studies of the mechanism of I₂ oxidative addition to Pt(II) phosphine complexes.

Results and Discussion

We found that addition of a toluene solution of iodine to a solution of **1a** immediately resulted in a color change to dark yellow and the formation of complex **2** was observed by ³¹P NMR spectroscopy (Scheme 3).[12] The ³¹P NMR spectrum of **2** shows a singlet at −21.99 ppm (J_{PtP} = 1749.4 Hz). A singlet at −116.76 ppm was also observed in the ¹⁹F NMR spectrum. Complex **2** was crystallized at −30 °C from pentane, and its X-ray structure is shown in Figure 1. The platinum atom is located in an octahedral environment with the two phosphine ligands occupying the apical positions. Each of the iodo ligands is located trans to the aryl group.
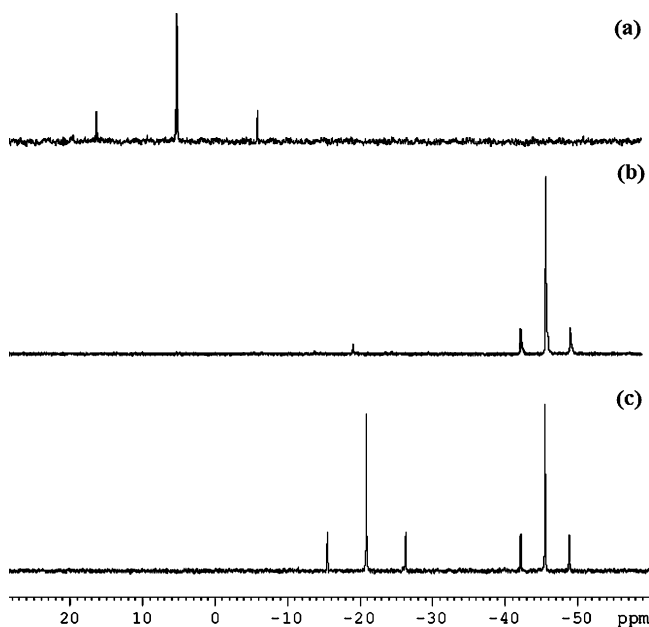
(9) Formation of kinetic Pt(IV) products with phosphine ligands was observed but not studied in detail: (a) Bennett, M. A.; Bhargava, S. K.; Ke, M.; Willis, A. C. *J. Chem. Soc., Dalton Trans.* **2000**, 3537−3545. (b) Crespo, M.; Puddephatt, R. J. *Organometallics* **1987**, *6*, 2548−2550.

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The metal−carbon bond distances of 2.089(5) and 2.101-(6) Å are within the range for the Pt−C bonds in other Pt(IV) complexes.[5a] Similarly, the Pt−I bond lengths of 2.7719(5) and 2.7961(4) (s) Å compare well with those in Pt(IV) complexes, being trans to a carbon atom.[8f]
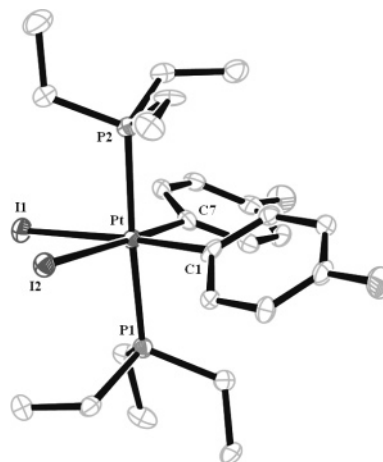
Figure 1. ORTEP structure of a molecule of **2** (50% probability). The hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Pt−C1 2.089-(5), Pt−C7 2.101(6), Pt−I1 2.7719(5), Pt−I2 2.7961(4), C1−Pt−C7 94.1(2), P2−Pt−P1 177.23(5), I1−Pt−I2 83.812-(13), C1−Pt−I2 89.39(16).

Performing the reaction between **1a** and I₂ in toluene at −90 °C showed the immediate formation of the new complex **3** (Scheme 3), which rapidly disappeared upon warming to room temperature to cleanly produce **2** (Figure 2b,c). The NMR spectra of complex **3** demonstrate the equivalent aryl groups (a singlet in the ¹⁹F NMR at −119.79 ppm) as well as phosphine ligands. The latter give rise to a singlet at a very high field (−44.22 ppm) with a low Pt−P coupling constant of 1104.8 Hz. The NMR signals in acetone were virtually identical to those in toluene (Table 1). The ¹³C NMR spectrum of **3** reveals a large phosphine splitting for the ipso-carbon atoms of the aryl ligands (J_{obs} = 145.5 Hz), effectively excluding the trans positioning of the phosphine ligands. In addition, no virtual coupling, commonly found in the phosphine-trans-to-phosphine systems,[13] was observed for the ethyl groups, indicating the mutual cis arrangement of the phosphines. Thus, the NMR features of **3** could be indicative of the two intermediate complexes, namely, the trans Pt(IV) diiodide (shown in Scheme 3) or η^1 platinum(II) addition complex of I₂ (vide infra). A similar complex was previously reported by van Koten and co-workers in the amine pincer system and proposed to be an intermediate in the I₂ oxidative addition reaction to a d^8 metal center.[7] While the reported Pt(II) adduct was inert in

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Figure 2. ^{31}P NMR spectra of complexes **1a** (a) and **3** (b) and mixture of **3** and **2** at ca. 50% conversion (c).

Table 1. Selected NMR Data for Complexes 1–4 in Different Solvents

complex	$\delta\ ^{31}P\{^1H\}$	J_{PtP}	$\delta\ ^{195}Pt$	$\delta\ ^{19}F\{^1H\}$
1a	3.18[d]	1798.9[d]	−4551.29[d]	−120.91[d]
	3.34[c]		−4546.70[c]	
1b	9.36[a]	2790.4[a]	−4422.63[a]	−121.79[a]
	9.44[b]	2786.3[b]		
	10.68[c]	2781.3[c]		−120.79[c]
3	−44.22[a]	1104.8[a]	−4333.70[a]	−119.79[a]
	−43.96[c]	1114.3[c]		−119.16[c]
4	−28.33[a]	1667.3[a]	−4524.8[a]	−118.52[a]
	−28.45[c]	1658.8[c]		
2	−21.99[a]	1749.4[a]	−3555.03[a]	−116.76[a]
	−22.24[b]	1764.7[b]		−116.18[b]
	−20.59[c]	1759.8[c]		
	−21.23[d]	1763.3[d]		−116.36[d]

[a] In toluene. [b] In benzene. [c] In acetone. [d] In CDCl$_3$.

the actual oxidative addition step, probably as a result of the rigid square planar structure of the tridentate pincer ligand and low electron density on the metal, the more electron rich aryl complex gave the cis oxidative addition product.[7,11] In our case, the observed intermediate underwent smooth conversion to the oxidative addition product upon warming to room temperature. Kinetic analysis of the conversion of **3** to **2** at different temperatures in toluene, obtained using ^{31}P NMR spectrometry, gave the activation parameter values of 9.97 kcal/mol and −40.5 cal/mol·K^{-1} for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, respectively (Table 2). The highly negative value of the activation entropy was previously observed in the C−X bond activation as an indication of the highly ordered S$_N$2-type process.[8d] The conversion followed first-order kinetics and no intermediates were observed. Interestingly, when the same reaction was performed in acetone, the conversion of **3** to **2** occurred at a much *slower* rate. $\Delta H^{\ddagger}$ of 23.25 kcal/mol and $\Delta S^{\ddagger}$ of 4.0 cal/mol·K^{-1} were obtained in this case (Figure 3). The solvent effect on multistep reactions, such as an oxidative addition−rearrangement sequence, is not always straightforward to rationalize. For example, oxidative addition to an Ir(I) chelate was assisted by polar solvents,[14] while a
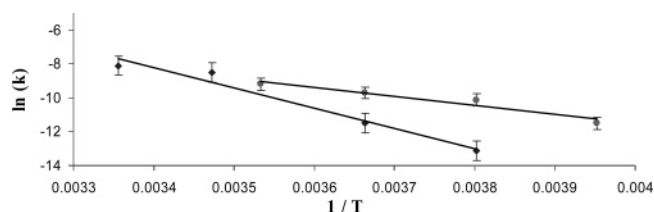
Figure 3. Eyring plot of conversion of **3** to **2** in acetone (◆) and toluene (△).

significant rate acceleration in a nonpolar solvent versus acetone was reported for the isomerization of an Ir(III) dihydride phosphine complex.[3c] The efficient solvation by acetone might stabilize **3** and deactivate it toward further transformations. The formation of a six-coordinate metal complex might also account for this effect.[7c] It is plausible that acetone stabilizes the unobserved cationic intermediate, slowing the cis−trans rearrangement reaction (vide infra).

The observation of cis complex **3** alone, however, does not explain the mutual trans orientation of the phosphine ligands in the final product. The formation of **2** must be preceded by ligand dissociation from **3** or another, unobserved intermediate. Addition of free Et$_3$P to a solution of **3** in toluene at −90 °C resulted in the immediate precipitation of the Et$_3$P(I)$_n$ species and regeneration of complex **1a**, ruling out the possibility of phosphine ligand dissociation under the reaction conditions. Attempts to follow the reaction by UV−vis spectroscopy did not provide new mechanistic information. A new shoulder at 444 nm was observed in the UV−vis spectrum upon addition of I$_2$ to **1a** at low temperatures, this shoulder rapidly disappearing upon conversion to **2**. The latter shows signals at 355 and 327 nm. Similar inconclusive results were observed for the previously reported Pt−I$_2$ complexes.[7b] Little evidence in support of the intermediate structures could be obtained from the ^{195}Pt NMR measurements. While the Pt(II) complex **1a** shows a triplet at −4551.29 ppm in its ^{195}Pt NMR spectrum, the Pt(IV) complex **2** exhibits a triplet at −3555.03 ppm. Complex **3**, on the other hand, gives a signal at −4333.70 ppm, making it difficult to unequivocally assign the structure of **3**. The correlation between the complex structure and position of its ^{195}Pt NMR signal should be treated with caution, as it can vary dramatically with the ligand environment.[15]

As complex **2** appears to be the thermodynamic product for (Et$_3$P)$_2$Pt(Ar)$_2$I$_2$, we were also interested to investigate its formation in the reaction of the trans isomer of **1a** with I$_2$. Addition of I$_2$ to a solution of the trans complex **1b** at −90 °C showed no formation of **3** (Scheme 4). Instead, the formation of the new complex **4** was observed. The same product was formed even at −110 °C in Et$_2$O. Complex **4** rapidly converted to **2** even at −30 °C. Complex **4** shows the ^{31}P NMR signal in the area expected for the Pt(IV) diiodo complex (−28.33 ppm) with a J_{PtP} value of 1667.3 Hz, close to that in **2**. The ^{195}Pt NMR spectrum of **4** showed a triplet at −4524.80 ppm, compared with −4422.63 for the starting

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Table 2. Observed Kinetic Parameters for Conversion of Complexes 3 and 4

complex	solvent	k_{263}, (s^{-1})	$\Delta G^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (cal/mol·K^{-1})	$\Delta H^{\ddagger}$ (kcal/mol)
3	toluene	$(4 \pm 1) \times 10^{-5}$	20.63 ± 0.4	-40.5 ± 2.3	9.97 ± 1.0
	acetone	$(2 \pm 0.02) \times 10^{-6}$	22.19 ± 0.05	$+4.0 \pm 1.2$	23.25 ± 0.5
4	acetone	$(2 \pm 0.1) \times 10^{-4}$	19.79 ± 0.1	-4.8 ± 0.4	18.52 ± 0.2

Scheme 4
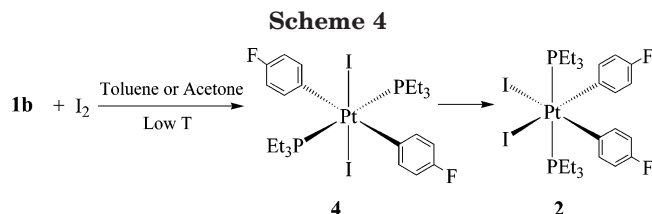
1b. The ^{13}C NMR spectrum showed a virtual triplet for the CH₂ group of the Et₃P ligands, indicating their mutual trans arrangement. Also, no large J_{PC} coupling was observed for the aromatic ipso-carbon, showing the cis positioning of the aryl group versus the phosphine ligands. The combined NMR features suggested the all-trans structure for complex **4**. As in the case of **3**, no significant changes in the NMR spectra of **4** were observed upon performing the measurements in acetone instead of toluene. Kinetic investigation of the isomerization of **4** to **2** in acetone using ^{31}P NMR spectroscopy (Figure 4b,c) resulted in the activation enthalpy and
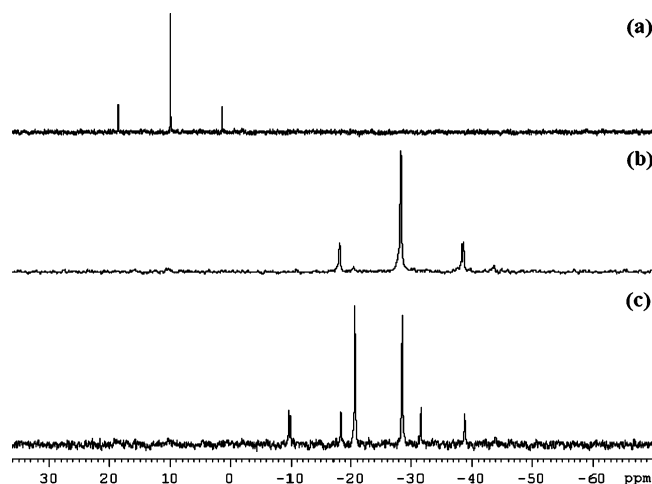
Figure 4. ^{31}P NMR spectra of complexes **1b** (a) and **4** (b) and mixture of **4** and **2** at ca. 50% conversion (c).

entropy of 18.52 kcal/mol and -4.8 cal/mol·K^{-1}, respectively (Table 2). The activation barrier for this rearrangement reaction is ca. 2.5 kcal/mol lower than that observed in **3**. Thus, it appears that the oxidative addition of I₂ to the geometric isomers **1a** and **1b** does not proceed via a common intermediate.

Finally, we tried to investigate the effect of the added I$^-$ on the reaction rates. Unfortunately, the results were inconclusive. Addition of 1–10 equiv of Bu₄N$^+$I$^-$ to a solution of **3** in acetone significantly accelerated the reaction rate. However, other unstable products were also observed along with the starting material. Similar results were also obtained upon addition of Bu₄N$^+$I$^-$ to a solution of **4** in acetone at -50 °C. Large amounts of the starting Pt(II) complex **1b** were observed almost immediately after the addition along with **2** and other products. This reactivity is attributed to aggregation between I$^-$ and I₂. When a preformed 1:1 mixture of Bu₄N$^+$I$^-$ and I₂ was reacted with **1a** at room tempera-

ture, rapid isomerization to **1b** was observed, akin to that reported for the I$^-$-promoted cis-to-trans isomerization of Pt(II) complexes.[16] The complex behavior of the I$^-$ anion in organometallic chemistry is well documented.[17]

Although the proposed structures of **3** and **4** cannot be unambiguously confirmed without X-ray analysis, the ^{31}P NMR features suggest that **3** corresponds to the Pt(IV) product of the trans addition of I₂ to **1**. A large chemical shift difference from **1** and significantly lower J_{PtP} are indicative of the Pt(IV) complex.[9,18] Due to nearly identical ^{31}P NMR signals of **3** in toluene and acetone, the cationic Pt(IV) structure is highly unlikely.[9b] Similar to the reaction with **1a**, the addition of I₂ to (dmpe)PtAr₂ gave the trans addition product, which showed a greater than 45 ppm upfield shift in the ^{31}P NMR spectrum (-25.85 ppm, versus 21.46 ppm for (dmpe)PtAr₂) and a low Pt–P coupling constant of 1195.8 Hz versus 1709.3 in (dmpe)PtAr₂. The trans addition structure assigned to **3** also explains the dramatic difference in the reaction rates in toluene and acetone. Since no phosphine dissociation occurs, the formation of **2** must be preceded by the dissociation of the iodide ligand. If this step is faster than the rearrangement of the resulting pentacoordinate intermediate, the latter would be stabilized by a coordinating solvent, such as acetone. In toluene, the iodide dissociation is unfavorable and most probably produces a highly unstable tight ion pair. The reorganization of this intermediate, via the pseudorotation or turnstile routes,[19] accounts for the large negative activation entropy. In the trans complex **4**, the phosphine ligands are already located in the "right" position and only a minor rotation is required. Together with the lower thermodynamic stability of **4**, this results in a significantly faster conversion to **2**.

The combined data provide some quantitative information about the proposed mechanism for the I₂ oxidative addition to the d^8 square planar Pt(II) phosphine complexes (Scheme 5). While not detected in this work, the formation of the pentacoordinate η^1 iodine adduct might take place in the S$_N$2-type mechanism. The trans oxidative addition step produces the intermediate complex where the two iodo ligands are located at the axial positions of an octahedron, with the equatorial ligands retaining the configuration of the parent square planar complex. If such a product is not the thermodynamically

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Scheme 5
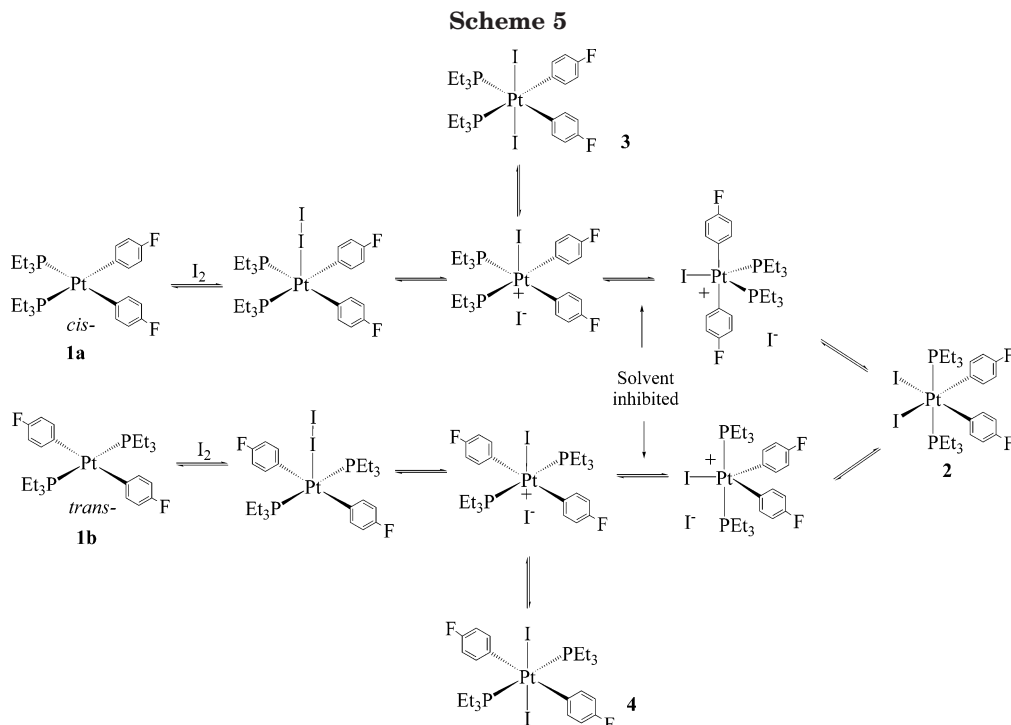
stable one, it undergoes isomerization to give the most stable isomer. The isomerization most likely proceeds via the pseudorotation pathway preceded by the dissociation of I^- from the metal center. Coordinating solvents, such as acetone, stabilize the cationic intermediate and slow the rearrangement process.

Experimental Part

General Procedures. All operations with air- and moisture-sensitive compounds were performed in a nitrogen-filled Innovative Technology glovebox. All solvents were degassed and stored under high-purity nitrogen over activated 4 Å molecular sieves. All deuterated solvents were stored under high-purity nitrogen on 3 Å molecular sieves. Commercially available reagents were used as received. The NMR spectra were recorded on Bruker AC 200 MHz and Bruker AMX 400 MHz spectrometers. ^1H and ^{13}C NMR signals are reported in ppm downfield from TMS. ^1H signals are referenced to the residual proton of a deuterated solvent (7.26 ppm for CDCl$_3$, 7.15 ppm for C$_6$D$_6$, 2.11 ppm for toluene-d_8, 2.09 ppm for acetone-d_6). For ^{13}C NMR spectra, the following signals were used as a reference: 77.36 ppm for CDCl$_3$, 128.62 ppm for C$_6$D$_6$, 21.10 ppm for toluene-d_8, and 30.60 for acetone-d_6. ^{31}P chemical shifts are reported in ppm downfield from H$_3$PO$_3$ and referenced to an external 85% phosphoric acid sample. ^{19}F chemical shifts are reported in ppm downfield from CClF$_3$. ^{195}Pt chemical shifts are reported in ppm downfield from external K$_2$PtCl$_6$. UV–vis measurements were recorded on a Scinco s-1300. Elemental analysis was performed in the laboratory for microanalysis at the Hebrew University of Jerusalem. The platinum complexes *cis-* and *trans-*(PEt$_3$)$_2$Pt-(*p*-FC$_6$H$_4$)$_2$ (**1a,b**) were prepared by ligand exchange with the corresponding (1,5-cyclooctadiene)PtAr$_2$ and (PEt$_3$)$_2$PtI$_2$, respectively, as previously reported.[12,20]

Synthesis of 2. In a typical procedure, a freshly prepared solution of I$_2$ (1 mL of 0.018 M) in an appropriate solvent was added dropwise (while stirring) to a solution of **1a** or **1b** (0.018 mmol) in the same solvent (1 mL) at 23 °C. After several

minutes, the $^{31}P\{^1H\}$ NMR spectrum showed the disappearance of the starting material and formation of **2**. Evaporation of the solvent gave **2** in a quantitative yield. A precise amount of I$_2$ must be used to avoid the formation of side products and a tedious cleaning process.

Low-Temperature Experiments. Freshly prepared toluene or acetone solutions (0.032 mmol) of **1a** (or **1b**) were cooled to −90 °C in an NMR tube using an ethanol/liquid N$_2$ bath. A cold I$_2$ solution (1 equiv) was then added at once, the mixture was rapidly shaken to ensure complete mixing, and the tube was placed into the NMR spectrometer precooled to the desired temperature.

2 (CDCl$_3$, 23 °C): $^{31}P\{^1H\}$ −21.23 (s, J_{PtP} = 1763.3 Hz); $^{19}F\{^1H\}$ −116.36 (s, Ar–F); ^1H 0.99 (m, CH$_3$, 18H), 2.24 (m, CH$_2$, 12H), 6.70 (br t, J = 8.5 Hz, Ar–H, 4H), 7.12−7.72 (br m, Ar–H, 4H); $^{13}C\{^1H\}$ 10.15 (s, CH$_3$), 19.20 (t, J_{PC} = 17.6 Hz, CH$_2$), 113.94 (br m, J_{PC}= 18.2 Hz, Ar), 128.68 (br m, Ar–Pt), 141.10 (br s, Ar), 161.34 (d, C–F, $J_{F–C}$ = 245.4 Hz); ^{195}Pt NMR (C$_6$D$_6$) −3555.03 (t). Anal. for C$_{24}$H$_{38}$F$_2$I$_2$P$_2$Pt: found (calc): C 32.11 (32.93), H 4.35 (4.38). FAB-MS M−I: found (calc) 748 (748).

3 (acetone-d_6, −50 °C): $^{31}P\{^1H\}$ −43.96 (s, J_{PtP} = 1114.3 Hz) (at the same temperature in toluene the signal appears at −44.22 with $J_{Pt–P}$ = 1104.8 Hz); $^{19}F\{^1H\}$ −119.16 (s, Ar–F); ^1H NMR 1.09 (m, CH$_3$, 18H), 2.30 (m, CH$_2$, 12H), 6.66 (t, J = 8.3 Hz, Ar–H, 4H), 7.92 (m, Ar–H, 4H); $^{13}C\{^1H\}$ 10.98 (s, CH$_3$), 20.37 (m, CH$_2$), 114.14 (m, Ar), 132.52 (dd, Ar–Pt, J_{PcisC} = 5.8 Hz, $J_{PtransC}$ = 145.5 Hz), 147.28 (br s, Ar), 161.67 (d, C–F, $J_{F–C}$ = 240.2 Hz); ^{195}Pt NMR (toluene, −50 °C) −4333.70 (t).

4 (toluene-d_8, −50 °C): $^{31}P\{^1H\}$ −28.33 (s, J_{PtP} = 1667.3 Hz) (at the same temperature in acetone the signal appears at −28.45 with J_{PtP} = 1658.8 Hz); $^{19}F\{^1H\}$ −118.52 (s, Ar–F); ^1H 0.54 (m, CH$_3$, 18H), 1.94 (br s, CH$_2$, 12H), 6.89 (br t, J = 8.5 Hz, Ar–H, 4H), 8.79 (br m, Ar–H, 4H); $^{13}C\{^1H\}$ 10.24 (br s, CH$_3$), 19.93 (br t, J_{PC} = 17.5 Hz, CH$_2$), 115.14 (m, J_{PC} = 17.0 Hz, Ar), 148.94 (br s, J_{PtC} = 160.2 Hz, Ar–Pt), 162.08 (d, C−F, $J_{F–C}$ = 242.5 Hz), 130.49 (overlapped); ^{195}Pt NMR (acetone, −50 °C) −4524.80 (t).

Kinetic Experiments. In a typical experiment, a freshly prepared solution of **1a** or **1b**, in an appropriate solvent, was cooled to −90 °C in an NMR tube using an ethanol/liquid N$_2$ bath. A cold I$_2$ solution (1 equiv) was then added at once, the

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mixture was rapidly shaken to ensure complete mixing, and the tube was placed into the NMR spectrometer precooled to -10 °C. The reaction progress was followed by ^{31}P NMR spectrometry. In each spectrum 120 scans were taken (2 min), with the time intervals between the spectra being 20 min. At higher temperatures, shorter time intervals and a smaller number of scans were used. The maximal monitored conversion was 45%. For the kinetic analysis, each measurement was repeated at least twice.

Supporting Information Available: Crystallographic data for **2** (CIF), ^{195}Pt NMR spectra for complexes **1**−**4**, and ^{1}H, ^{31}P, and ^{19}F spectra for complex **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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