Cationic intermediates in oxidative addition reactions of alkyl halides to d8 complexes: evidence for the SN2 mechanism

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Cationic Intermediates in Oxidative Addition Reactions of Alkyl Halides to d^8 Complexes: Evidence for the S_N2 Mechanism

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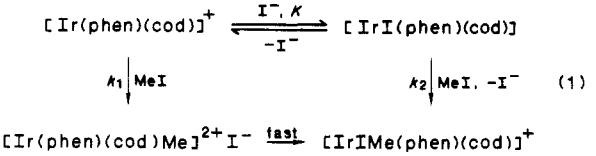
The oxidative addition reactions of RX to $[PtMe_2L_2]$ (1) to give $[PtXMe_2RL_2]$ (3) (L_2 = 2,2'-bipyridine, RX = MeI, $PhCH_2Br$; L = PMe_2Ph, RX = MeI) are shown to occur by way of an ionic intermediate, $[PtSMe_2RL_2]^+X^-$ (2), when the solvent (S) = CD_3CN and, for RX = MeI and L_2 = 2,2'-bipyridine, when S = CD_3OD or acetone-d_6. The intermediates 2 were detected and characterized by low-temperature ^1H and, when L = PMe_2Ph, ^{31}P NMR studies. At temperatures above -20 °C the ligand substitution of X^- for S occurred rapidly and hence the intermediates were detected only for the most reactive systems, which underwent oxidative addition at temperatures below -20 °C. Less reactive systems, for example, EtI with $[PtMe_2(bpy)]$ or MeI with $[IrCl(CO)(PPh_3)_2]$, failed to give detectable ionic intermediates. The observation of ionic intermediates provides strong evidence for the S_N2 mechanism of oxidative addition.

Introduction

The S_N2 mechanism of oxidative addition of alkyl halides was first proposed on the bases of the kinetic order and the similarity of the activation parameters, for reaction of MeI with *trans*-$[IrCl(CO)(PPh_3)_2]$, to those for the Menschutkin reaction.[1] An S_N2 mechanism should lead to inversion of configuration for chiral alkyl halides, and this has been confirmed in some cases.[2] However, free radical chain and non-chain mechanisms are also important in many oxidative additions, and there have been difficulties in distinguishing between the possible mechanisms in some cases.[2,3]

The oxidative addition of MeI to square-planar d^8 complexes is of especial interest because of its role in the Monsanto process for acetic acid.[4] In some cases the reaction is accelerated in the presence of iodide, due to a preequilibrium involving formation of a five-coordinate 18-electron complex (eq 1, phen = 1,10-phenathroline, cod = 1,5-cyclooctadiene).[5]

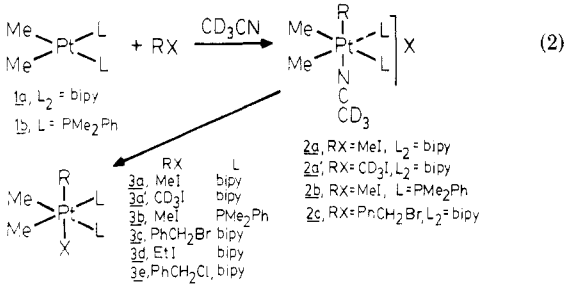


(1)

Both $[Ir(phen)(cod)]^+$ and [IrI(phen)(cod)] reacted by the S_N2 mechanism, but the ratio $k_2/k_1 \approx 7$. The proposed intermediate $[Ir(phen)(cod)Me]^{2+}$ was not identified presumably because iodide addition to give the product $[IrIMe(phen)(cod)]^+$ was very fast.[5] The observation of such cationic intermediates would be good evidence for the S_N2 mechanism of oxidative addition, since they are not expected in free radical or concerted mechanisms of reaction.[2,3] However, numerous attempts to identify such species from 16-electron precursors have been unsuccessful.[2-6] The observation by low-temperature NMR of an intermediate, *fac*-$[PtMe_3(SMe_2)_2(CD_3CN)]^+I^-$, during oxidative addition of MeI to *cis*-$[PtMe_2(SMe_2)_2]$ in CD_3CN to give *fac*-$[PtMe_3I(SMe_2)_2]$ was therefore surprising[7] and led us to make a more general study of the conditions under which such cationic intermediates could be detected. The results are reported below.

Results and Discussion

The scope of the reaction of eq 2 was investigated.



(2)

The reactions were carried out at low temperature in an NMR tube using CD_3CN solvent, monitoring the progress of the reaction at -40, -20, and 0 °C. When RX = MeI and L_2 = 2,2'-bipyridine, the spectrum at -40 °C contained peaks due to both **2a** and **3a** (but none due to **1a**). On further warming peaks due to **2a** decayed and pure **3a** was present.[8,9] The initial oxidative addition was shown to be trans by use of CD_3I as reagent. Initially, neither the intermediate **2a'** nor the product **3a'** showed resonances at δ 0.47 or 0.58 for the methylplatinum resonance trans to CD_3CN or I, respectively (Figure 1). However, on further reaction **2a'** decayed to give **3a'** and scrambling of the CH_3 and CD_3 groups occurred, this scrambling occurring faster for **2a'** than for **3a'** (Figure 1). The intermediate **2a** is characterized by a high value of $^2J(PtCH_3)$ = 78 Hz for the methyl group trans to CD_3CN, which has a low trans influence.[9]

Very similar results were obtained with *cis*-$[PtMe_2(PMe_2Ph)_2]$ (**1b**) though it reacts less rapidly than **1a**. In this case reaction occurred at -20 °C to give **2b**, and then, on warming to 0 °C, complex **3b** was formed. This reaction

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Table I. ^1H and ^{31}P NMR Data[a]

	R trans to X $\delta(H)$ (J_{PtH}) (J_{HH})	Me trans to N $\delta(H)$ (J_{PtH})	bpy resonances $\delta(H_3)$, $\delta(H_4)$, $\delta(H_5)$, $\delta(H_6)$
$[PtMe_2(bpy)]$ (**1a**)		0.89 (86)	8.22, 8.19, 7.59, 9.17
$[PtMe_3I(bpy)]$ (**3a**)	0.58 (76), Me	1.36 (70)	8.66, 8.17, 7.71, 8.95
$[PtMe_2EtI(bpy)]$ (**3d**)	1.39 (72) (7.6), CH_3 0.01 (68) (7.6), CH_2	1.35 (71)	8.55, 8.29, 7.82, 9.04
$[PtMe_2BzCl(bpy)]$ (**3e**)	2.75 (92), CH_2Ph 6.3 (m)–6.6 (m), Ph	1.32 (70)	8.20, 8.04, 7.55, 8.66
$[PtMe_2BzBr(bpy)]$ (**3c**)	2.80 (93), CH_2Ph 6.3 (m)–6.6 (m), Ph	1.40 (70)	8.17, 8.01, 7.51, 8.63
$[PtMe_3(CD_3CN)(bpy)]I$ (**2a**)	0.47 (78), Me	1.14 (68)	8.52, 8.27, 7.82, 8.87
$[PtMe_3(CD_3OD)(bpy)]I$ (**2d**)[b]	0.54 (80), Me	1.13 (66)	
$[PtMe_3(CH_3I)(bpy)]I$ (**2f**)[c]	0.64 (80), Me	1.01 (71)	
$[PtMe_3(CD_3COCD_3)(bpy)]I$ (**2e**)[c]	0.60 (80), Me	1.17 (68)	
$[PtMe_2Bz(CD_3CN)(bpy)]Br$ (**2c**)	2.84 (96), CH_2Ph	1.30 (67)	

	MePt- $\delta(H)$ (J_{PtH}) (J_{PH})	PMe_2Ph- $\delta(Me)$ (J_{PtH}) (J_{PH})	$\delta(P)$ (J_{PtP})
$[Pt(CD_3)_2(PMe_2Ph)_2]$ (**1b'**)		1.41 (20) (7.9)	−12.29 (1842)
$[Pt(CD_3)_2MeI(PMe_2iPh)_2]$ (**3b'**)	0.63 (70) (7.6)	1.63 (12) (9) 1.70 (11) (5.3)	−36.28 (1200)
$[Pt(CD_3)_2Me(CD_3CN)(PMe_2Ph)_2]I$ (**2b'**)	0.59 (75) (8.6)	1.51 (11) (5.3) 1.56 (11) (5.7)	−46.51 (1192)

	$\delta(H)$ (J_{PH})
$[IrClI(CH_3)(CO)(PPh_3)_2]$	0.98 (5.7)
$[IrI_2(CH_3)(CO)(PPh_3)_2]$	1.14 (5.3)

[a] Solvent CD_3CN unless otherwise stated. J values in hertz. [b] Solvent CD_3OD. [c] Solvent $(CD_3)_2CO$.

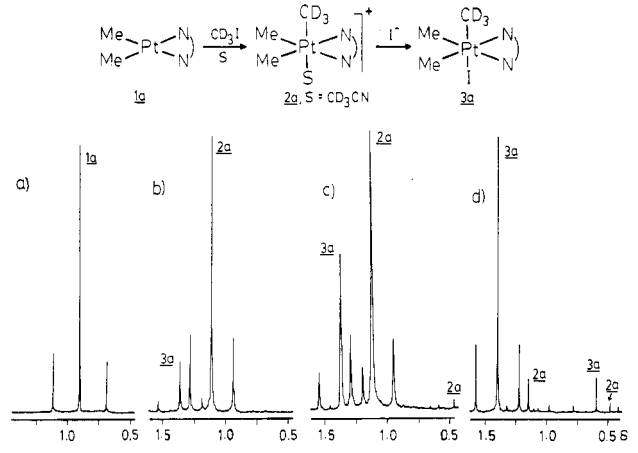

Figure 1. ^1H NMR spectra (200 MHz) during the reaction of CD_3I with $[PtMe_2(bpy)]$ in CD_3CN: (a) before addition of CD_3I; (b) spectrum at −40 °C; (c) spectrum at −20 °C; (d) spectrum at 0 °C.

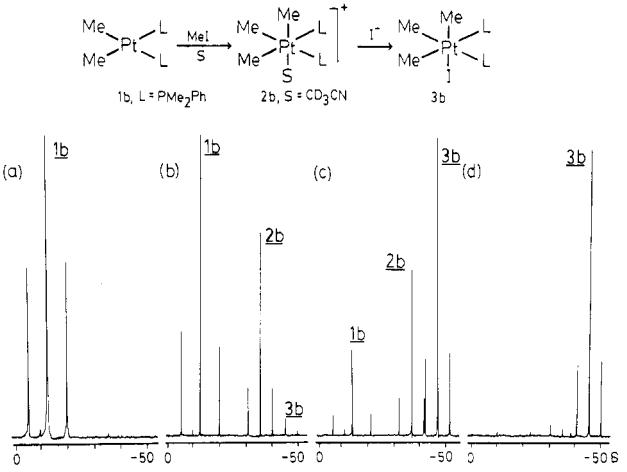

Figure 2. $^{31}P\{^1H\}$ NMR spectra (121.5 MHz) during the reaction of MeI with *cis*-$[PtMe_2(PMe_2Ph)_2]$ in CD_3CN: (a) at −40 °C; (b) at −20 °C; (c) at 0 °C; (d) at 20 °C.

was monitored by both ^1H and ^{31}P NMR spectroscopy (Figure 2). The value of $^1J_{PtP}$ fell from 1842 Hz for **1b** to 1200 Hz for **2b** and 1192 Hz for **3b**, the changes being typical of those expected on oxidation of platinum(II) to platinum(IV).[12] Oxidative addition was again trans, as shown by reaction of MeI with *cis*-$[Pt(CD_3)_2(PMe_2Ph)_2]$, and no scrambling of CH_3 and CD_3 groups occurred at room temperature in this system.

No ionic intermediate analogous to **2** could be detected on reaction of *trans*-$[IrCl(CO)(PPh_3)_2]$ with MeI in CD_3CN. No reaction was observed at temperatures up to −20 °C, and at 0 °C reaction occurred to give $[IrClIMe(CO)(PPh_3)_2]$.[12,13] This complex reacted further at room temperature to give $[IrI_2Me(CO)(PPh_3)_2]$, which was prepared independently from $[IrCl(CO)(PPh_3)_2]$ with MeI in the presence of NaI. Attempts to detect ionic intermediates in reactions of EtI or $PhCH_2Cl$ to $[PtMe_2(bpy)]$ in CD_3CN were also unsuccessful. Again reaction occurred at 0 °C to give the final products **3d** and **3e**. Qualitatively, it seems that the ionic intermediates can be detected only when oxidative addition occurs at −20 °C or lower. Above this temperature, the reaction of **2** to give **3** occurs rapidly, and hence **2** cannot be detected. There is good evidence that the reactions of **1a** with EtI and $PhCH_2Cl$ occur by the S_N2 mechanism,[14] and so the ionic intermediate **2** is expected to be formed.

Now, knowing that only the most reactive alkyl halides in combination with the most reactive transition-metal complexes were likely to give detectable ionic intermediates, the reaction of $PhCH_2Br$ with **1a** was studied.[15] The ionic intermediate **2c** was detected at −40 °C (Table I), and further reaction to give **3c** was complete at 0 °C. Only trans addition was observed in both **2c** and **3c**.

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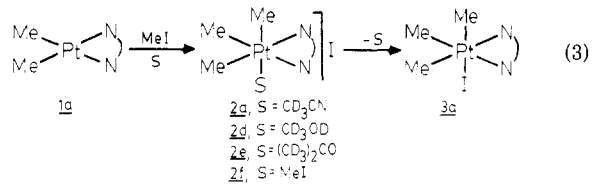
Solvents Which Give Ionic Intermediates. A survey of some polar solvents was made to determine which gave detectable ionic intermediates in eq 3.



(3)

The intermediate was most easily detected when S = CD_3CN. However, when S = CD_3OD, the ionic intermediate **2d** could be detected at −80 °C along with **3a**. On warming, **2d** reacted further to give **3a**. When S = $(CD_3)_2CO$, two intermediates were detected at −80 °C and are thought to be **2e** and **2f**. The relative abundances of **2e** and **2f** were found to change as the concentration of MeI was changed, **2f** being more abundant at higher concentration of MeI. This situation presumably arises because MeI is a better ligand for platinum than is acetone. Both intermediates had disappeared at −20 °C, and only **3a** was present. NMR data are given in Table I.

Conclusions

This work has shown that ionic intermediates can be detected by low-temperature NMR spectroscopy during oxidative addition of alkyl halides to platinum(II) complexes, provided the oxidative addition occurs at about −20 °C or lower. It is essential that the oxidative addition step should be faster than the subsequent substitution of halide for solvent in the ionic intermediate (eq 2 and 3), if the intermediate is to be detectable. It is then clear that the cationic intermediate is formed as a result of kinetic control, providing good evidence for the S_N2 mechanism of oxidative addition. We consider it likely that the solvent coordination (eq 2 and 3) occurs synchronously with the oxidative addition step, thus contributing to the large negative entropies of activation observed[9] and reducing the incipient positive charge buildup on the platinum center. The other experimental evidence, for example the trans stereochemistry of addition, is consistent with but does not prove this hypothesis.

For octahedral platinum(IV) complexes the ligand substitution step is expected to occur by a dissociative (D or I_d) mechanism.[15] Normally such substitutions in platinum(IV) complexes are very slow, but in this case it should be accelerated due to the high trans influence of the methyl group trans to solvent (eq 2 and 3) and the poor coordinating ability of the solvent molecules. As expected, the ligand substitution occurs more rapidly for the oxygen donor solvents, S = CD_3OD or acetone-d_6, than for the nitrogen donor, S = CD_3CN.

Our attempts to identify ionic intermediates in oxidative addition to Vaska's iridium(I) complex have been unsuccessful. This is due to a slower rate of oxidative addition for the iridium(I) complex and, most probably, a higher rate of ligand substitution for the iridium(III) cationic intermediate.[1,2,16] Nevertheless, the direct observation of ionic intermediates in oxidative addition to platinum(II), together with the strong similarity in solvent effects on rates and in activation parameters for oxidative addition of methyl iodide to iridium(I) and platinum(II) systems, strongly supports the S_N2 mechanism in both cases for reactions involving methyl iodide.[1,2,9,13,17]

Experimental Section

NMR spectra were recorded by using Varian XL200 (^1H) or XL300 (^{31}P) NMR spectrometers, and chemical shifts are referenced to Me_4Si (^1H) or $(MeO)_3PO$ (^{31}P). The complexes $[PtMe_2(bpy)]$ and *cis*-$[PtMe_2(PMe_2Ph)_2]$ were prepared by literature methods.[11,18] Most of the final products of oxidative addition were known complexes and were identified by comparison of the NMR spectra (Table I) with those of authentic samples.[1,2,8,9,11,13,14] The NMR spectral studies showed that the products were formed in essentially quantitative yields (e.g. Figures 1 and 2), and they were isolated after crystallization in yields of at least 70%. The following new complexes were prepared.

$[PtClMe_2(CH_2Ph)(bpy)]$. To a solution of $[PtMe_2(bpy)]$ (10 mg) in acetone (10 mL) was added $PhCH_2Cl$ (10 μL). After 15 min the product was isolated by evaporation of the solvents and purified by recrystallization from CH_2Cl_2/pentane; yield 75%. Anal. Calcd for $C_{19}H_{21}ClN_2Pt$: C, 44.9; H, 4.2; N, 5.5. Found: C, 44.5; H, 4.4; N, 5.0%.

$[PtBrMe_2(CH_2Ph)(bpy)]$ was prepared in a similar way; yield 78%. Anal. Calcd for $C_{19}H_{21}BrN_2Pt$: C, 41.3; H, 3.8; N, 5.1. Found: C, 41.2; H, 3.9; N, 5.3.

Detection of Intermediates. Typically a solution of $[PtMe_2(bpy)]$ (5 mg) in CD_3CN (0.5 mL) in an NMR tube was cooled to −45 °C, and CD_3I (3 μL) was added. The tube was then placed in the cooled probe of the NMR spectrometer, and spectra were recorded at −40, −20, 0, and 20 °C. Results are given in Table I and Figures 1 and 2.

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Registry No. **1a**, 52594-52-2; **1b**, 24917-48-4; **1b′**, 69721-14-8; **2a**, 110638-29-4; **2a′**, 110638-30-7; **2b**, 110638-31-8; **2b′**, 110638-32-9; **2c**, 110661-47-7; **2d**, 110638-33-0; **2e**, 110638-34-1; **2f**, 110638-35-2; **3a**, 38194-05-7; **3a′**, 110638-36-3; **3b**, 24833-69-0; **3b′**, 110661-48-8; **3c**, 62343-16-2; **3d**, 62342-98-7; **3e**, 110638-37-4; *trans*-$[IrCl(CO)(PPh_3)_2]$, 15318-31-7; $IrClIMe(CO)(PPh_3)_2$, 24315-50-2; $IrI_2Me(CO)(PPh_3)_2$, 110716-19-3.

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