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Diorganoplatinum(II) complexes with chelating PN ligand 2-(diphenylphosphinoamino)pyridine; synthesis and kinetics of the reaction with MeI†

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New organoplatinum(II) complexes [PtR_2(PN)] (PN = 2-(diphenylphosphinoamino)pyridine, R = Me, **1a**, or *p*-MeC_6H_4, **1b**) were synthesized by the reaction of [$Pt(p\text{-}MeC_6H_4)_2(SMe_2)_2$] or [$Me_2Pt(\mu\text{-}SMe_2)_2PtMe_2$] with 1 and 2 equiv. of PN, respectively. The reaction of Pt(II) complexes **1** with MeI gave the Pt(IV) complexes [PtR_2(PN)MeI] (R = Me; **2a**, and *p*-MeC_6H_4; **2b**). All the complexes were fully characterized using multinuclear (^1H, ^{31}P, ^{13}C, and ^{195}Pt) NMR spectroscopy. Density functional theory calculations have been performed to find approximate structures for all described complexes. The platinum(II) complexes have a $5d_\pi$(Pt)-π*(PN) metal-to-ligand charge-transfer band, which was used to easily follow the kinetics of their reactions with MeI. The classical S_N2 mechanism was suggested. The rates of the reactions at different temperatures were measured and were consistent with the proposed mechanism, large negative $\Delta S^{\ddagger}$ values were found in each reaction. The PN chelating complexes [PtR_2(PN)], **1**, reacted almost 100 or 300 times slower with MeI as compared to that of the NN chelating complex [PtR_2(bpy)] (bpy = 2,2′-bipyridine) in acetone or benzene, respectively. This was attributed to the π-acceptance through the P ligating atom of PN ligand, which decreases the electron density of Pt(II) in PN chelating complexes.

Introduction

The area of homogeneous, transition metal catalyzed alkane functionalization reactions has significantly progressed over the last several decades.[1] Among the metal complexes, platinum species have been extensively applied as catalyst for many reactions in the petrochemical industries.[2] This has led to an increased level of research in the area of oxidative addition reactions by platinum complexes, and the number of platinum complexes that have been shown to activate C–X (X = halide) bonds to form stable alkyl and aryl complexes has developed considerably in the last several years. The dimethylplatinum(II) complexes [$PtMe_2$(NN)], in which NN are various diimine ligands such as 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen), have been extensively investigated by Puddephatt *et al.*[3] and we have recently studied the oxidative addition of some alkyl halides,[4] *e.g.* EtI, EtBr, ^{n}PrI, ^{n}PrBr, ^{n}BuI and an epoxide[5a] to [$PtMe_2$(NN)] or metallacycle analog [$Pt\{(CH_2)_4\}$(NN)]. A secondary α-deuterium KIE study involving the reaction of MeI/CD_3I with some organoplatinum(II) complexes has also been reported to confirm the operation of the S_N2 mechanism in the oxidative addition of MeI to some organoplatinum(II) complexes.[6] So it is well established that these reactions proceed by an S_N2 mechanism; however, sometimes the concerted three-center mechanism is also a possibility, but although it has been proposed for some reactions, it has never been demonstrated by experimental evidence.[3] The concerted three-center mechanism is usually proposed in the oxidative addition of C–H and C–C bonds,[3b,c] and also we have proposed it in the oxidative addition of the O–O bonds in H_2O_2 and dibenzoyl peroxide to some diarylplatinum(II) complexes [$PtAr_2$(NN)] (in which Ar is Ph or some simple substituted Ph groups).[5b] The kinetics of reaction of MeI with some binuclear organoplatinum(II) complexes, including a bridging biphosphine ligand, have recently been studied and a step-wise oxidative addition of MeI to the platinum(II) centers of each complex were described.[7]

On the other hand, bidentate ligands with a nitrogen and a phosphorus donor atom (P,N ligands) have attracted considerable attention in the field of transition metal catalysis.[8] The development and application of P,N ligands is a significant field of homogeneous catalysis, and this ligand type has proven its value in many reactions.[8] The chemistry of this class of ligand has been reviewed.[8c–e]

In spite of the comparative ease of phosphorus–nitrogen bond forming reactions compared to those in which

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† Electronic supplementary information (ESI) available: Table S1, DFT calculated bond angles (deg) of compounds **1–2**; Fig. S1, absorbance-time curves; Fig. S2, plots of first-order rate constants *versus* concentration of MeI; and Fig. S3, Eyring plots. See DOI: 10.1039/b9nj00523d

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phosphorus–carbon bonds are formed, relatively few examples of transition metal complexes with pyridine–phosphine (PN), in which the donor atoms (*i.e.* P and N) are separated by amino groups, are known.[9]

In continuation of our interest in the oxidative addition reactions of alkyl halides with organoplatinum(II) complexes, in the present work, new organoplatinum complexes [PtR_2(PN)] (PN = 2-(diphenylphosphinoamino)pyridine, R = Me, **1a**, or *p*-MeC_6H_4, **1b**) were synthesized and the oxidative addition of MeI to these complexes was studied and the results obtained here were compared with complexes containing NN ligands. The kinetics of oxidative addition to platinum complexes including PN ligands has not been studied, despite the fact that the PN ligands, especially in which an amine acts as spacer between the aromatic ring and the phosphine, are of great interest because of their possible role in catalysis and coordination chemistry of transition metals.[8]

Experimental

The ^{1}H NMR spectra were recorded on a Bruker Avance DPX 250 MHz spectrometer. ^{31}P, ^{13}C and ^{195}Pt NMR spectra were recorded on a Bruker Avance DRX 500 MHz. References were TMS (^{1}H, ^{13}C), H_3PO_4 (^{31}P), and aqueous K_2PtCl_4 (^{195}Pt). $CDCl_3$ was used as solvent. All the chemical shifts and coupling constants are in ppm and Hz, respectively. Kinetic studies were carried out by using a Perkin-Elmer Lambda 25 spectrophotometer with temperature control using an EYELA NCB-3100 constant-temperature bath. The microanalysis was performed using a Thermofinnigan Eager 300 CHN–O elemental analyzer. Complex *cis*-[Pt(*p*-$MeC_6H_4)_2(SMe_2)_2$],[10] the dimeric precursor *cis*,*cis*-[$Me_2Pt(\mu$-$SMe_2)_2PtMe_2$][11] and 2-(diphenylphosphinoamino)-pyridine (PN)[8l,12] were prepared by the literature methods.

[$PtMe_2$(PN)], 1a

To a solution of *cis*,*cis*-[$Me_2Pt(\mu$-$SMe_2)_2PtMe_2$] (125.5 mg, 0.22 mmol) in acetone (30 ml) was added a solution of PN (121.5 mg, 0.44 mmol) in acetone (10 ml) and stirred at room temperature for 1 h. The solvent was removed under reduced pressure to yield the sponge-like product. The product was washed with cold dry ether to yield a solid white powder. Yield: 88%; Anal. Calcd. for $C_{19}H_{21}N_2PPt$: C, 45.3; H, 4.2, N, 5.6. Found: C, 44.6; H, 4.3, N, 5.2%. NMR in $CDCl_3$: δ (^{1}H) 0.78 [d, ^2J(PtH) = 65.0 Hz, ^3J(PH) = 7.5 Hz, 3H, Me ligand *trans* to P], 0.91 [d, ^2J(PtH) = 87.5 Hz, ^3J(PH) = 7.5 Hz, 3H, Me ligand *cis* to P], 5.84 [bd, ^2J(PH) = 5.0 Hz, 1H attached to N], 8.81 [d, ^3J(HH) = 5 Hz, ^3J(PtH) = 20 Hz, 1H, pyridyl C[6] proton of coordinated pyridine]; δ (^{13}C) −23.8 [d, ^1J(PtC) = 730 Hz, $^2J(CP_{cis})$ = 4 Hz, Me ligand *cis* to P], 14.0 [d, ^1J(PtC) = 678 Hz, $^2J(CP_{trans})$ = 114 Hz, Me ligand *trans* to P]; δ(^{31}P) 73.2 [s, ^1J(PtP) = 2126 Hz]; δ (^{195}Pt) −2333 [d, ^1J(PtP) = 2129 Hz].

[$PtMe_3I$(PN)], 2a

Excess of MeI (100 μl) was added to solution of [$PtMe_2$(PN)] (68 mg, 0.14 mmol) in acetone (30 ml) and stirred at room temperature for 1 h. The solvent was removed under reduced pressure. The off- white solid product was washed with cold dry ether. Yield: 84%; Anal. Calcd. for $C_{20}H_{24}IN_2PPt$: C, 37.3; H, 3.8, N, 4.3. Found: C, 38.0; H, 3.9, N, 4.3%. NMR in $CDCl_3$: δ (^{1}H) 0.65 [d, ^2J(PtH) = 70.0 Hz, ^3J(PH) = 7.5 Hz, 3H, Me ligand *trans* to I], 1.49 [d, ^2J(PtH) = 70.0 Hz, ^3J(PH) = 7.5 Hz, 3H, Me ligand *cis* to P], 1.60 [d, ^2J(PtH) = 60.0 Hz, ^3J(PH) = 7.5 Hz, 3H, Me ligand *trans* to P], 6.15 [bd, ^2J(PH) *not observed*, 1H attached to N], 8.42 [d, ^3J(HH) = 7.5 Hz, ^3J(PtH) = *not resolved*, 1H, pyridyl C[6] proton of coordinated pyridine]; δ (^{31}P) 45.4 [s, ^1J(PtP) = 1275 Hz].

[Pt(*p*-$MeC_6H_4)_2$(PN)], 1b

To solution of *cis*-[Pt(*p*-$MeC_6H_4)_2(SMe_2)_2$] (320 mg, 0.68 mmol) in acetone (30 ml) was added a solution of PN (189 mg, 0.68 mmol) in the same solvent (10 ml) and the solution was stirred at room temperature for 1.5 h. The solvent was removed under reduced pressure. The off-white solid product was washed with *n*-pentane. Yield: 91%; Anal. Calcd. for $C_{31}H_{29}N_2PPt$: C, 56.7; H, 4.5, N, 4.3. Found: C, 55.9; H, 4.9, N, 4.0%. NMR in $CDCl_3$: δ (^{1}H) 2.08 and 2.17 [s, 6 H, 2 Me groups on the *p*-tolyl ligands], 5.90 [bd, ^2J(PH) = 4.2 Hz, 1H attached to N], 8.20 [d, ^3J(HH) = 5 Hz, ^3J(PtH) = 20 Hz, 1H, pyridyl C[6] proton of coordinated pyridine]; δ (^{13}C) 13.1 and 14.9 [s, 2 Me groups on the *p*-tolyl ligands], PN carbons 160-110; δ (^{31}P) 69.5 [s, ^1J(PtP) = 2016 Hz].

[PtMeI(*p*-$MeC_6H_4)_2$(PN)], 2b

Excess of MeI (100 μl) was added to solution of [Pt(*p*-$MeC_6H_4)_2$(PN)] (40.8 mg, 0.062 mmol) in acetone and stirred at room temperature for 6 h. The solvent was removed under reduced pressure. The yellow oily product was washed with cold dry ether to yield light yellow powder. Yield: 84%; Anal. Calcd. for $C_{32}H_{32}IN_2PPt$: C, 48.2; H, 4.0, N, 3.5. Found: C, 47.8; H, 4.1, N, 3.4%. NMR in $CDCl_3$: δ (^{1}H) 1.45 [d, ^2J(PtH) = 68.43 Hz, 3H, Me ligand *trans* to I], 2.20 and 2.30 [s, 6 H, 2 Me groups on the *p*-tolyl ligands], 6.15 [bd, ^2J(PH) = 4.2 Hz, 1H attached to N] 8.42 [d, ^3J(HH) = 7.5 Hz, 1H, pyridyl C[6] proton of coordinated pyridine]; δ (^{31}P) 48.2 [s, ^1J(PtP) = 1247 Hz].

Kinetic studies of the reaction of [$PtMe_2$(PN)] and [Pt(*p*-$MeC_6H_4)_2$(PN)] with MeI

A solution of [$PtMe_2$(PN)], **1a**, in benzene (3 ml, 2.6×10^{-4} M) and [Pt(*p*-$MeC_6H_4)_2$(PN)], **1b**, in acetone (3 ml, 5.0×10^{-4} M) in a cuvette was thermostatted at 25 °C and a known excess of MeI was added using a microsyringe. After rapid stirring, the absorbance at λ = 350 and 340 nm for **1a** and **1b**, respectively, was collected with time (Fig. 3 and S1†). The pseudo-first-order rate constants (k_{obs}) were evaluated by nonlinear least-squares fitting of the absorbance-time profiles to a first order equation (eqn (1)):

$$Abs_t = Abs_\infty + (Abs_0 - Abs_\infty) \exp(-k_{obs}t) \qquad (1)$$

A plot of k_{obs} *versus* [MeI] was linear and the slope gave the second-order rate constant. The same method was used at

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other temperatures (Fig. S2†) and activation parameters were obtained from the Eyring equation (eqn (2) and Fig. S3†).

$$\ln\left(\frac{k_2}{T}\right) = \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT} \qquad (2)$$

Similar methods were used to study the other reactions at the corresponding λ_{max} and the data are collected in Table 2.

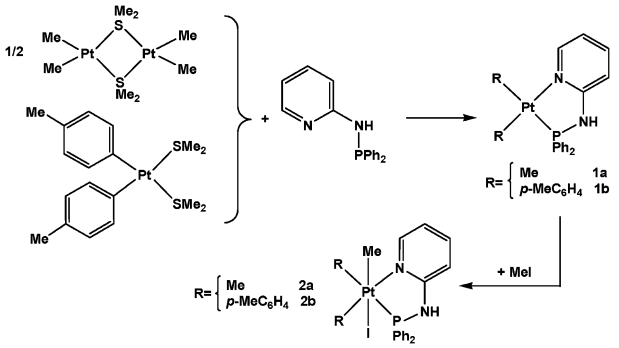
Computational details

Density functional calculations were performed with the program suite Gaussian98.[13] The LANL2DZ basis set was used with B3LYP method. All geometries were optimized. To evaluate and ensure the optimized structures of the molecules, frequency calculations were carried out using analytical second derivatives. In all cases only real frequencies were obtained for the optimized structures.

Results and discussion

Synthesis and characterization of the complexes

Very recently, Goldberg *et al.* reported[8m] the synthesis of the platinum(II) complex [$PtMe_2P'N'$], where P′N′ = 2-((di*tert*-butylphosphino)methyl)pyridine, by reaction of the bidentate ligand 2-((di*tert*-butylphosphino)methyl)pyridine with the Pt(II) dimethyl complex [$(\mu\text{-}SEt_2)PtMe_2]_2$ in toluene at high temperature (100 °C) for 90 min. Also, it has been shown that attempts to synthesize and isolate the complex **1a**, through the slow addition of PN ligand to a solution of [$PtMe_2$(cod)] in CH_2Cl_2, from the reaction mixture has not been successful due to its extremely high solubility in all common solvents.[8l] But we have synthesized the complex **1a** very easily by reaction of *cis*,*cis*-[$Me_2Pt(\mu\text{-}SMe_2)_2PtMe_2$] with 2-(diphenylphosphinoamino)pyridine ligand at room temperature in acetone and isolated the complex as pure and stable product. The analogous arylplatinum complex [$Pt(p\text{-}MeC_6H_4)_2$(PN)], **1b**, was synthesized similarly by the reaction of [$Pt(p\text{-}MeC_6H_4)_2(SMe_2)_2$] with 1 equimolar of PN. The preparative methods are described in the Scheme 1. The platinum(II) complexes, **1a** and **1b**, reacted cleanly with MeI to give the corresponding organoplatinum(IV) complexes, **2**. The complexes were fully characterized using ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H} and ^{195}Pt{^{1}H} NMR spectroscopy and elemental analysis. Full data are collected in the experimental section.



Scheme 1

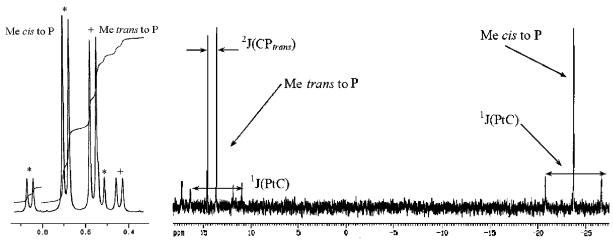


Fig. 1 ^{1}H (left) and ^{13}C (right) NMR spectra of complex **1a** in the Me region. Assignments are given on the spectra.

The ^{1}H NMR spectrum of **1a** in $CDCl_3$ at room temperature contains one signal as a broad doublet for NH proton at δ = 5.84 with ^2J(PH) = 5.0 Hz as well as four for the inequivalent pyridyl protons on the ligand, the furthest downfield of which at δ = 8.81 has ^{195}Pt satellites, ^3J(PtH) = 20 Hz. The presence of two inequivalent Pt–Me groups (see Fig. 1) is evident from the Pt–CH_3 signals of equal intensity (δ = 0.91 and 0.78 ppm), both with coupling to one ^{31}P nucleus as well to ^{195}Pt (^2J(PtH) = 87.5 Hz and ^3J(PH) = 7.5 Hz; *cis* to P and ^2J(PtH) = 65.0 Hz and ^3J(PH) = 7.5 Hz; *trans* to P, respectively). The ^{31}P{^{1}H} NMR spectrum of **1a** shows one signal with ^{195}Pt satellites characteristic of a phosphorus *trans* to a methyl on Pt(II) (δ = 73.2, ^1J(PtP) = 2126 Hz). In the ^{13}C NMR spectrum of **1a**, two methyl ligands (see Fig. 1) appear as two different set of doublets at δ = −23.8 ppm, accompanied by platinum satellites with ^1J(PtC) = 730 Hz, $^2J(CP_{cis})$ = 4 Hz for Me group *cis* to P, and δ = 14.0 ppm accompanied by platinum satellites with ^1J(PtC) = 678 Hz, $^2J(CP_{trans})$ = 114 Hz for Me group *trans* to P. Its ^{195}Pt NMR spectrum shows a doublet at δ = −2333 with ^1J(PtP) = 2126 Hz. Similar spectral data are obtained for complex [$Pt(p\text{-}MeC_6H_4)_2$(PN)], **1b**, except instead of Me–Pt, two singlets were observed at δ = 2.08 and 2.17 for the Me substituents on the Ar ligands.

In the ^{1}H NMR spectrum of complex [$PtMe_3I$(PN)], **2a**, a doublet at δ = 0.65 with ^2J(PtH) = 70.0 Hz and ^3J(PH) = 7.5 Hz was assigned to the Me ligand *trans* to I. A doublet at δ = 1.49 with ^2J(PtH) = 70.0 Hz and ^3J(PH) = 7.5 Hz was assigned to the Me ligand *cis* to P and a doublet at δ = 1.60 with ^2J(PtH) = 60.0 Hz and ^3J(PH) = 7.5 Hz were attributed to the Me ligand *trans* to P. The hydrogen attached to N appeared as a broad doublet at δ = 6.15. The pyridyl C[6] proton of coordinated pyridine appeared at δ = 8.42 with ^3J(HH) = 7.5 Hz. The ^{31}P{^{1}H} NMR spectrum of [$PtMe_3I$(PN)], **2a**, is representative of the product. The value of ^1J(PtP) in this platinum(IV) complex is 1275 Hz, which is considerably lower than the corresponding value of 2126 Hz for the starting platinum(II) complex [$PtMe_2$(PN)], **1a**.

DFT-computed geometries for complexes 1 and 2

The possible geometries for complexes **1** and **2** were calculated theoretically. The calculated bond distances and bond angles from DFT-optimized structures (B3LYP/LANL2DZ)[13] for compounds **1** and **2** are included in the Table 1 and 1S. The DFT-optimized structures for these complexes are shown in Fig. 2.

As can be seen from Table 1, for complex **1a**, the Pt–C bond lengths for the two methyl groups are within the expected

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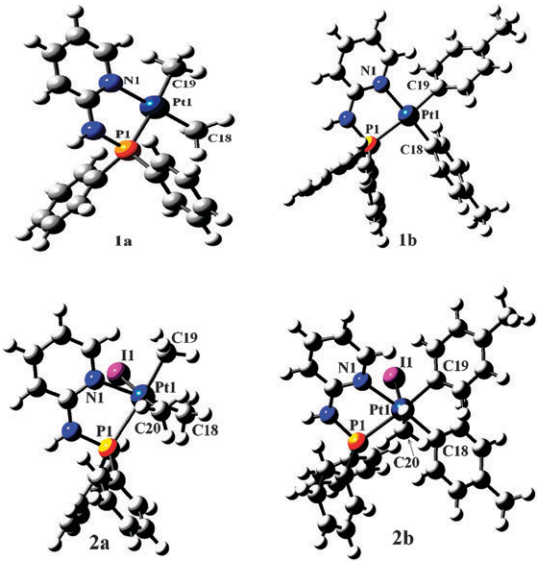

Fig. 2 Optimized structures of complexes **1** and **2**.

Table 1 DFT calculated bond lengths (Å) of complexes **1–2** based on the optimized structures

	1a	1b	2a	2b
Pt1–P1	2.402	2.422	2.548	2.539
Pt1–N1	2.210	2.204	2.268	2.269
Pt1–C18	2.069	2.033	2.080	2.050
Pt1–C19	2.079	2.041	2.088	2.071
Pt1–C20	—	—	2.100	2.109
Pt1–I1	—	—	2.912	2.937

range for a Pt(II)-Me moiety.[14] The Pt–C bond *trans* to the phosphorus is longer (2.079 Å) than that *trans* to nitrogen (2.069 Å), as would be expected based on *trans* influence arguments and is in agreement with ^{2}J(PtH) values reported for complex [$PtMe_2$(PN)], **1a**. Also, as expected, the bond lengths of platinum(II) complexes, **1**, is shorter than the corresponding bonds for the product platinum(IV) complexes, **2**. For example the Pt–P bond in complex **1a** is shorter (2.402 Å) than that in **2a** (2.548 Å). This confirms the larger ^{1}J(PtP) value of the complex **1a** compared to that of the complex **2a**. Also, the Pt–P bond lengths for complexes **1a** and **1b** are 2.402 and 2.422 Å, respectively, which is in agreement with the ^{1}J(PtP) values found for these complexes in ^{31}P NMR spectra (2126 or 2016 Hz for complex **1a** or **1b**, respectively).

The kinetic study

The kinetics of oxidative addition of MeI to [PtR_2(PN)] (R = Me, **1a**, in benzene and R = *p*-MeC_6H_4, **1b**, in acetone) were studied by using UV-vis spectroscopy. In each case, a known excess of MeI reagent was used and the disappearance of the MLCT band for **1a** at λ = 350 nm and for **1b** at λ = 340 nm was used to monitor the reaction. The reactions followed good first-order kinetics (Fig. 3 and S1†). Graphs of these first-order rate constants against the concentration of the MeI gave good straight line plots passing through origin, showing a first-order dependence of the rate on the concentration of MeI (Fig. S2†). Thus, the overall second-order rate constants were determined. The activation parameters were also

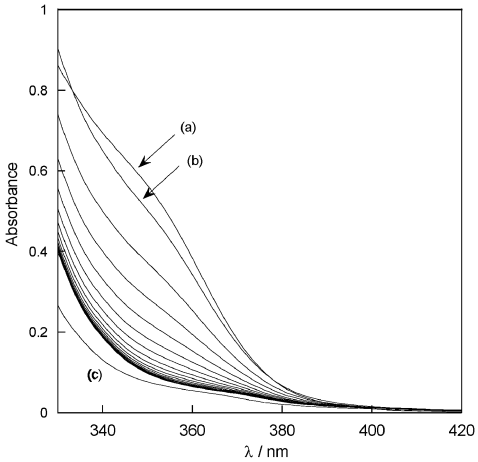

Fig. 3 The changes in the UV-vis spectrum during the reaction of [$PtMe_2$(PN)] (2.64×10^{-4} M) and MeI (0.27 M) in benzene at T = 25 °C: (a) initial spectrum (before adding MeI); (b) spectrum at t = 0; successive spectra recorded at intervals of 30 s, (c) final spectrum.

determined from measurement at different temperatures (Fig. S3†) and the data are given in Table 2. These reactions followed good second-order kinetics, first order in both platinum(II) and MeI reagent, with remarkable reproducibility (±5%). These observations suggest an S_N2 mechanism of oxidative addition of methyl iodide to the platinum(II) complex.[3] Also, the large negative values of $\Delta S^{\ddagger}$ are typical of oxidative addition by a common S_N2 mechanism which involves nucleophilic attack of the metallic center to methyl group of MeI and formation of a cationic intermediate $[PtR_2(PN)Me]^{+}I^{-}$.

As shown in Table 2, in reactions of the Pt(II)–NN complexes or the PN analog with MeI at different temperatures and different solvents, the NN complexes reacted more than 100–300 times faster than the corresponding PN analog. For example, MeI in acetone at 25 °C reacted nearly 100 times faster with [Pt(*p*-$MeC_6H_4)_2$(bpy)][6] ($k_2 = 6.2 \times 10^{-1}$ L mol^{-1} s^{-1}) than with [Pt(*p*-$MeC_6H_4)_2$(PN)] ($k_2 = 6.3 \times 10^{-3}$ L mol^{-1} s^{-1}). The same behavior has been seen in the reaction of dimethyl analogues with MeI in benzene. This trend could be explained by the influence of donating/accepting character of P and N atoms. The π-acceptor character of the phosphorous ligands stabilizes a metal center in a low oxidation state,[8d] so ligands with P ligating atom, such as PN, decrease electron density on platinum(II) core and make it reluctant to oxidative/addition reactions based on S_N2 mechanism. On the other hand nitrogen σ-donor ability in NN ligand, such as 2,2′-bipyridine makes the metal core more susceptible to oxidative addition reactions[8d] that help to stabilize intermediate oxidation states, so complexes with NN ligands undergo oxidative addition reactions readily.

Conclusions

New organoplatinum complexes [PtR_2(PN)] (R = Me, **1a**, and *p*-MeC_6H_4, **1b**, 2-(diphenylphosphinoamino)pyridine (= PN)) were synthesized by the reaction of [Pt(*p*-$MeC_6H_4)_2(SMe_2)_2$] or [$Me_2Pt(\mu\text{-}SMe_2)_2PtMe_2$] with 1 and 2, respectively, equiv. of PN and the kinetic of reaction of MeI with [PtR_2(PN)] complexes was studied.

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Table 2 Second-order rate constants[a] and activation parameters for reaction of MeI with [Pt(*p*-$MeC_6H_4)_2$(PN)] or [Pt(*p*-$MeC_6H_4)_2$(bpy)] in acetone and [$PtMe_2$(PN)] or [$PtMe_2$(bpy)] in benzene

		10^2 k_2/Lmol^{-1} s^{-1} at different T/°C						
Complex	Solvent	10	20	25	30	40	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
[Pt(*p*-$MeC_6H_4)_2$(PN)]	Acetone	0.25	0.47	0.63	0.87	1.50	41.8 ± 0.6	−147 ± 5
[Pt(*p*-$MeC_6H_4)_2$(bpy)][b]	Acetone	28	48	62	83	133	34.9 ± 0.4	−132 ± 2
[$PtMe_2$(PN)]	Benzene	1.48	2.48	3.24	4.13	6.22	33.4 ± 0.7	−161 ± 7
[$PtMe_2$(bpy)][c]	Benzene	636	888	1093	1200	1699	21.6 ± 1.4	−153 ± 5

[a] Estimated errors in k_2 values are ±5%. [b] bpy = 2,2′-bipyridine, from ref. 6. [c] From ref. 15.

According to the kinetic results, the oxidative addition reaction of MeI with [PtR_2(PN)] follows a good second order kinetic, first order with respect to both reactants. The entropy of activation, $\Delta S^{\ddagger}$, has a large negative value in each reaction consistent with an S_N2-type mechanism. The operative mechanism involves nucleophilic attack of platinum(II) on the carbon atom of MeI to give the transient cationic platinum(IV) intermediate, [PtR_2(PN)Me]$^+I^-$, which rapidly rearranges to [PtR_2(PN)MeI].

It is interesting to note that the observed rate constants for the reaction of PN complexes, [PtR_2(PN)], with MeI are lower than the related rate constants reported typically for NN complexes *e.g.* [$PtMe_2$(bpy)][3,15] and [Pt(*p*-$MeC_6H_4)_2$(bpy)].[6] This was attributed to the π-acceptance through the P atom of PN ligand, which decreases the electron density of Pt(II) in the complex with PN containing ligand.

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