

Exchange of pyridine and bipyridine ligands in trimethylplatinum(IV) iodide complexes: Substituent and solvent effects

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Table S1 Selected bond distances [$\text{\AA}$] and angles [$^\circ$] for $[\text{PtMe}_3(\text{L-L})\text{I}]$ complexes (L-L = 4-Mebipy, 4-MeObipy, 4-Me₂Nbipy) complexes

	$[\text{PtMe}_3(4\text{-Mebipy})\text{I}] \cdot 0.5(\text{C}_6\text{H}_6)$	$[\text{PtMe}_3(4\text{-MeObipy})\text{I}]$	$[\text{PtMe}_3(4\text{-Me}_2\text{Nbipy})\text{I}]$
Pt1-C1	2.028(5)	2.041(6)	2.065(12)
Pt1-C2	2.035(5)	2.024(8)	2.134(16)
Pt1-C3	2.045(5)	2.070(7)	2.068(15)
Pt1-N1	2.146(3)	2.135(6)	2.124(10)
Pt1-N2	2.149(3)	2.158(5)	2.140(10)
Pt1-I1	2.7813(4)	2.7744(5)	2.7937(11)
C1-Pt1-C2	84.7(2)	85.7(3)	85.9(6)
C2-Pt1-C3	87.5(3)	88.2(3)	89.9(6)
C1-Pt1-C3	87.7(2)	88.3(3)	85.9(6)
C1-Pt1-N1	174.84(17)	173.2(2)	174.0(5)
C2-Pt1-N1	98.80(18)	99.6(2)	99.5(5)
C3-Pt1-N1	88.62(17)	87.7(2)	91.4(5)
C1-Pt1-N2	99.90(18)	98.3(3)	98.7(5)
C2-Pt1-N2	174.24(19)	175.5(2)	175.2(5)
C3-Pt1-N2	89.2(2)	89.8(3)	88.7(5)
C1-Pt1-I1	91.75(14)	89.56(19)	91.5(4)
C2-Pt1-I1	93.7(2)	91.2(2)	90.5(5)
C3-Pt1-I1	178.68(18)	177.76(19)	177.3(4)
N1-Pt1-I1	91.85(9)	94.56(12)	91.1(2)
N2-Pt1-I1	89.74(9)	90.99(14)	91.1(2)
N1-Pt1-N2	76.42(13)	76.25(18)	75.9(4)

Table S2 ^1H NMR data^a for the reaction of an 1:1 mixture of $[\text{PtMe}_3\text{L}_2\text{I}]$ (L = pyridines) and corresponding 2,2'-bipyridines at 300 K in CDCl_3 and in nitrobenzene- d_5

Reaction	Pt(IV) species present in solution	$\delta(\text{Pt-CH}_3)^{b, c}$		Trans ligand
		in CDCl_3	in nitrobenzene- d_5	
1:1 mixture of $[\text{PtMe}_3(\text{py})_2\text{I}]$ and bipy	$[\text{PtMe}_3(\text{py})_2\text{I}]$	A 1.50 (70.3)	A 1.70 (70.4)	Py
		B 1.20 (69.6)	B 1.29 (68.9)	I
	$[\text{PtMe}_3(\text{bipy})\text{I}]$	C 1.56 (70.5)	C 1.81 (70.5)	Bipy
		D 0.64 (73.1)	D 0.78 (72.6)	I
	$[\text{PtMe}_3(\text{bipy})(\text{py})\text{I}]$	E 1.23 (67.1)	E 1.31 (67.2)	Bipy
		F 0.57 (70.3)	F 0.61 (70.5)	Py
1:1 mixture of $[\text{PtMe}_3(4\text{-Mepy})_2\text{I}]$ and 4-Mebipy	$[\text{PtMe}_3(4\text{-Mepy})_2\text{I}]$	A 1.45 (70.0)	A 1.69 (70.1)	4-MePy
		B 1.17 (70.0)	B 1.28 (69.2)	I
	$[\text{PtMe}_3(4\text{-Mebipy})\text{I}]$	C 1.51 (70.3)	C 1.78 (70.3)	4-Mebipy
		D 0.63 (73.5)	D 0.81 (72.9)	I
	$[\text{PtMe}_3(4\text{-Mebipy})(4\text{-Mepy})\text{I}]$	E 1.14 (66.9)	E 1.25 (67.2)	4-Mebipy
		F 0.52 (70.6)	F 0.61 (70.5)	4-Mepy
1:1 mixture of $[\text{PtMe}_3(4\text{-MeOpy})_2\text{I}]$ and 4-MeObipy	$[\text{PtMe}_3(4\text{-MeOpy})_2\text{I}]$	A 1.42 (70.0)	A 1.69 (70.2)	4-MeOpy
		B 1.15 (70.2)	B 1.29 (69.4)	I
	$[\text{PtMe}_3(4\text{-MeObipy})\text{I}]$	C 1.48 (70.2)	C 1.77 (70.5)	4-MeObipy
		D 0.65 (73.7)	D 0.86 (73.0)	I
	$[\text{PtMe}_3(4\text{-MeObipy})(4\text{-MeOpy})\text{I}]$	E 1.09 (67.2)	E 1.23 (67.4)	4-MeObipy
		F 0.50 (70.4)	F 0.64 (70.5)	4-MeOpy
1:1 mixture of $[\text{PtMe}_3(4\text{-Me}_2\text{Npy})_2\text{I}]$ and 4-Me ₂ Nbipy	$[\text{PtMe}_3(4\text{-Me}_2\text{Npy})_2\text{I}]$	A 1.35 (69.3)	- ^d	4-Me ₂ Npy
		B 1.14 (71.5)		I
	$[\text{PtMe}_3(4\text{-Me}_2\text{Nbipy})(4\text{-Me}_2\text{Npy})\text{I}]$	C 0.94 (67.0)	C 1.13 (67.1)	4-Me ₂ Nbipy
		D 0.43 (70.3)	D 0.65 (70.0)	4-Me ₂ Npy
	$[\text{PtMe}_3(4\text{-Me}_2\text{Npy})_3\text{I}]$	E 0.92 (66.7)	E 1.04 (66.7)	4-Me ₂ Npy

^a Chemical shifts quoted in ppm are relative to internal solvent peaks (in the case of CDCl_3 , $\delta = 7.26$ ppm; in the case of nitrobenzene- d_5 , $\delta = 8.11$ ppm, 7.67 and 7.50 ppm). ^{b2} $J_{\text{Pt-H}}$ /Hz in parentheses. ^c labelling refers to Schemes 3 and 4. ^dIn nitrobenzene- d_5 , the compound $[\text{PtMe}_3(4\text{-Me}_2\text{Npy})_2\text{I}]$ was not present in solution.

Table S3 Population of different Pt(IV) complexes in 1:1 mixture of [PtMe₃(py)₂I] and bipy at 300 K in CDCl₃

Reaction time	In CDCl ₃				
	Pyridine complex (I)	Bipyridine complex (II)	Bipyridine complex (III)	Bipyridine complexes (II + III) /pyridine complex (I)	Bipyridine Complex III /bipyridine Complex II
After 1d	37.7%	57.4%	4.9%	1.65	0.08
After 3d	19.8%	72.3%	7.9%	4.05	0.11
After 7d	8.6%	78.4%	13%	10.63	0.17
After 14d	6%	79.5%	14.5%	15.67	0.18

Table S4 Population of different Pt(IV) complexes in 1:1 mixture of [PtMe₃(py)₂I] and bipy at 300 K in nitrobenzene-d₅

Reaction time	In nitrobenzene-d ₅				
	Pyridine complex (I)	Bipyridine complex (II)	Bipyridine complex (III)	Bipyridine complexes (II + III)/pyridine complex (I)	Bipyridine Complex III /bipyridine Complex II
After 1d	46%	36%	18%	1.17	0.50
After 3d	24.6%	48.4%	27%	3.06	0.56
After 7d	10.8%	57.3%	31.9%	8.26	0.56
After 14d	7%	60.4%	32.6%	13.28	0.54

Table S5 Population of different Pt(IV) complexes in 1:1 mixture of [PtMe₃(4-Mepy)₂I] and 4-Mebipy at 300 K in CDCl₃

Reaction time	In CDCl ₃				
	Pyridine complex (I)	Bipyridine complex (II)	Bipyridine complex (III)	Bipyridine complexes (II + III) /pyridine complex (I)	Bipyridine Complex III /bipyridine Complex II
After 1d	47.2%	40.6%	12.2%	1.12	0.30
After 3d	27.3%	50.8%	21.9%	2.66	0.43
After 7d	9.8%	56.3%	33.9%	9.20	0.60
After 14d	7.6%	56%	36.4%	12.16	0.65

Table S6 Population of different Pt(IV) complexes in 1:1 mixture of [PtMe₃(4-Mepy)₂I] and 4-Mebipy at 300 K in nitrobenzene-d₅

Reaction time	In nitrobenzene-d ₅				
	Pyridine complex (I)	Bipyridine complex (II)	Bipyridine complex (III)	Bipyridine complexes (II + III) /pyridine complex (I)	Bipyridine Complex III /bipyridine Complex II
After 1d	51%	26.5%	22.5%	0.96	0.85
After 3d	34.5%	33.1%	32.4%	1.90	0.98
After 7d	22.9%	36.6%	40.5%	3.37	1.11
After 14d	20%	38.1%	41.9%	4.00	1.10

Table S7 Population of different Pt(IV) complexes in 1:1 mixture of [PtMe₃(4-MeOpy)₂I] and 4-MeObipy at 300 K in CDCl₃

Reaction time	In CDCl ₃				
	Pyridine complex (I)	Bipyridine complex (II)	Bipyridine complex (III)	Bipyridine complexes (II + III) /pyridine complex (I)	Bipyridine Complex III /bipyridine Complex II
After 1d	53.2%	23.4%	23.4%	0.88	1.00
After 3d	29.4%	29.4%	41.2%	2.40	1.40
After 7d	11.7%	33.0%	55.3%	7.55	1.68
After 14d	10.5%	30.0%	59.5%	8.52	1.98

Table S8 Population of different Pt(IV) complexes in 1:1 mixture of [PtMe₃(4-MeOpy)₂I] and 4-MeObipy at 300 K in nitrobenzene-d₅

Reaction time	In CDCl ₃				
	Pyridine complex (I)	Bipyridine complex (II)	Bipyridine complex (III)	Bipyridine complexes (II + III) /pyridine complex (I)	Bipyridine Complex III /bipyridine Complex II
After 1d	61.7%	13.6%	24.7%	0.62	1.82
After 3d	43.1%	19.8%	37.1%	1.32	1.87
After 7d	27.8%	22.6%	49.6%	2.60	2.19
After 14d	23.3%	23.7%	53%	3.29	2.24

Table S9 Population of different Pt(IV) complexes in 1:1 mixture of [PtMe₃(4-Me₂Npy)₂I] and 4-Me₂Nbipy at 300 K in CDCl₃

Reaction time	In CDCl ₃		
	Pyridine complex (I)	Bipyridine complex (III)	Bipyridine complex (III) /pyridine complex (I)
After 1d	35%	65%	1.86
After 3d	12.4%	87.6%	7.06
After 7d	8.8%	91.2%	10.36
After 14d	5.0%	95.0%	19.00

Table S10 Population of different Pt(IV) complexes in 1:1 mixture of [PtMe₃(4-Me₂Npy)₂I] and 4-Me₂Nbipy at 300 K in nitrobenzene-d₅

Reaction time	In nitrobenzene-d ₅		
	Pyridine complex (I)	Bipyridine complex (III)	Bipyridine complex (III) /pyridine complex (I)
After 1d	20.6%	79.4%	3.85
After 3d	9.7%	90.3%	9.31
After 7d	7.4%	92.6%	12.51
After 14d	6%	94%	15.67

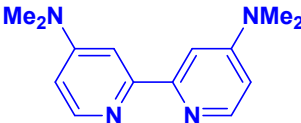


Fig. S2 The 400 MHz ^1H NMR spectrum of $[\text{PtMe}_3(4\text{-Mebipy})\text{I}]$ in CDCl_3 at 300 K.

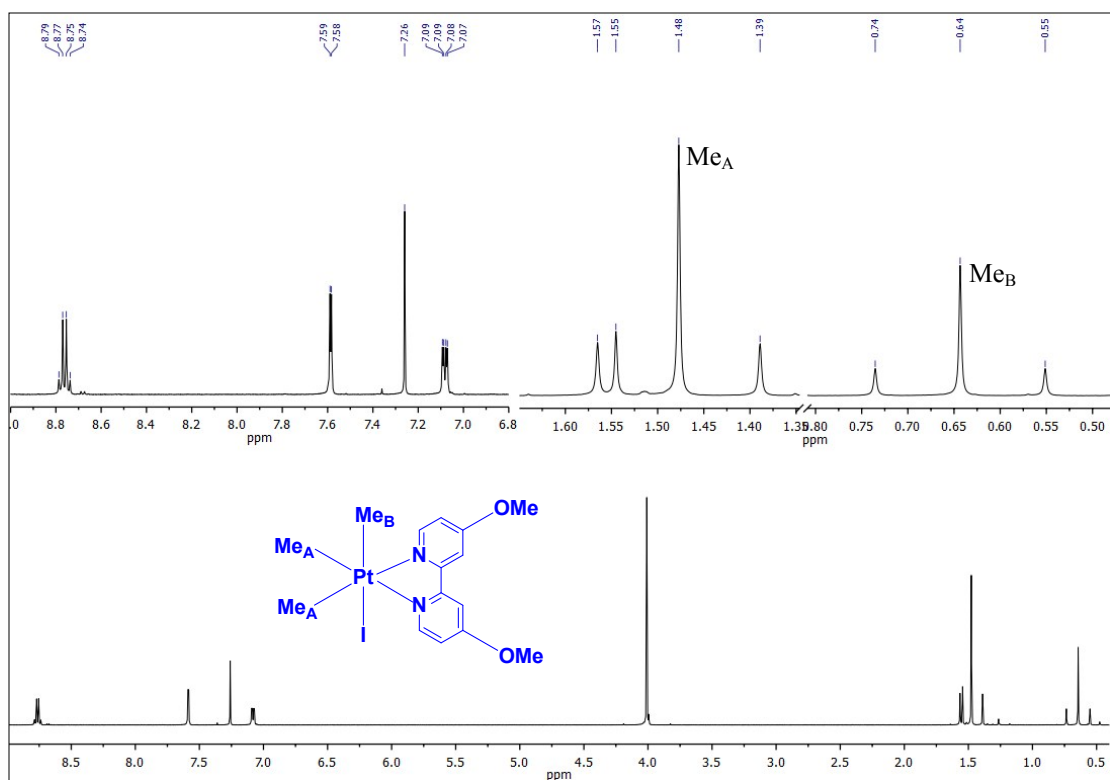


Fig. S3 The 400 MHz ^1H NMR spectrum of $[\text{PtMe}_3(4\text{-MeObipy})\text{I}]$ in CDCl_3 at 300 K.

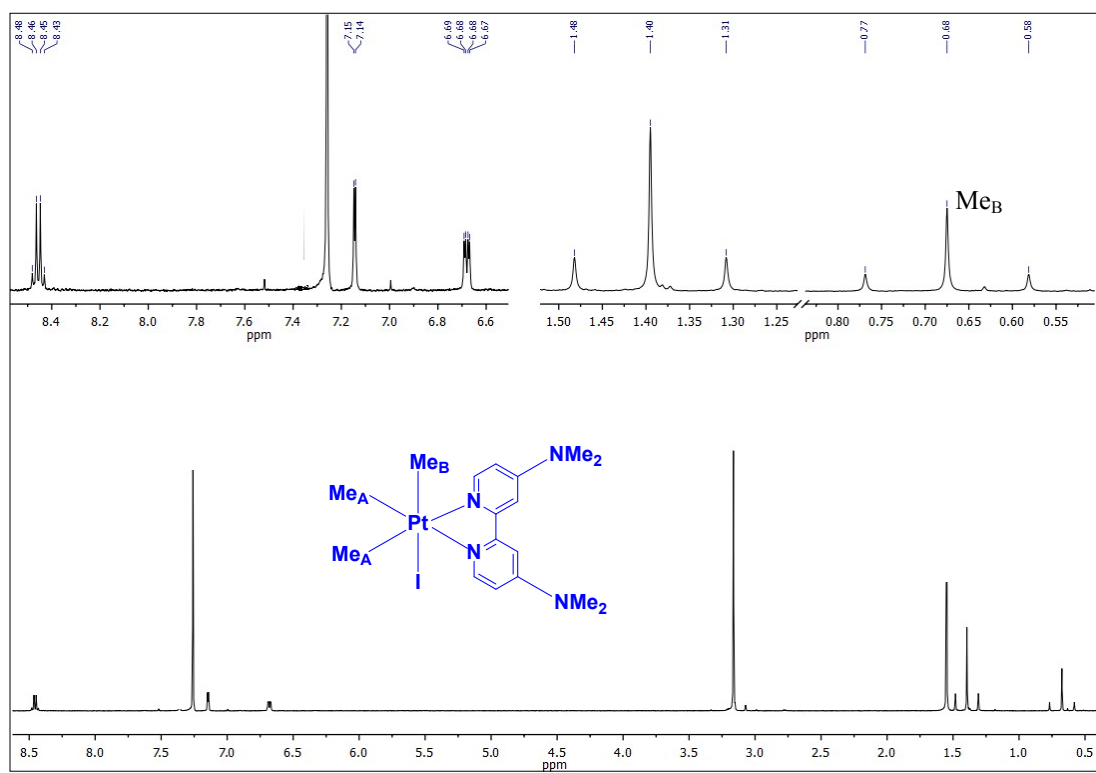


Fig. S4 The 400 MHz ^1H NMR spectrum of $[\text{PtMe}_3(4\text{-Me}_2\text{Nbipy})\text{I}]$ in CDCl_3 at 300 K.

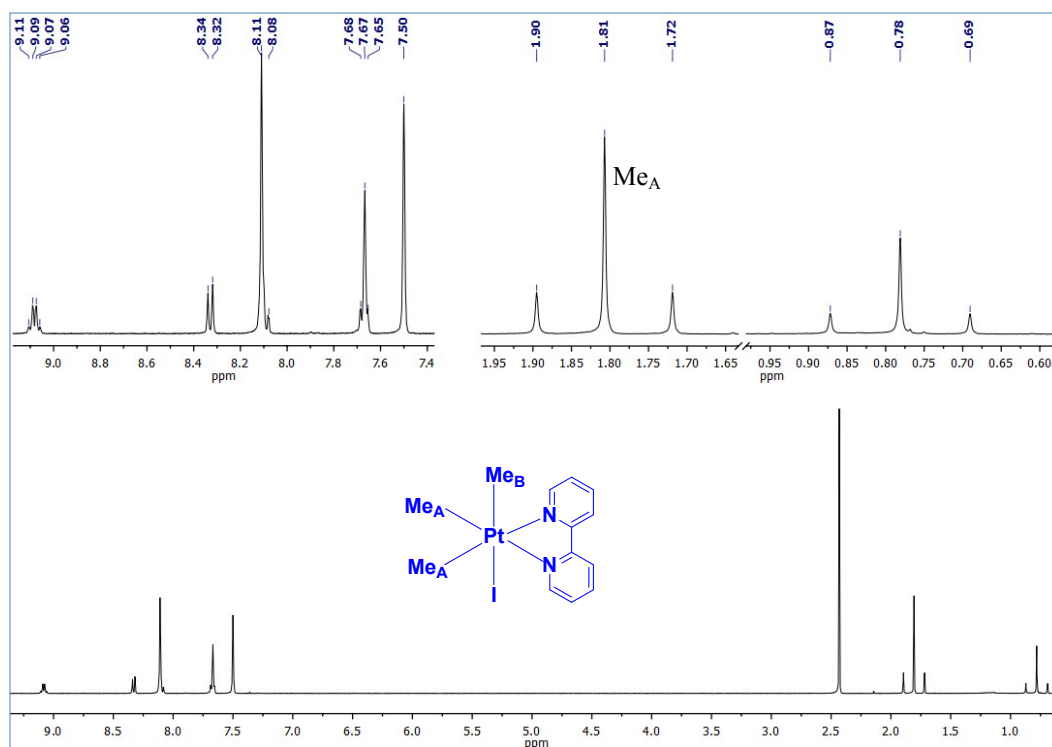


Fig. S5 The 400 MHz ^1H NMR spectrum of $[\text{PtMe}_3(\text{bipy})\text{I}]$ in nitrobenzene- d_5 at 300 K.

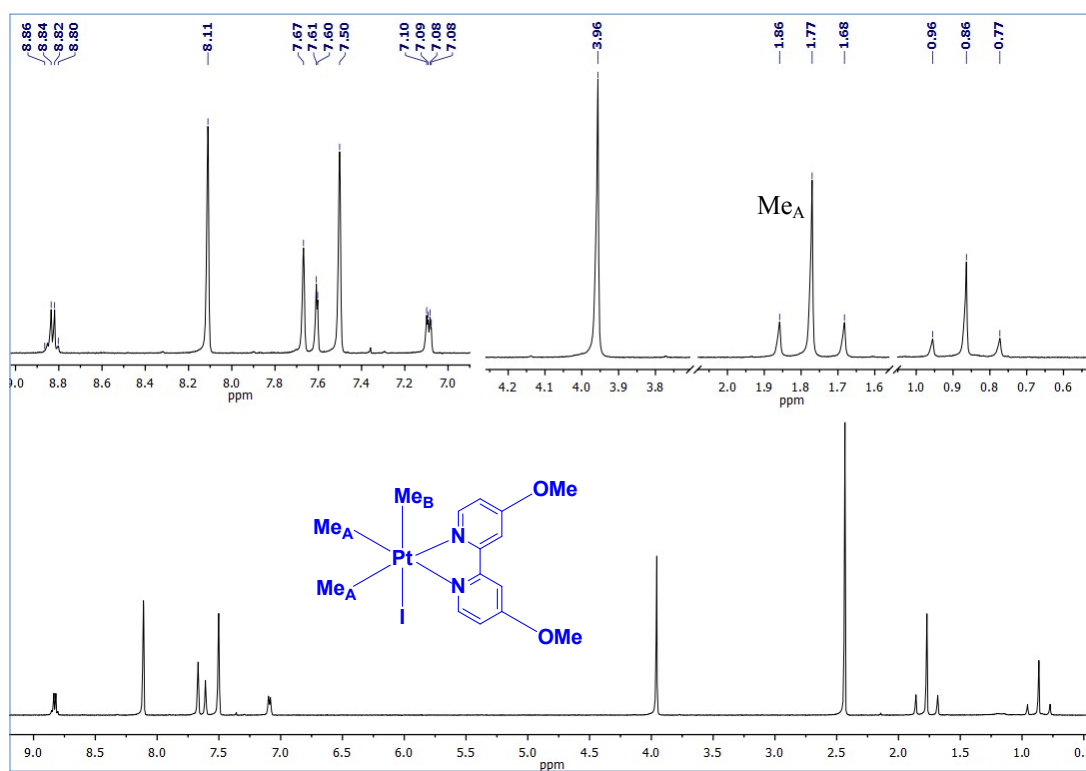


Fig. S6 The 400 MHz ^1H NMR spectrum of $[\text{PtMe}_3(4\text{-MeObipy})\text{I}]$ in nitrobenzene- d_5 at 300 K.

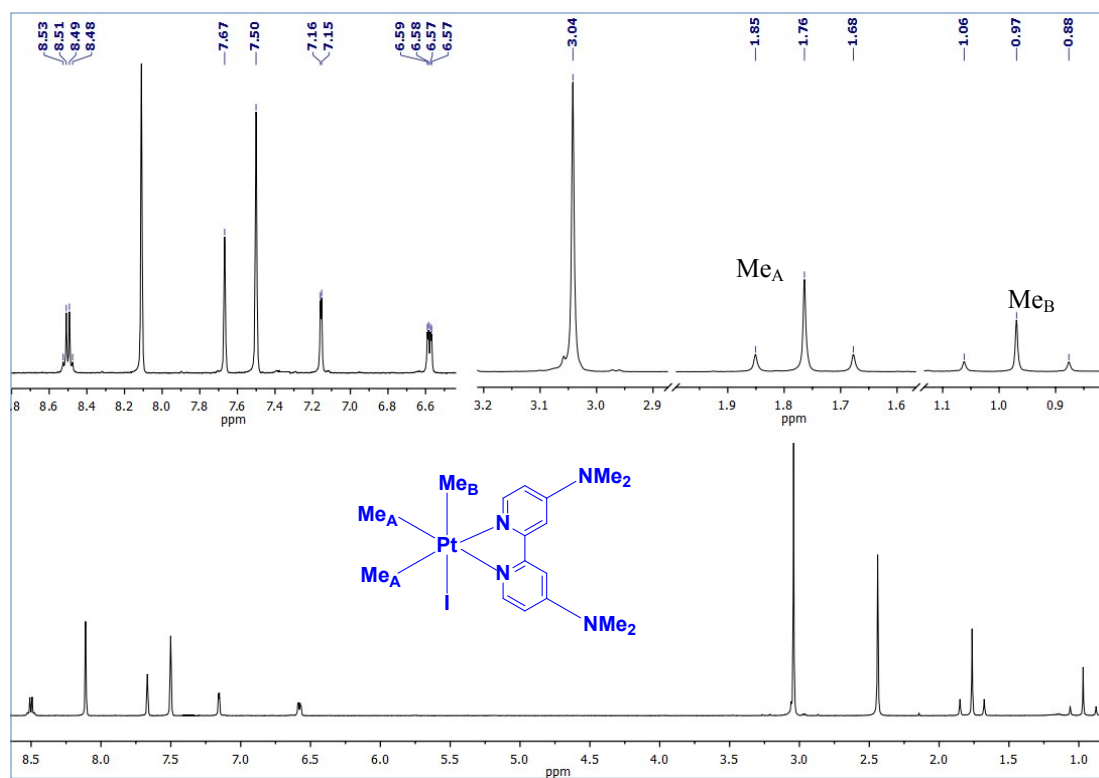


Fig. S7 The 400 MHz ^1H NMR spectrum of $[\text{PtMe}_3(4\text{-Me}_2\text{Nbipy})\text{I}]$ in nitrobenzene- d_5 at 300 K.

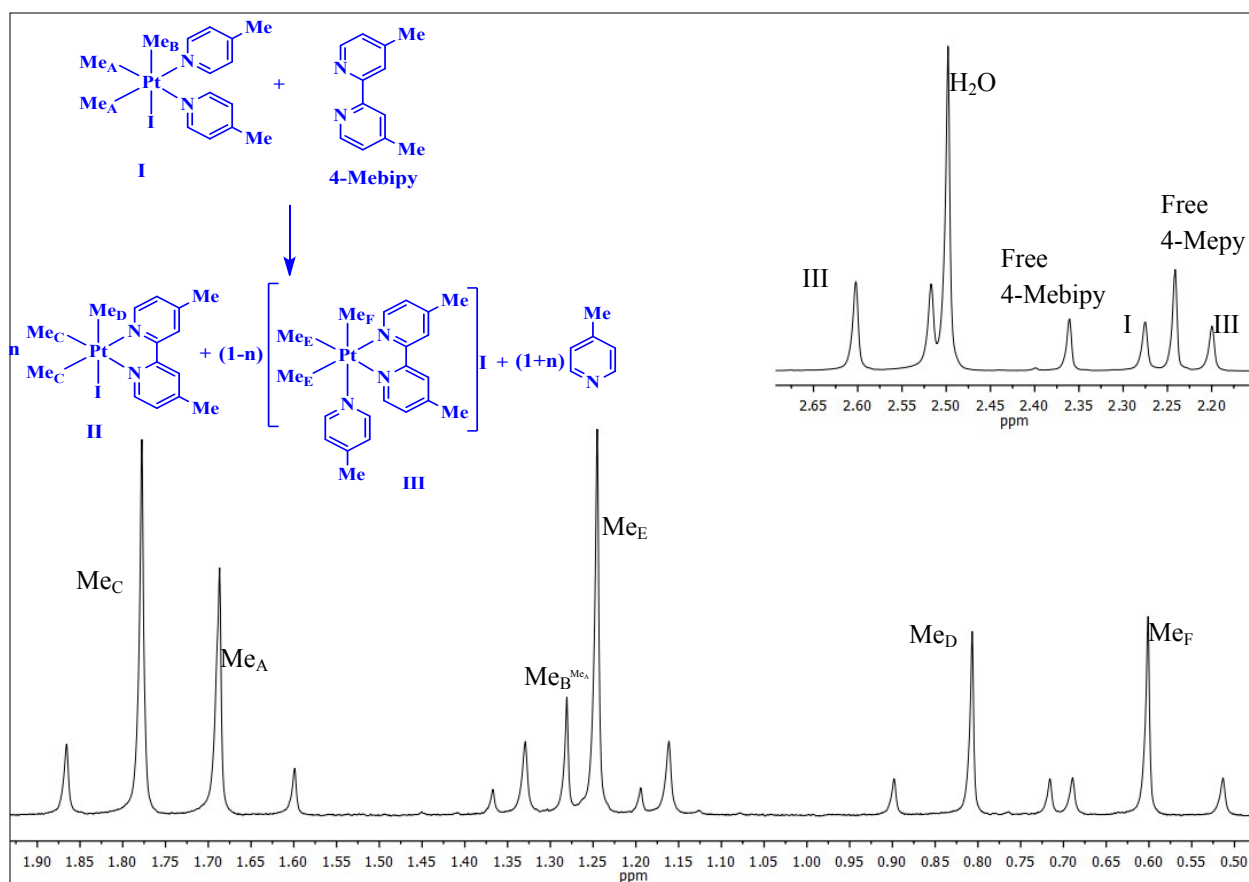


Fig. S8 The platinum-methyl region in the ^1H NMR spectrum of an equimolar mixture of $[\text{PtMe}_3(4\text{-Mepy})_2\text{I}]$ and 4-Mebipy in nitrobenzene- d_5 at 300 K after 14 days, showing presence of three platinum(IV) complexes **I**, **II** and **III** in solution. Inset showing the methyl region for the spectrum and also the reaction scheme. The signal at the left correspond to the methyl group of 4-Mebipy in complex **III**, while the signal at the utmost right correspond to the methyl group of 4-Mepy in **III**.

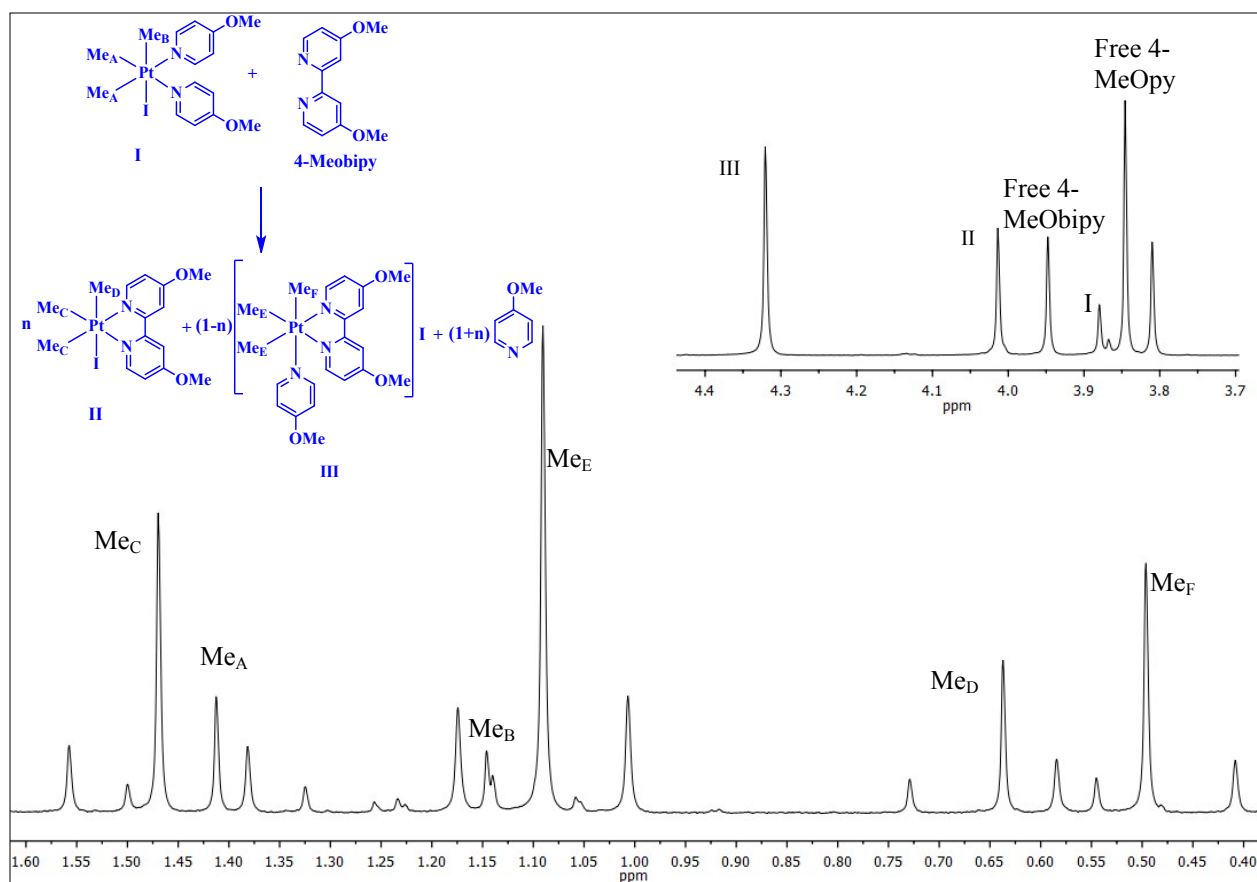


Fig. S9 The platinum-methyl region in the ^1H NMR spectrum of an equimolar mixture of $[\text{PtMe}_3(4\text{-MeOpy})_2]$ and 4-MeObipy in CDCl_3 at 300 K showing presence of three platinum(IV) complexes **I**, **II** and **III** in solution. Inset showing the methoxy region for the spectrum. The signal at the left correspond to the methoxy group of 4-MeObipy in complex **III**, while the signal at the utmost right correspond to the methoxy group of 4-MeOpy in **III**.

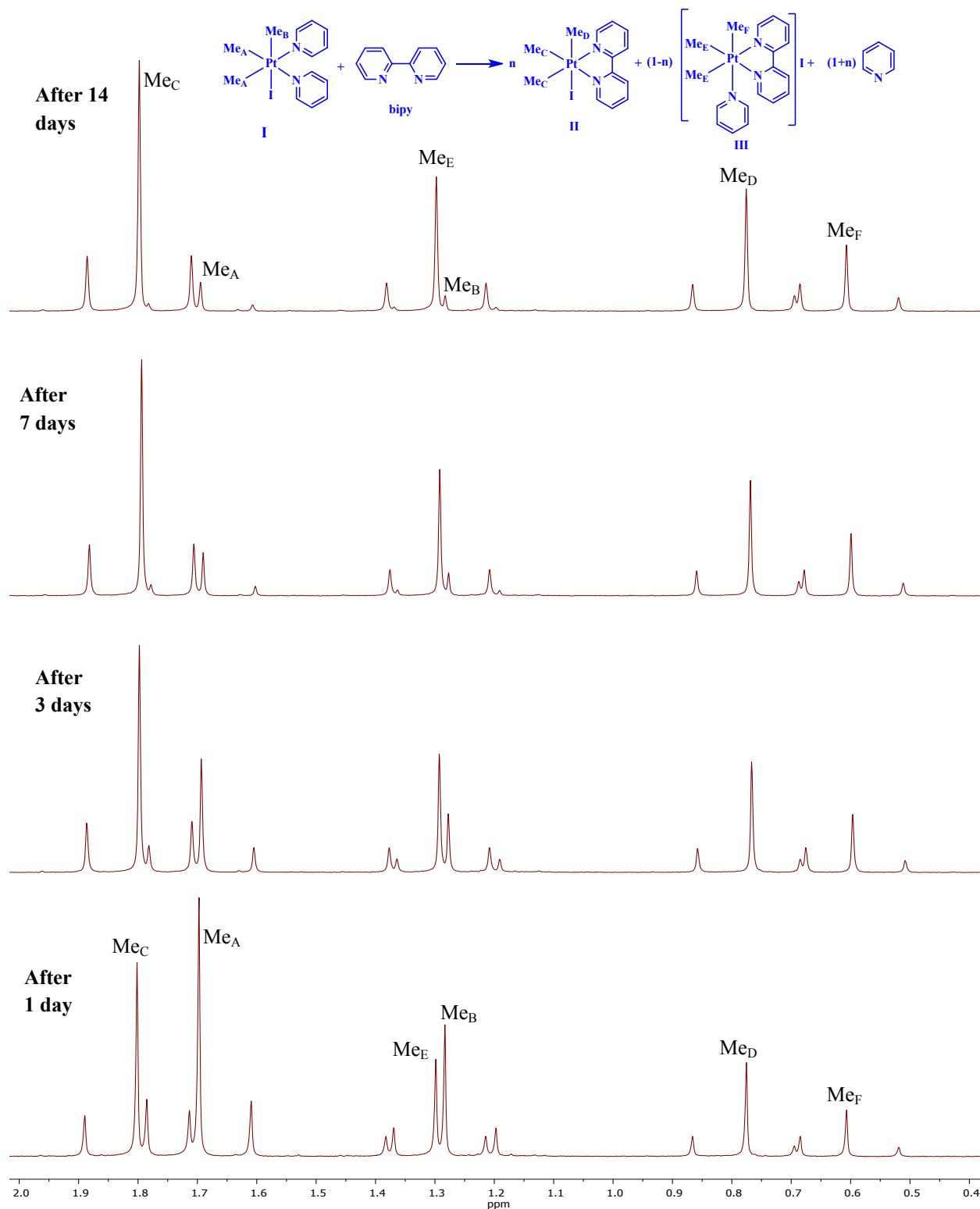


Fig. S10 The platinum-methyl region in the ¹H NMR spectrum of an 1:1 mixture of [PtMe₃(py)₂] and bipy in nitrobenzene-d₅ at 300 K at different time interval, showing presence of three platinum(IV) complexes **I**, **II** and **III** in solution.

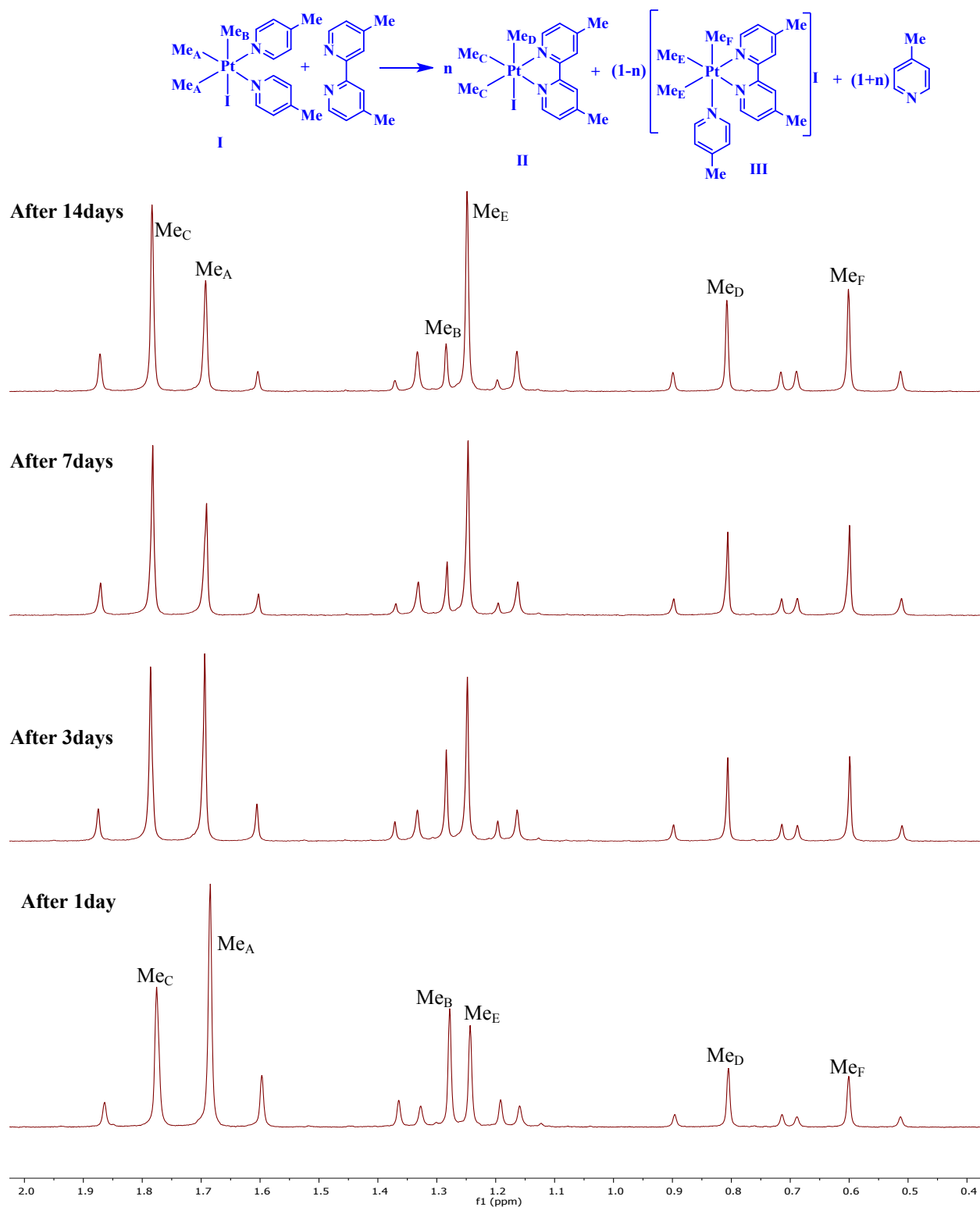


Fig. S11 The platinum-methyl region in the ^1H NMR spectrum of an 1:1 mixture of $[\text{PtMe}_3(4\text{-Mepy})_2\text{I}]$ and 4-Mepy in nitrobenzene- d_5 at 300 K at different time interval, showing presence of three platinum(IV) complexes **I**, **II** and **III** in solution.

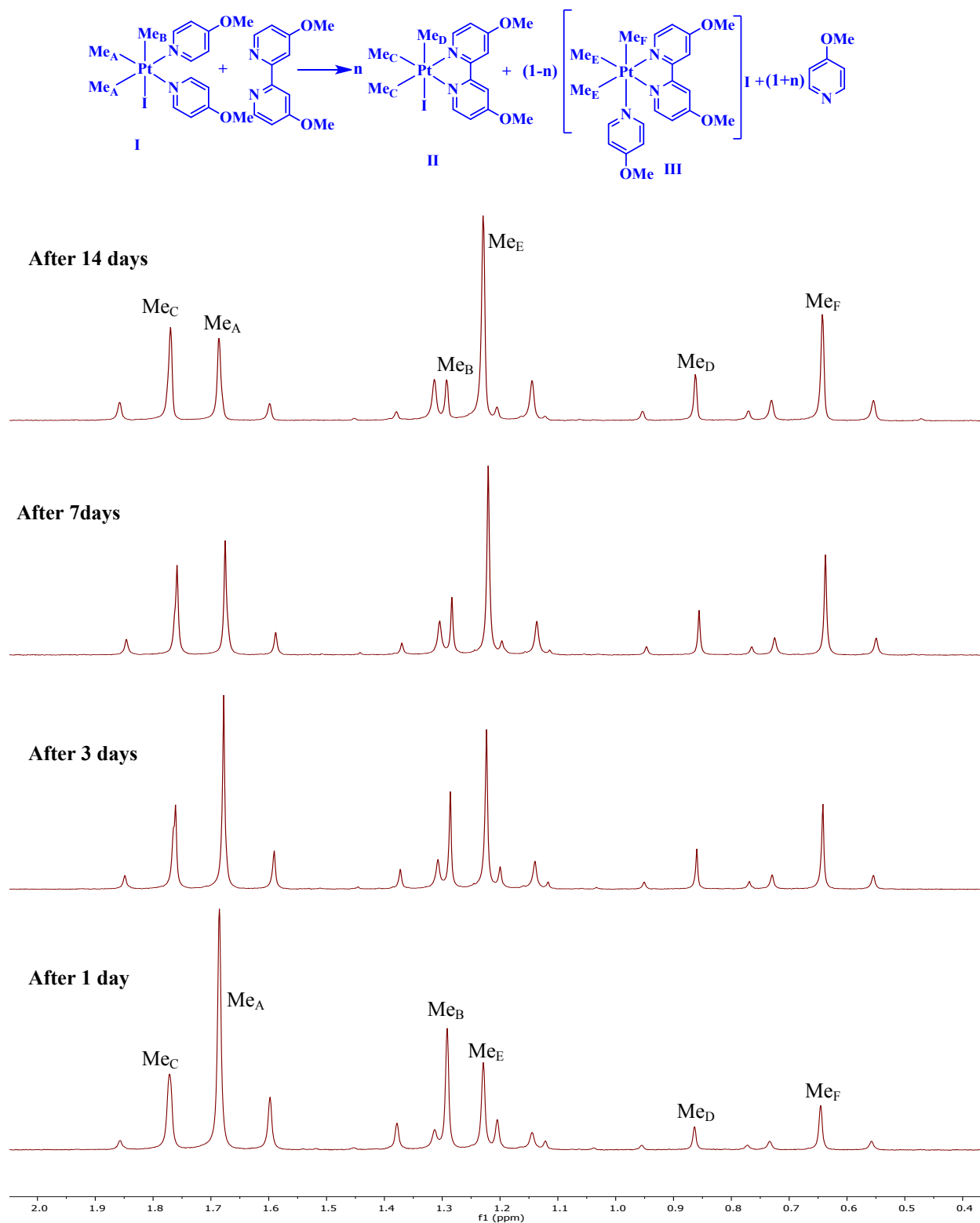


Fig. S12 The platinum-methyl region in the ¹H NMR spectrum of an 1:1 mixture of [PtMe₃(4-MeOpy)₂]I and 4-MeObipy in nitrobenzene-d₅ at 300 K at different time interval, showing presence of three platinum(IV) complexes **I**, **II** and **III** in solution.

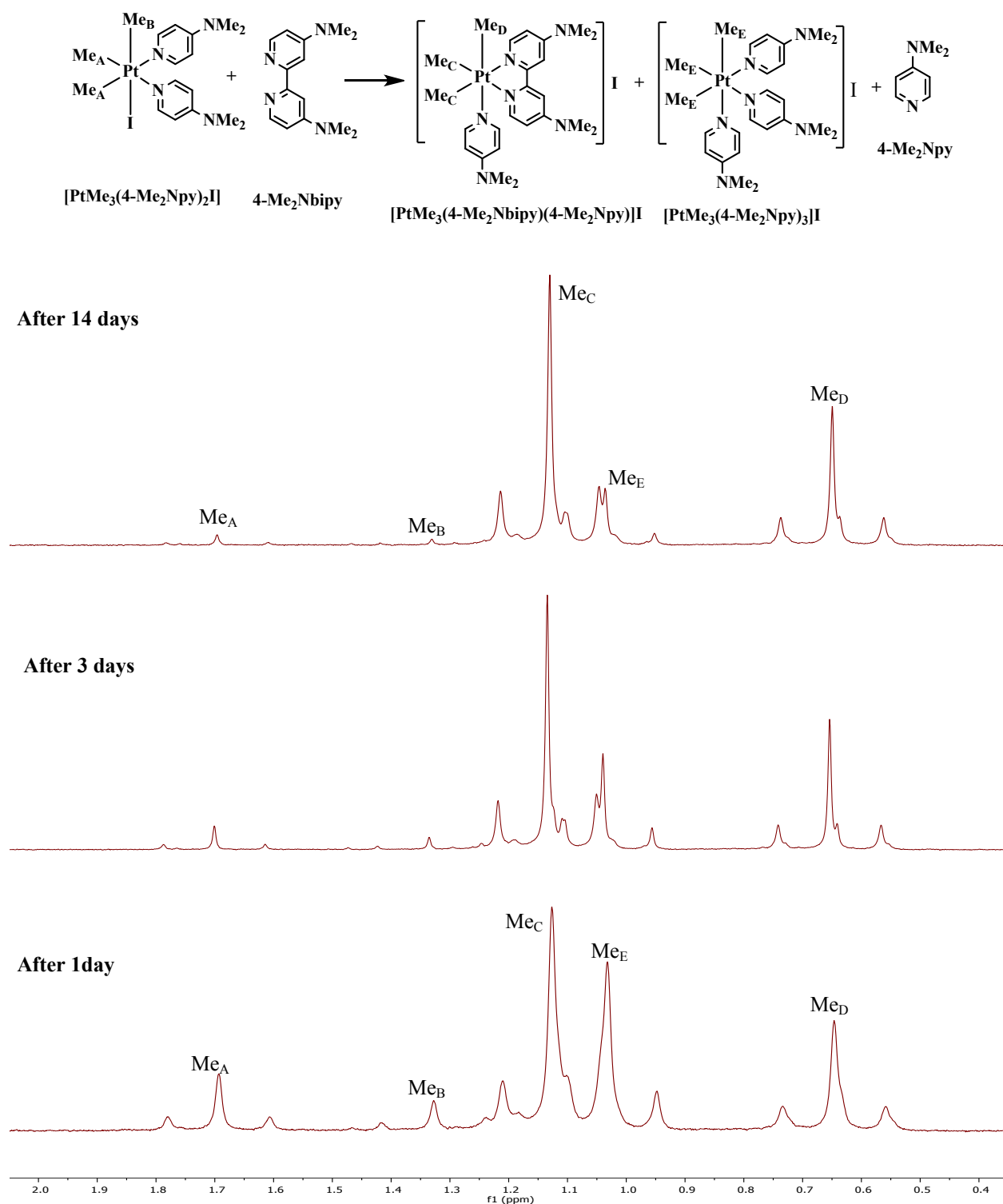


Fig. S13 The platinum-methyl region in the ^1H NMR spectrum of an 1:1 mixture of $[\text{PtMe}_3(4\text{-Me}_2\text{Npy})_2]\text{I}$ and 4-Me₂Nbipy in nitrobenzene-d₅ at 300 K at different time interval, showing presence of three platinum(IV) complexes **I** and **III** in solution.

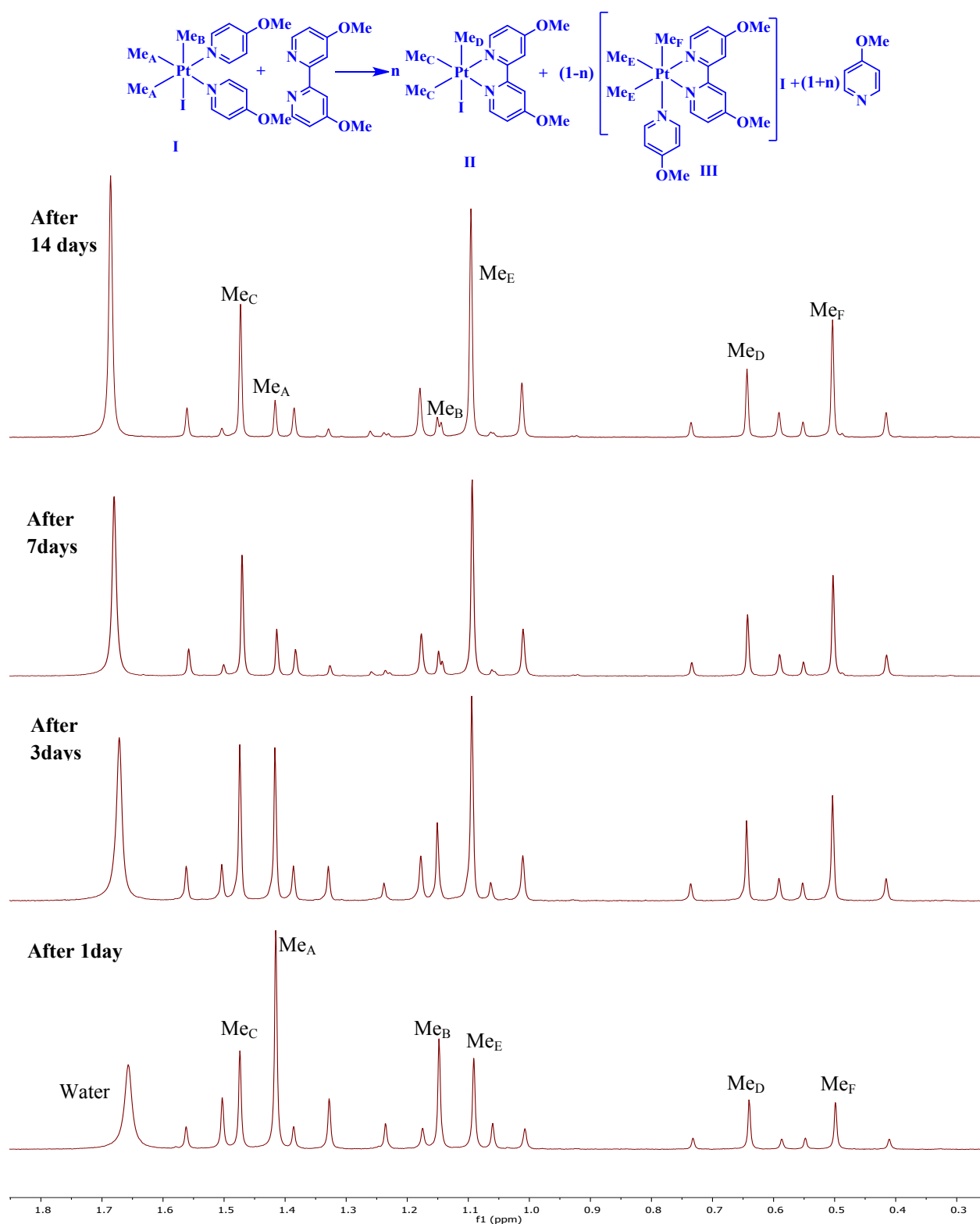


Fig. S14 The platinum-methyl region in the ^1H NMR spectrum of an 1:1 mixture of $[\text{PtMe}_3(4\text{-MeOpy})_2]\text{I}$ and 4-MeObpy in CDCl_3 at 300 K at different time interval, showing presence of three platinum(IV) complexes **I**, **II** and **III** in solution.

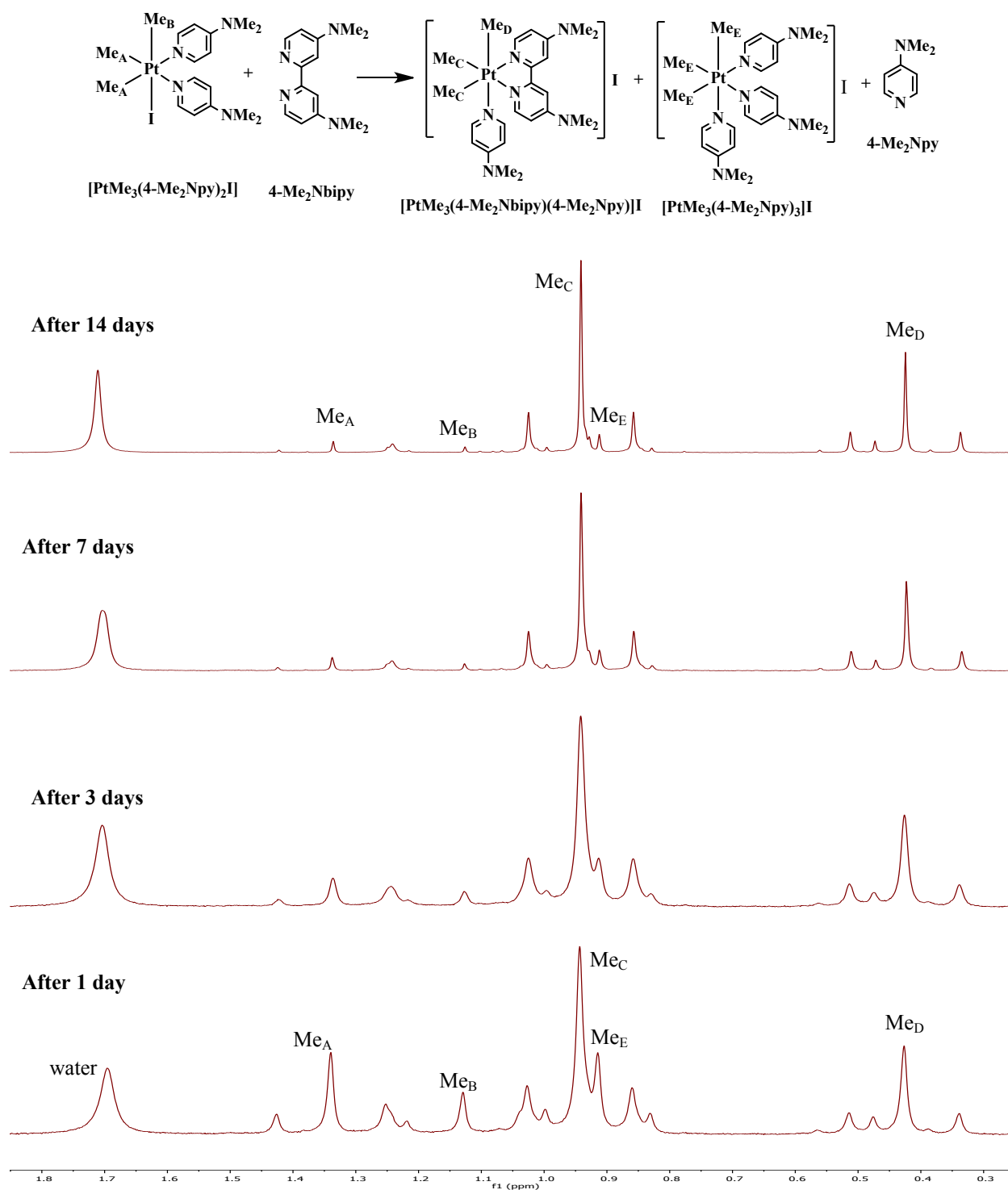


Fig. S15 The platinum-methyl region in the ¹H NMR spectrum of an 1:1 mixture of $[\text{PtMe}_3(4\text{-Me}_2\text{Npy})_2]\text{I}$ and 4-Me₂Nbipy in CDCl₃ at 300 K at different time interval, showing presence of three platinum(IV) complexes **I** and **III** in solution.