Journal of Organometallic Chemistry, 303 (1986) 139–149
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

DISPLACEMENT OF NORBORNADIENE (NBD) FROM $PtMe_2$(NBD) BY N-DONORS, DIMETHYLSULFOXIDE, AND CYANIDE, AND REACTIONS OF *cis*-$PtMe_2L_2$ WITH IODOMETHANE

TREVOR G. APPLETON, JOHN R. HALL*, and MARK A. WILLIAMS
Department of Chemistry, University of Queensland, Brisbane 4067 (Australia)

(Received September 23rd, 1985)

Summary

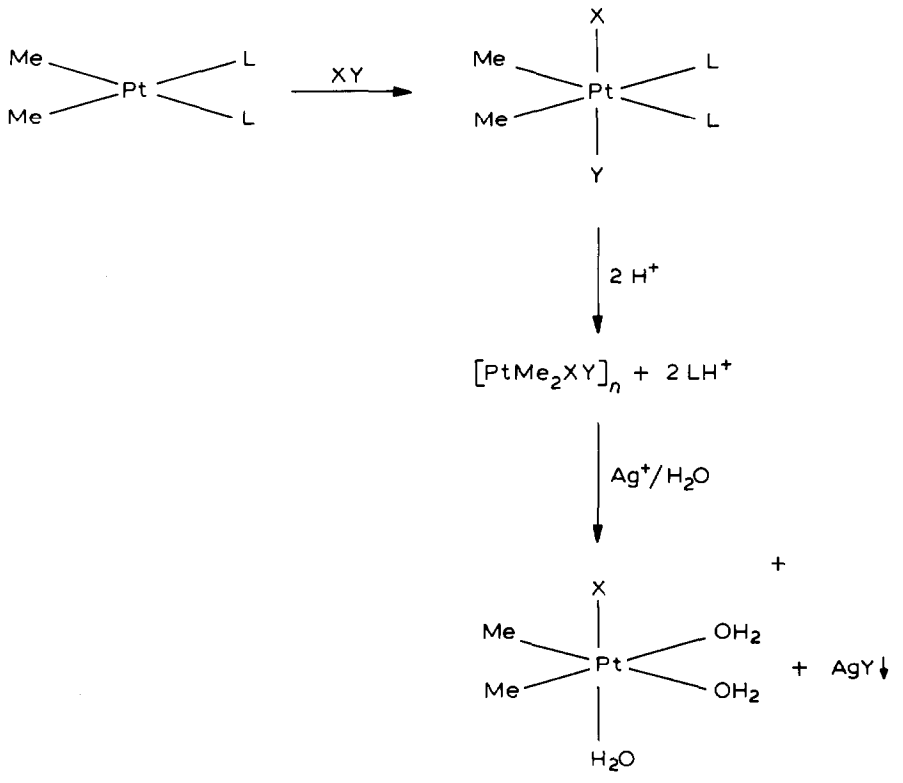
Norbornadiene (NBD) was displaced from $PtMe_2$(NBD) by a range of ligands L to form *cis*-$PtMe_2L_2$ (L = pyridine (py), NH_3, dimethylsulfoxide (DMSO); L_2 = 2,2′-bipyridyl (bipy), ethylenediamine (en), *N,N,N′,N′*-tetramethylethylenediamine (tmen) – but not L = acetonitrile, benzonitrile, *N,N*-dimethylformamide, or water). These reactions occur more readily than the corresponding displacements of 1,5-cyclooctadiene (COD) from $PtMe_2$(COD). Cyanide readily displaced the diolefin from either $PtMe_2$(NBD) or $PtMe_2$(COD) to form *cis*-$PtMe_2(CN)_2^{2-}$, but no reaction occurred with bromide, chloride, and acetylacetonate. Thiocyanate and iodide slowly reacted, but no methyl-platinum product was obtained.

The reaction of each of the compounds $PtMe_2L_2$ with MeI was studied in benzene. $PtMe_2$(NBD) gave $[PtMe_3I]_4$. With L = py, $\frac{1}{2}$(bipy), or $\frac{1}{2}$(tmen), $PtMe_3IL_2$ was obtained rapidly at room temperature. For the sparingly soluble compounds with L = NH_3 or $\frac{1}{2}$(en), heating was necessary for reaction. The product from $PtMe_2$(en) was $PtMe_3I$(en), but *cis*-$PtMe_2(NH_3)_2$ gave a mixture of $[PtMe_3(NH_3)(\mu\text{-}I)]_2$ and *fac*-$[PtMe_3(NH_3)_3]I$. With L = DMSO, heating initially gave $PtMe_3I(DMSO)_2$, which slowly lost DMSO to form $[PtMe_3I]_4$. For L = py, $\frac{1}{2}$(tmen), treatment with acid readily removed L from $PtMe_3IL_2$.

Introduction

Most organometallic compounds of platinum(II) contain tertiary phosphines or arsines, or isonitriles as "stabilizing ligands". Once bound to the metal these ligands are not easily removed. We wished to make platinum(IV) compounds $[PtMe_2XY]_n$ and *fac*-$PtMe_2X(H_2O)_3^+$ for use as starting materials for preparation of a series of new dimethylplatinum(IV) compounds. One possible route would involve oxidative addition of XY to *cis*-$PtMe_2L_2$ to form $PtMe_2XYL_2$, with subsequent removal of L. Suitable ligands for this purpose might be N-donors, which could, in principle, be removed from $PtMe_2XYL_2$ by acid (Scheme 1).

0022-328X/86/$03.50



SCHEME 1

$PtMe_2$(bipy) is a well-known compound, conveniently prepared from $PtMe_2$(COD) and bipy [1]. It has been reported that *cis*-$PtMe_2py_2$ [2] and $PtMe_2$(tmen) [3] may be prepared in a similar way.

In this paper, we describe an improved preparative route to compounds *cis*-$PtMe_2L_2$ where L is a relatively weak ligand. The reactions of these compounds with iodomethane were then studied, as a convenient test system for oxidative addition by reagents XY, since many of the expected products, $PtMe_3IL_2$ are known from reaction of $[PtMe_3I]_4$ with L.

A preliminary account of some of this work has appeared [4].

Experimental

Instrumentation and general methods

Positive values of NMR shifts denote lower shielding. 100 MHz ^1H NMR spectra were recorded with a JEOL PS-100 spectrometer; in organic solvents, tetramethylsilane (TMS) was used as internal reference, and in D_2O, sodium 3-trimethylsilylpropanesulfonate (TSS). 25 MHz ^{13}C spectra were recorded on a JEOL FX-100 Fourier Transform instrument with a 10 mm tunable probe, 16K data points, double precision mode, and internal lock on solvent deuterium; in organic solvents, TMS was used as internal reference, and shifts for aqueous solutions are relative to external TMS, with dioxane (δ(C) 67.73 ppm) as internal standard.

C, H, and N microanalyses were carried out by J. Kent in this Department.

Starting materials

$PtCl_2(COD)$ and $PtCl_2(NBD)$ were prepared by Drew and Doyle's method [5]. $PtMe_2(COD)$ was prepared as described by Clark and Manzer [3], except that $PtCl_2(COD)$, rather than $PtI_2(COD)$, was treated with methyllithium. $PtMe_2(bipy)$ was prepared from $PtMe_2(COD)$ and bipy [1].

Preparation of $PtMe_2(NBD)$ (1)

Some NMR data have been reported for $PtMe_2(NBD)$, without details of its preparation [6]. The method used was mainly similar to that previously described for $PtMe_2(COD)$ [3].

11.6 ml of a 1.6 *M* methyllithium solution in ether (18.6 mmol) was added to an ice-cold solution of 3.0 g of $PtCl_2(NBD)$ (8.4 mmol) in 30 ml of distilled ether under nitrogen. The solution was stirred for 2 h, then treated at 0°C with an ice-cold solution of ammonium chloride. The ether layer was separated, and the aqueous layer extracted with three 20 ml portions of ether. The combined ether fractions were dried over magnesium sulfate, and a small amount of activated charcoal was added. After filtration, ether was removed under reduced pressure to give colourless crystals. Yield was 2.5 g (94%).

Preparation of cis-$PtMe_2py_2$ (2)

0.30 g of **1** (0.95 mmol) was dissolved in 10 ml of dry distilled benzene under nitrogen. The reaction vessel was protected from light and 0.45 ml of freshly distilled pyridine (5.6 mmol) was added in three equal aliquots during 1 h. This produced a solution, containing **2** and free NBD, which could be used directly for some reactions. If solid was required, it was obtained by removal of the solvent under reduced pressure. The yield of the pale yellow solid, under optimum conditions, was 0.35 g (97%), but yields were much lower if the reactants contained trace impurities.

The product was readily soluble in all common organic solvents except ether, and sparingly soluble in water. Solutions were light sensitive, and, even in the dark under nitrogen, chloroform and benzene solutions decomposed over 24 h. The solid was stable for several weeks at room temperature, and for months if stored at 0°C in the dark under nitrogen.

Preparation of $PtMe_2$(tmen)

0.30 g of **1** (0.95 mmol) was dissolved in 10 ml of distilled benzene. 0.15 ml of distilled *N,N,N',N'*-tetramethylethylenediamine (1.0 mmol) was added, and the solution was heated at 50°C for one hour. The volume of the solution was then reduced to 1 ml under reduced pressure, and ether was added to precipitate a white solid, which was filtered off, washed with ether, and air-dried. The yield was 0.31 g (96%). The product was similar to that described by Clark and Manzer [3], and was soluble in all common organic solvents except ether. The solid was quite stable.

Preparation of $PtMe_2$(en)

0.10 g of **1** (0.32 mmol) was dissolved in 10 ml of distilled benzene, and 0.22 ml of distilled ethylenediamine (0.32 mmol) was added through a microsyringe. A white precipitate formed immediately. Benzene was decanted off, and the solid was transferred to a sintered glass filter using two 5 ml portions of benzene, dried briefly in air, then under vacuum. The solid tended to retain small amounts of solvated

benzene. The yield of $PtMe_2(en) \cdot 0.1C_6H_6$ was 0.080 g (88%). The solid decomposed after several days at room temperature, but was stable for several weeks at 0°C in the dark under nitrogen. The solid was sparingly soluble in acetone, but insoluble in other common organic solvents and in water.

Preparation of cis-$PtMe_2(NH_3)_2$

0.10 g of **1** (0.32 mmol) was dissolved in 10 ml of distilled benzene in a Carius tube. The solution was degassed by standard freeze-thaw techniques. The solution was cooled with liquid nitrogen, and a 20-fold excess of dry ammonia was condensed into the tube. The tube was sealed, allowed to warm to room temperature, and allowed to stand for 2 h. During this time a white precipitate formed. The tube was opened, benzene was decanted off, and the solid transferred to a sintered glass filter using two 5 ml portions of benzene. It was dried briefly in air, then under vacuum. It was insoluble in all common non-coordinating organic solvents. Again, the solid tended to retain a small amount of solvated benzene. The yield of $PtMe_2(NH_3)_2 \cdot 0.06C_6H_6$ was 0.080 g (96%).

Preparation of cis-$PtMe_2(DMSO)_2$

0.20 g of **1** was dissolved in 10 ml of distilled benzene, and 0.4 ml of dimethylsulfoxide was added. After 2 h, the solvent was removed under reduced pressure until a colourless solid began to crystallize. The solution was then stored overnight in a vacuum desiccator under reduced pressure, to give colourless crystals in 3 ml of solvent. The crystals were collected on a sintered glass filter, washed with ether, and dried under vacuum. Yield was 0.188 g (78%). The product was soluble in common organic solvents, but only sparingly in ether. It was also quite soluble in water.

Preparation of cis-$K_2[PtMe_2(CN)_2]$

To a suspension of 0.10 g of **1** (0.32 mmol) in 2 ml of water was added 0.039 g of solid potassium cyanide (0.64 mmol). The mixture was warmed at 50°C until the solid dissolved. The solution was filtered, and water was removed under reduced pressure to yield a hygroscopic colourless solid, which was dried in a vacuum desiccator over silica gel. The yield of *cis*-$K_2[PtMe_2(CN)_2] \cdot 2H_2O$ was 0.09 g (77%).

*Reaction of **2** with MeI*

0.30 g of **2** (0.78 mmol) was dissolved in 10 ml of benzene and 0.049 ml of iodomethane (0.79 mmol) was added by microsyringe. The solution was concentrated to 1 ml under reduced pressure, and ether was added to precipitate an off-white solid, which was filtered off, washed with ether, and air-dried. The yield was 0.39 g (95%). The properties of the solid were similar to those of $PtMe_3Ipy_2$ prepared from $[PtMe_3I]_4$ and pyridine [7–10].

Reaction of $PtMe_2$(tmen) with MeI

A similar procedure to that described above yielded $PtMe_3I$(tmen) in 89% yield.

Reaction of $PtMe_2$(en) with MeI

0.20 g of $PtMe_2$(en) (0.70 mmol) was suspended in 5 ml of benzene and 5 ml of MeI was added. The mixture was refluxed for an hour. The solvent was decanted from the solid, which was transferred to a sintered glass filter using benzene, washed

with ether, and air-dried. This solid was insoluble in water and common organic solvents, and its properties corresponded to those reported for $PtMe_3I(en)$ prepared from $[PtMe_3I]_4$ and ethylenediamine [7]. The solid tended to incorporate solvated benzene.

Reaction of cis-$PtMe_2(NH_3)_2$ with MeI

0.20 g of $PtMe_2(NH_3)_2$ was suspended in 5 ml benzene, 5 ml of MeI was added, and the mixture refluxed for 2 h. The solid was filtered off, and the filtrate evaporated to dryness under reduced pressure to yield 0.13 g (44%) of $[PtMe_3(NH_3)(\mu\text{-}I)]_2$ (**4**), which retained a small amount of solvated benzene. The properties of this material corresponded to those reported by Hall and Swile [9]. The solid that had been filtered off was washed with acetone, then dissolved in 5 ml of water. The solution was filtered, then water was removed under reduced pressure to give a white solid, *fac*-$[PtMe_3(NH_3)_3]I$. After drying in a vacuum desiccator over phosphorus(V) oxide the yield was 0.13 g (40%). Again, the properties were as previously described [9].

*Reaction of **1** with MeI*

0.30 g of **1** (0.95 mmol) was dissolved in 5 ml of benzene, and 0.059 ml of MeI (0.95 mmol) was added by microsyringe. The solution was evaporated to dryness under reduced pressure to yield $[PtMe_3I]_4$ as a white solid, which was washed with ether and air dried. The yield was 0.34 g (97%).

Reactions of $PtMe_3IL_2$ with acid

0.30 g of $PtMe_3IL_2$ (L = py, $\frac{1}{2}$(tmen), $\frac{1}{2}$(en)) was suspended in 10 ml of water, and 0.5 ml of 70% perchloric acid was added. The mixture was refluxed (2 h for L = py, 3 h for L = $\frac{1}{2}$(tmen), 4 h for L = $\frac{1}{2}$(en)). The mixture was cooled, and the solid $[PtMe_3I]_4$ was filtered off, washed with acetone, and air-dried. For L = py, $\frac{1}{2}$(tmen), the product thus obtained was pure, and yield was near 90%. For L = $\frac{1}{2}$(en), the product was less pure; extraction of the solid with benzene, followed by filtration and removal of solvent yielded $[PtMe_3I]_4$ in 69% yield.

Results and discussion

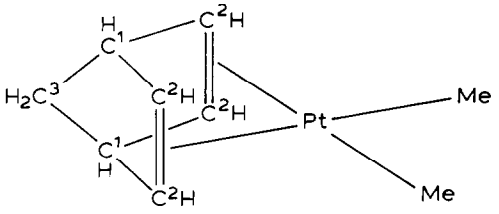
Analytical data are given in Table 1, and NMR data in Table 2.

*Preparation of cis-dimethylplatinum(II) complexes from $PtMe_2(NBD)$ (**1**)*

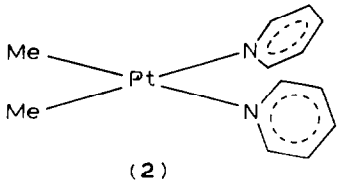
Kistner et al. [2] claimed that $PtMe_2py_2$ (**2**) can be obtained in 5% yield by heating a pyridine solution of $PtMe_2(COD)$. In our hands, this method did not yield any product which could be identified as **2**, and since Kistner et al. did not present any evidence that their product was **2**, it is not likely that they did make it. Reactions of $PtMe_2(COD)$ with stoicheometric and excess amounts of pyridine were studied, using as solvents chloroform, dichloromethane, acetone, methanol, and benzene (or their deuterated analogues). No reaction occurred in any of these solvents below 80°C. At this temperature, peaks which can now be assigned to **2** were observed in some NMR spectra, but did not persist. It became evident that, under the conditions necessary for pyridine to displace COD from $PtMe_2(COD)$, **2** rapidly decomposed. We therefore sought a starting compound, $PtMe_2$(diolefin), from which the diolefin could be more easily displaced than COD.

If COD is regarded as a chelating bidentate ligand, its "coordination bite" in a platinum(II) complex is near 86°C [11,12]. Crystal structure data are not available for analogous platinum(II) complexes with norbornadiene (NBD), but in rhodium(I) complexes the bite is near 66° [13,14]. In a formally square-planar complex, overlap between the bonding orbitals of the metal and the diolefin will be much further removed from the optimum for NBD than for COD, which might cause NBD to be more readily displaced by other ligands.

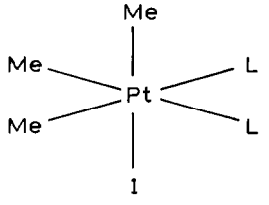
^{1}H NMR spectra were used to monitor reactions of pyridine with $PtMe_2$(NBD) (**1**) in various solvents. NBD was displaced at ambient temperature in $CDCl_3$ and CD_2Cl_2, but only in C_6D_6 was there clean production of a new species, and from ^{1}H and ^{13}C NMR spectra (Table 2) this was characterized as *cis*-$PtMe_2py_2$ (**2**). Peaks due to free NBD were also observed. The Pt–CH_3 coupling constant in **2**, 85.7 Hz, may be compared with that in $PtMe_2$(bipy), 85 Hz [15]. Because of the high *trans* influence of the methyl ligand [16], ^2J(Pt–CH_3) would be expected to be very much smaller if the complex were *trans*.



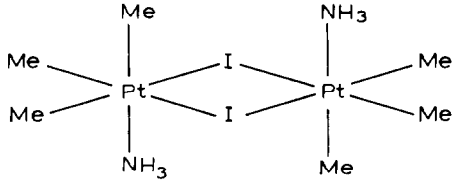
(1)



(2)



(3)



(4)

Removal of the benzene solvent from this solution under reduced pressure gave **2** as a pale yellow solid. This contrasts with the bright red colour of $PtMe_2$(bipy), which is ascribed to a transition from a platinum *d*-orbital to the lowest π^* orbital

TABLE 1

ANALYTICAL DATA

Compound	Analysis (Found (calcd.)(%))		
	C	H	N
$PtMe_2(NBD)$ (**1**)	34.1(34.1)	4.5(4.5)	–
$PtMe_2py_2$ (**2**)	37.7(37.6)	3.9(4.2)	7.4(7.3)
$PtMe_2$(tmen)	28.1(28.2)	6.5(6.5)	8.0(8.2)
$PtMe_2(en)\cdot 0.1C_6H_6$	18.7(18.9)	5.6(5.0)	9.2(9.6)
cis-$(PtMe_2(NH_3)_2\cdot 0.06C_6H_6$	10.9(10.8)	4.3(4.7)	10.2(10.6)
cis-$PtMe_2(DMSO)_2$	19.0(18.9)	4.5(4.8)	–
cis-$K_2[PtMe_2(CN)_2]\cdot 2H_2O$	12.5(12.3)	2.6(2.6)	7.0(7.2)
$PtMe_3Ipy_2$	29.8(29.7)	3.8(3.6)	5.1(5.3)
$PtMe_3I$(tmen)	22.9(22.4)	5.2(5.2)	5.8(5.8)
$PtMe_3I(en)\cdot 0.25C_6H_6$	17.5(17.5)	4.7(4.2)	6.2(6.3)
$[PtMe_3(NH_3)(\mu\text{-}I)]_2\cdot 0.3C_6H_6$	12.1(11.8)	3.5(3.3)	3.6(3.5)
$[PtMe_3(NH_3)_3]I$	8.8(8.6)	4.2(4.3)	10.0(10.1)

of bipy [1]. The solid dissolved in $CDCl_3$ to give a solution stable for several hours. Like other methylplatinum(II) compounds, **2** is not very air-sensitive, but exposure of a solution to normal laboratory light more than very briefly caused a loss of the signals due to **2** in NMR spectra, with the appearance of a multitude of new peaks. The presence of a large excess of pyridine during the preparation of **2** also caused side reactions: yields were best when the pyridine was added in several smaller aliquots.

Following the successful preparation of **2** from **1**, we considered the possibility that other compounds *cis*-$PtMe_2L_2$, where L is a N-donor ligand, might be conveniently prepared from **1**. $PtMe_2$(tmen) has been previously prepared by dissolving $PtMe_2$(COD) in *N,N,N',N'*-tetramethylethylenediamine, then heating to 100°C [3]. In our hands, the yield and quality of this product depended critically on control of temperature and reaction time. **1** did not react with tmen at room temperature, but at 50°C in benzene, $PtMe_2$(tmen) was obtained in good yield. Despite a small discrepancy between our ^1H NMR data, and those previously reported [3], the spectra allow unequivocal assignment of the product as $PtMe_2$(tmen). The lack of resolved platinum coupling to the ring carbon atoms in the ^{13}C spectrum (Table 2) was not unexpected, as ^2J(Pt–N–C) and ^3J(Pt–N–C–C) would be expected to be of opposite sign [17].

Reaction of **1** with ethylenediamine in benzene immediately produced a precipitate of $PtMe_2$(en), which was sufficiently soluble in $(CD_3)_2CO$ to give a ^1H NMR spectrum consistent with this formulation (Table 1). The low value of $^3J(Pt\text{–}N\text{–}CH_2)$, 11.2 Hz, is consistent with the high *trans* influence of the methyl ligand (cf. values in the series $Pt(en)L_2$, 52.5 Hz for $L = H_2O$, 32.0 Hz for $L = PPh_3$) [18].

Reaction of **1** with ammonia in benzene caused precipitation of *cis*-$PtMe_2(NH_3)_2$. When the reaction was carried out in C_6D_6, the filtrate showed ^1H NMR peaks from free NBD. The product was not sufficiently soluble in any solvent to allow NMR spectra to be obtained.

In these two reactions involving primary amines, there was no indication of any attack by the amine on the coordinated olefin. Both $PtMe_2$(en) and $PtMe_2(NH_3)_2$ were much less stable as solids than the other $PtMe_2L_2$ compounds. It is possible

TABLE 2

^1H AND ^{13}C NMR DATA

Compound	Solvent	δ(H) (J(Pt–H))			δ(C) (J(Pt–C))		
		Pt–Me		Other resonances	Pt–Me		Other resonances
		trans to L	*trans* to I		*trans* to L	*trans* to I	
$PtMe_2(NBD)$ (1) [a]	$CDCl_3$	0.67(89.8)		H^1 3.96; H^2 5.00(39.6); H^3 1.54	4.56(814.5)		C^1 48.54(39.1); C^2 87.80(46.9); C^3 72.29(43.9)
cis-$PtMe_2py_2$ (2)	$CDCl_3$				−8.18(688.5)		C^α 124.38(10.7); C^β 149.21; C^γ 136.66
	C_6D_6	1.57(86.1)		H^α 8.68(20.6)			
$PtMe_2$(tmen) [b]	$CDCl_3$	0.44(82.7)		N–Me 2.68(21.5) CH_2 2.49(11.3)	−23.67(826.2)		N–Me 48.93(7.8); $CH_2$61.95
$PtMe_2$(en)	$(CD_3)_2CO$	0.65(81.2)		CH_2 2.56(11.2)	[c]		[c]
cis-$PtMe_2(DMSO)_2$ [d]	D_2O	0.46(79.1)		S–Me 3.01(13.7)	−3.70(707.0)		S–Me 43.32(25.6)
cis-$K_2[PtMe_2(CN)_2]$	D_2O	0.13(69.8)			−9.00(562.5)		CN 153.70(774.4)
$PtMe_3Ipy_2$ [e]	$CDCl_3$	1.43(69.8)	1.14(70.3)		−8.00(674.8)	13.45(726.6)	C^α 125.38(10.7); C^β 149.75; C^γ 137.67
$PtMe_3I$(tmen)	$CDCl_3$	1.34(71.6)	0.92(70.5)	N–Me 3.36(10.8) 2.35(15.4) CH_2 complex	−7.14(673.8)	14.38(773.4)	N–Me 47.00, 55.87 CH_2 61.33
$[PtMe_3(NH_3)(\mu\text{-}I)]_2$ (4)	$CDCl_3$	1.68(72.3)	1.08(75.7)		−10.18(698.3)	9.16(724.3)	
fac-$[PtMe_3(NH_3)_3]I$	D_2O	0.31(70.3)			−9.89(688.6)		
$PtMe_3I(DMSO)_2$	$CDCl_3$	1.46(75.7)	1.09(73.1)	S–Me 2.97(13.2)			

[a] ^{13}C data previously reported [6]. For atom numbering see text figure. [b] ^1H data previously reported [3]. [c] Solubility too low for ^{13}C spectrum to be obtained. [d] ^1H data in $CDCl_3$ previously reported [20]. [e] ^1H data previously reported [9,10].

that the hydrogen atoms attached to nitrogen react with the methyl ligands to cause methane elimination, which initiates decomposition.

Reaction of **1** with DMSO in benzene gave *cis*-$PtMe_2(DMSO)_2$, previously obtained by Eaborn et al. [19,20] from the reaction of $PtCl_2(COD)$ with $SnMe_4$ in DMSO. This compound, as well as dissolving in most organic solvents, is quite soluble in water to give a solution stable for several hours. Our IR and NMR data agreed with those previously reported [20], which were interpreted as indicating coordination of the DMSO through sulfur in a *cis* complex. S-coordination was likewise postulated for the diaryl analogues [20], and this has been confirmed for *cis*-$PtPh_2(DMSO)_2$ by X-ray crystal structure determination [21].

1 did not react with acetonitrile, benzonitrile, or *N*,*N*-dimethylformamide, neat or in benzene, at 25°C or higher temperature. **1** was insoluble in water. No change occurred when an aqueous suspension was stirred at room temperature. When the suspension was heated under reflux for 30 min, the colour of the solid changed from pale yellow to white. This solid was now soluble in aqueous acids and alkalis. The ^1H NMR spectrum of a solution in dilute D_2SO_4/D_2O was identical to that of *cis*-$PtMe_2(D_2O)_4^{2+}$ [22]. The product from reaction of **1** with water was therefore formulated as $[PtMe_2(OH)_2(H_2O)_m]_n$ [23], a platinum(IV) product rather than "$PtMe_2(H_2O)_2$".

Addition of two molar equivalents of KCN to an aqueous suspension of either $PtMe_2(COD)$ or $PtMe_2(NBD)$ gave, with gentle heating, a solution of *cis*-$K_2[PtMe_2(CN)_2]$. A salt of $PtMe_2(CN)_2^{2-}$ has been previously prepared with a potassium crown ether complex as the counter-cation. Our ^1H NMR spectrum in D_2O was similar to those reported in organic solvents [24].

No reaction was observed between **1** and bromide, chloride, or acetylacetonate anions, under a variety of conditions. Thiocyanate and iodide did slowly react with **1** in acetone, but with loss of the methyl groups.

Displacement of pyridine from cis-$PtMe_2py_2$ (2)

Addition of excess ethylenediamine to a benzene solution of **2** caused immediate precipitation of $PtMe_2(en)$. Reaction of ammonia gas with a solution of **2** in benzene caused precipitation of *cis*-$PtMe_2(NH_3)_2$. Heating a benzene solution of **2** with an excess of tmen for 2 h at 50°C gave a solution of $PtMe_2(tmen)$. When **2** or $PtMe_2(NH_3)_2$ was dissolved in DMSO and the solution gently heated, *cis*-$PtMe_2(DMSO)_2$ was formed.

Reactions of complexes cis-$PtMe_2L_2$ with MeI, and reactions of the platinum(IV) products with acid

$PtMe_2(COD)$ has been previously shown [3] to react with MeI to give $[PtMe_3I]_4$, presumably by elimination of COD from an unstable platinum(IV) intermediate, "$PtMe_3I(COD)$". As expected, the NBD analogue, **1**, also reacted with MeI to give $[PtMe_3I]_4$.

$PtMe_2(bipy)$ reacts readily with MeI to form $PtMe_3I(bipy)$ (**3**, L_2 = bipy) [15,25]. Refluxing an aqueous suspension of this compound with dilute $HClO_4$ did not remove the bipyridyl ligand.

Cis-$PtMe_2L_2$, where L = py or $\frac{1}{2}$(tmen) reacted readily MeI to give $PtMe_3IL_2$ (**3**). No reaction occurred at room temperature when excess MeI was added to a benzene suspension of $PtMe_2(en)$, but, under reflux, $PtMe_3I(en)$ formed, insoluble in water

and common organic solvents. Each of these compounds has been previously prepared from $[PtMe_3I]_4$ and the ligand (L = py [7–10], ½(tmen) [26], ½(en) [7]). As previously reported [9], $PtMe_3Ipy_2$ gave a precipitate of $[PtMe_3I]_4$ when refluxed with dilute aqueous $HClO_4$. A similar reaction removed tmen from $PtMe_3I$(tmen). Reaction of $PtMe_2$(en) did not proceed as cleanly, but some $[PtMe_3I]_4$ was formed.

Cis-$PtMe_2(NH_3)_2$ reacted with MeI only when heated. Two products were obtained: *fac*-$[PtMe_3(NH_3)_3]I$ and $[PtMe_3(NH_3)(\mu\text{-}I)]_2$ (**4**). Hall and Swile [9] have reported that all attempts to prepare $PtMe_3I(NH_3)_2$ from $[PtMe_3I]_4$ and ammonia gave the same mixture of compounds.

Cis-$PtMe_2(DMSO)_2$ also reacted with MeI in benzene only upon heating. The ^1H NMR spectrum of the initial product showed two platinum-methyl signals (with satellites) with intensity ratio 2/1, and a singlet with satellites from coordinated DMSO (Table 2). From peak integration it was clear that two DMSO ligands were coordinated per platinum atom, and the compound was formulated as $PtMe_3I$-$(DMSO)_2$ (**3**, L = DMSO). With continued heating, or prolonged standing, peaks due to $[PtMe_3I]_4$ and free DMSO increased in intensity at the expense of those due to the DMSO complex.

Conclusions

For the preparation of new complexes, $[PtMe_2XY]_n$, direct oxidation of $PtMe_2$(NBD) (**1**) may sometimes suffice, as demonstrated by the reaction of **1** with MeI to give $[PtMe_3I]_4$. Reactions of this type have been previously reported with $PtMe_2$(COD) [3], but with some reagents a platinum(IV) product is not obtained. For example, $PtMe_2$(COD) with CF_3I gives $Pt(CF_3)_2$(COD) [3], and **1** reacts similarly [4,27]. Where this direct route is not available, the most suitable starting material for preparation of $[PtMe_2XY]_n$ and *fac*-$PtMe_2X(H_2O)_3^+$ according to Scheme 1 is *cis*-$PtMe_2py_2$ (**2**) since it would be expected from the "model" reaction with MeI that:

(i) **2** would react readily with oxidative addition reagents, XY, under mild conditions; (ii) **2** would be expected to yield a well-defined platinum(IV) product, $PtMe_2XYL_2$ and (iii) it should be possible to remove pyridine from the latter product with acid.

The compounds *cis*-$PtMe_2L_2$ with $L = NH_3$, ½(en), ½(bipy) DMSO, are all inferior to **2** in at least one of these respects. From the reaction with MeI $PtMe_2$(tmen) would appear to have some potential for these syntheses, but, in some circumstances, the steric hindrance from the *N*-methyl groups might be expected to reduce reactivity.

The preparations of new compounds $[PtMe_2XY]_n$ and *fac*-$PtMe_2X(H_2O)_3^+$ from **2** will be described in a subsequent publication [28].

Acknowledgements

We thank the Australian Research Grants Scheme for financial support. M. Williams acknowledges receipt of an Australian Commonwealth Postgraduate Scholarship. We thank Mr. K. Abel for assistance with the preparation of some of the compounds.

References

1 N. Chaudhury and R.J. Puddephatt, J. Organomet. Chem., 84 (1975) 105.
2 C.R. Kistner, J.H. Hutchinson, J.R. Doyle, and J.C. Storlie, Inorg. Chem., 2 (1963) 1255.
3 H.C. Clark and L.E. Manzer, J. Organomet. Chem., 59 (1973) 411.
4 T.G. Appleton, J.R. Hall, D.W. Neale, and M.A. Williams, J. Organomet. Chem., 276 (1984) C73.
5 D. Drew and J.R. Doyle, Inorg. Synth., 13 (1972) 47.
6 H.C. Clark, L.E. Manzer, and J.E.H. Ward, Can. J. Chem., 52 (1974) 1165.
7 W.J. Lile and R.C. Menzies, J. Chem. Soc., (1949) 1168.
8 A.D. Gel'man and E.A. Gorushkina, Dokl. Akad. Nauk SSSR, 57 (1947) 259.
9 J.R. Hall and G.A. Swile, J. Organomet. Chem., 42 (1972) 479.
10 J.M. Homan, J.M. Kawamoto, and G.L. Morgan, Inorg. Chem., 9 (1970) 2533.
11 G.K. Barker, M. Green, J.A.K. Howard, J.L. Spencer, and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1978) 1839.
12 M. Green, J.A.K. Howard, A. Laguna, L.E. Smart, J.L. Spencer, and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1977) 278.
13 K. Toriumi, T. Ito, H. Takaya, T. Souchi, and R. Noyori, Acta Cryst., B, 38 (1982) 807.
14 N.C. Payne and D.W. Stephan, Inorg. Chem., 21 (1982) 182.
15 J. Kuyper, R. van der Laan, F. Jeanneaus, and K. Vrieze, Trans. Met. Chem., 1 (1976) 199.
16 T.G. Appleton, H.C. Clark, and L.E. Manzer, Coord. Chem. Rev., 10 (1973) 335.
17 J.E. Sarneski, L.E. Erickson, and C.N. Reilley, J. Magn. Reson., 37 (1980) 155.
18 T.G. Appleton and J.R. Hall, Inorg. Chem., 10 (1971) 1717.
19 Z. Dawoodi, C. Eaborn, and A. Pidcock, J. Organomet. Chem., 170 (1979) 95.
20 C. Eaborn, K. Kundu, and A. Pidcock, J. Chem. Soc., Dalton Trans., (1981) 933.
21 R. Bardi, A. Del Pra, A.M. Piazzessi, and M. Trozzi, Cryst. Struct. Commun., 10 (1981) 301.
22 N.H. Agnew, T.G. Appleton, and J.R. Hall, Aust. J. Chem., 35 (1982) 881.
23 J.R. Hall and G.A. Swile, J. Organomet. Chem., 122 (1976) C19.
24 M.E. Fakley and A. Pidcock, J. Chem. Soc., Dalton Trans., (1977) 1444.
25 J.K. Jawad and R.J. Puddephatt, J. Chem. Soc., Dalton Trans., (1977) 1466.
26 J.R. Hall and G.A. Swile, unpublished results.
27 T.G. Appleton, J.R. Hall, and D.W. Neale, to be submitted.
28 T.G. Appleton, J.R. Hall, and M.A. Williams, to be submitted.