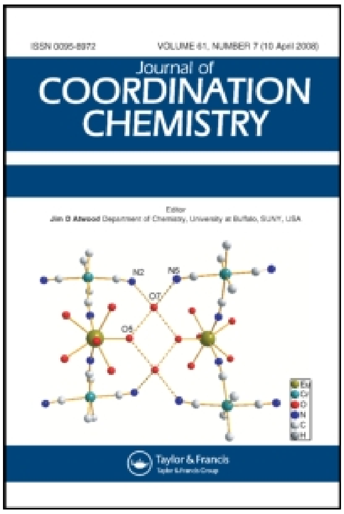

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Trimethylplatinum(IV) Complexes with *N,N'*-Dialkyl-1,2-Diiminoethane

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NOTE

TRIMETHYLPLATINUM(IV) COMPLEXES WITH *N,N'*-DIALKYL-1,2-DIIMINOETHANE

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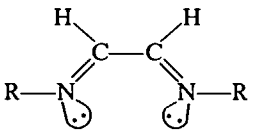
Trimethylplatinum(IV) complexes of the type [$PtMe_3X(R\text{-dim})$] (R-dim = *N,N'*-dialkyl-1,2-diiminoethane, R = Pr^i, Bu^i, Bu^t, *c*-Hx; X = Cl, Br, I) have been prepared and characterized by elemental analyses and ^1H and ^{13}C NMR spectral data. The R-dim ligand acts as a chelating bidentate.

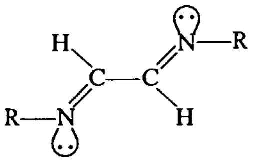
Keywords: Trimethylplatinum(IV), diimines, complexes, synthesis, NMR

INTRODUCTION

N,N'-Dialkyl-1,2-diiminoethane exists in *s-cis*(I) and *s-trans*(II) conformations with *E* (*anti*) configuration at both C=N double bonds.[1,2] Interconversion between the two forms is rapid in solution, and on complexation only one form is utilized. Thus the *s-cis* conformer forms a five-membered chelate ring,[3,4] while the *s-trans* form gives either σ,σ-*N,N'*-bridging with the N=C—C=N skeleton in the *anti* configuration,[5,6] σ-*N*-monodentate[4,7] or σ-*N*↔σ-*N'*-fluxional[4,8] modes of bonding. The flexibility of the N=C—C=N skeleton makes these ligands more versatile than bidentate nitrogen donors such as 2,2'-bipyridine, 1,10-phenanthroline, *etc.*



E-*s-cis*-E **(I)**



E-*s-trans*-E **(II)**

Recently, a number of triorganoplatinum(IV) compounds with chalcogen ligands have been synthesized and many interesting fluxional processes have been demonstrated.[9–11] The R-dim ligand with its flexible N=C—C=N skeleton might behave

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in a different fashion from usual bidentate nitrogen donors towards the trimethylplatinum(IV) moiety. In this paper we report the synthesis and characterization of trimethylplatinum(IV) complexes with R-dim.

EXPERIMENTAL

Trimethylplatinum halides[9,12] and R-dim[1] were prepared according to literature methods. Analytical grade solvents were used throughout the experiments. ^{1}H NMR spectra were recorded on a Varian FT-80A or a Bruker AC-200 spectrometer in $CDCl_3$ and chemical shifts are reported in ppm from internal chloroform peak (δ7.26 ppm). ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian FT-80A spectrometer operating at 20 MHz. Chemical shifts are relative to the $CDCl_3$ peak (δ77.0 ppm). Microanalyses were provided by the Analytical Chemistry Division of this research centre. Melting points were determined in capillary tubes and are uncorrected.

Synthesis of $[PtMe_3I(Bu^tN{=}CHCH{=}NBu^t)]$

To a dichloromethane solution of $[PtMe_3I]_4$ (107 mg; 0.073 mmol) a solution of $Bu^tN{=}CHCH{=}NBu^t$ (47 mg; 0.279 mmol) was added and the reactants were stirred at room temperature for 3 h. The solvent was evaporated *in vacuo* and the residue was recrystallized from dichloromethane-hexane as an orange crystalline solid (104 mg; 68%). Similarly, the other compounds were prepared. Pertinent data for these complexes are given in Table I.

RESULTS AND DISCUSSION

Treatment of trimethylplatinum halides with R-dim afforded complexes of the type $[PtMe_3X(\text{R-dim})]$ (R-dim = RN=CHCH=NR; R=Pr^i, Bu^i, Bu^t, *c*-Hx; X = Cl, Br, I) as pale yellow to orange coloured crystalline solids.

^{1}H and ^{13}C NMR data for these complexes are given in Tables II and III. The ^{1}H NMR spectra exhibited two Pt-Me resonances in a 1:2 ratio, each flanked with platinum satellites. The resonance at higher field with integration corresponding to one methyl group was attributed to the Pt-Me *trans* to X, while the one appearing at lower field was assigned to the methyl group *trans* to nitrogen. $^2J(^{195}Pt\text{-}^1H)$ lies in the range 68–74 Hz, the magnitude of $^2J(Pt\text{-}H)$ being greater for the methyl group *trans* to X. There is a small variation in $^2J(Pt\text{-}H)$ with changes in the R group in R-dim. The observed trends in chemical shifts and coupling constants, $^2J(^{195}Pt\text{-}^1H)$, are in good agreement with reported trimethylplatinum(IV) compounds with ligands such as bipyridine and 1,10-phenanthroline.[13–15]

The ^{1}H resonances of the diimine ligand undergo significant downfield shifts on coordination with trimethylplatinum(IV) halides. The imine protons showed $^3J(^{195}Pt\text{-}^1H)$ of the magnitude of 20–28 Hz. For four and five coordinate platinum(II)

TABLE I
Analytical data for the [$PtMe_3X$(R-dim)] complexes.

Complex*	m.p. (°C)	% Analyses found (calcd.)		
		C	H	N
[$PtMe_3Cl(Pr^iN{=}CHCH{=}NPr^i)$]	215–225**	31.4	5.5	7.1
		(31.8)	(6.1)	(6.7)
[$PtMe_3Br(Pr^iN{=}CHCH{=}NPr^i)$]	210	28.0	5.1	6.0
		(28.7)	(5.5)	(6.1)
[$PtMe_3I(Pr^iN{=}CHCH{=}NPr^i)$]	167	25.2	4.9	4.9
		(26.0)	(5.0)	(5.5)
[$PtMe_3Cl(Bu^iN{=}CHCH{=}NBu^i)$]	162	34.4	6.2	6.1
		(35.2)	(6.6)	(6.3)
[$PtMe_3Br(Bu^iN{=}CHCH{=}NBu^i)$]	180	31.1	5.9	5.7
		(32.0)	(6.0)	(5.7)
[$PtMe_3I(Bu^iN{=}CHCH{=}NBu^i)$]	157	28.3	5.2	5.2
		(29.2)	(5.5)	(5.2)
[$PtMe_3Cl(Bu^tN{=}CHCH{=}NBu^t)$]	225–235**	34.4	6.5	5.8
		(35.2)	(6.6)	(6.3)
[$PtMe_3Br(Bu^tN{=}CHCH{=}NBu^t)$]	220–230**	31.8	6.2	5.4
		(32.0)	(6.0)	(5.7)
[$PtMe_3I(Bu^tN{=}CHCH{=}NBu^t)$]	185–195**	28.6	5.5	4.9
		(29.2)	(5.5)	(5.2)
[$PtMe_3Cl$(*c*-HxN=CHCH=NHx-*c*)]	215–225**	40.9	6.2	5.5
		(41.2)	(6.7)	(5.6)
[$PtMe_3Br$(*c*-HxN=CHCH=NHx-*c*)]	240–250**	37.5	6.5	5.1
		(37.8)	(6.1)	(5.2)
[$PtMe_3I$(*c*-HxN=CHCH=NHx-*c*)]	229	34.8	6.3	4.8
		(34.8)	(5.7)	(4.8)

* All complexes were recrystallized from dichloromethane/hexane in 28–76% yield as yellow to orange crystalline solids. ** Decomposed.

complexes, [$PtCl_2$(R-dim)] and [$PtCl_2(>C{=}C<)$(R-dim)] these values are ~90 and ~40 Hz, respectively.[8] The methyl groups of R-dim ligands where $R = Pr^i$ or Bu^i, in the complexes are anisochronous as the two sets of methyl resonances were observed. For [$PtCl_2(Pr^iN{=}CHCH{=}NPr^i)$] only one doublet for the methyl groups has been reported.[8]

As with the ^1H NMR spectra, the ^{13}C NMR spectra exhibited two signals for platinum-methyl carbons, each flanked by ^{195}Pt sattelites. The methyl carbon resonance *trans* to X showed marked halogen dependence and dishielded with increasing size of the X atom, while carbons *trans* to N were little affected. Due to the low intensity of the Pt-Me signal, ^{195}Pt satellites could not be identified with confidence in some cases. Coupling constants for the methyl group *trans* to X are larger than those of *trans* to N. $^1J(^{195}Pt\text{-}^{13}C)$ decreases with increasing halogen size.

The ^{13}C resonances for ligand carbons showed a small down field shift. Ligand carbons appeared as singlets except for the C—N resonance which was flanked by ^{195}Pt

TABLE II
^{1}H NMR Spectral data for $[\mathrm{PtMe_3X(R\text{-}dim)}]$ in $CDCl_3$.

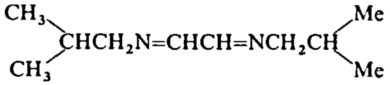
Complex	Pt-Me protons	Ligand protons
$\mathrm{Pr^iN{=}CHCH{=}NPr^i}$		7.88 (s, N=CH, 2-H); 3.47 (m, >CHN, 2H); 1.18 (d, 6.3 Hz, Me)
$[\mathrm{PtMe_3Cl(Pr^iN{=}CHCH{=}NPr^i)}]$	0.40 (s, Me, *trans* to Cl) J(Pt-H) = 74.7 Hz; 1.15 (s, 2Me, *trans* to N) J(Pt-H) = 68.8 Hz	8.62 (s, N=CH, 2H; J(Pt-H) = 27.3 Hz); 4.41 (m, >CHN, 2H); 1.40 (d, 6.7 Hz, CH_3, 6H) 1.34 (d, 6.3 Hz, CH_3, 6H)
$[\mathrm{PtMe_3Br(Pr^iN{=}CHCH{=}NPr^i)}]$	0.55 (s, Me, *trans* to Br) J(Pt-H) = 71 Hz; 1.30 (s, 2Me, J(Pt-H) = 68 Hz) *trans* to N	8.58 (s, N=CH, 2H, J(Pt-H) = 28 Hz); 4.52 (m, CHN, 2H); 1.40, 1.55 (d, 6.5 Hz, CH_3, 6H each)
$[\mathrm{PtMe_3I(Pr^iN{=}CHCH{=}NPr^i)}]$	0.63 (s, Me, J(Pt-H) = 72.3 Hz; *trans* to I); 1.40 (s, 2Me, J(Pt-H) = 70.5 Hz; *trans* to N)	8.60 (s, N=CH, 2H, J(Pt-H) = 27.7 Hz) 4.55 (m, >CHN, 2H); 1.51 (d, 6.6 Hz, 6H, Me); 1.38 (d, 6.6 Hz, 6H, Me)
$\mathrm{Bu^tN{=}CHCH{=}NBu^t}$		7.95 (s, N=CH, 2H); 1.25 (s, Me, 18H)
$[\mathrm{PtMe_3Cl(Bu^tN{=}CHCH{=}NBu^t)}]$	0.65 (s, Me, J(Pt-H) = 71 Hz; *trans* to Cl) 1.48 (s, 2Me, J(Pt-H) = 69.5 Hz; *trans* to N)	8.60 (s, N=CH, 2H, J(Pt-H) = 20 Hz; 1.55 (s, Me, 18H)
$[\mathrm{PtMe_3Br(Bu^tN{=}CHCH{=}NBu^t)}]$	0.75 (s, Me, J(Pt-H) = 72.5 Hz; *trans* to Br) 1.58 (s, 2Me, J(Pt-H) = 69.5 Hz; *trans* to N)	8.60 (s, N=CH, 2H, J(Pt-H) = 20 Hz) 1.55 (s, Me, 18H)
$[\mathrm{PtMe_3I(Bu^tN{=}CHCH{=}NBu^t)}]$	0.83 (s, Me, J(Pt-H) = 70.9 Hz; *trans* to I) 1.71 (s, 2Me, J(Pt-H) = 72 Hz; *trans* to N)	8.58 (s, N=CH, 2H, J(Pt-H) = 21 Hz); 1.55 (s, Me, 18H)
 $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!\mathrm{CHCH_2N{=}CHCH{=}NCH_2CH}\!<\!\begin{matrix}Me\\Me\end{matrix}$		7.72 (s, >N=CH, 2H), 3.22 (d, 6.5dl Hz, NCH_2, 4H); 2.20 (m, -CH-, 2H); 0.76 (d, 6.5 Hz, Me, 12H)
$[\mathrm{PtMe_3Cl(Bu^iN{=}CHCH{=}NBu^i)}]$	0.35 (s, Me, J(Pt-H) = 72 Hz; *trans* to Cl) 1.15 (s, 2Me, J(Pt-H) = 70.6 Hz; *trans* to N)	8.35 (s, N=CH, 2H, J(Pt-H) 26.5 Hz); 0.95 (d, 7 Hz, 2Me); 0.90 (d, 7Hz, 2Me); 3.70 (m, $>NCH_2$) 2.25 (m, -CH)
$[\mathrm{PtMe_3Br(Bu^iN{=}CHCH{=}NBu^i)}]$	0.34 (s, Me, J(Pt-H) = 74 Hz; *trans* to Br) 1.11 (s, Me, 6H) J(Pt-H) = 70 Hz; *trans* to N)	8.24 (s, N=CH, 2H, J(Pt-H) = 27 Hz) 3.60 (m, $>NCH_2$, 4H); 2.20 (m, -CH-, 2H) 0.85 (d, 6.6 Hz, 2Me); 0.80 (d, 6.6 Hz, 2Me)
$[\mathrm{PtMe_3I(Bu^iN{=}CHCH{=}NBu^i)}]$	0.52 (s, Me, J(Pt-H) = 72 Hz; *trans* to I) 1.30 (s, 2Me, J(Pt-H) = 70.8 Hz; *trans* to N)	8.30 (s, N=CH, 2H, J(Pt-H) = 27 Hz) 3.82 (m, CH_2, 4H) 2.29 (m, CH, 2H) 0.94 (d, 6.3 Hz; 2Me) 0.87 (d, 6.3 Hz; 2Me)

TABLE II

Continued.

Complex	Pt-Me protons	Ligand protons
-HxN=CHCH=NHx-*c*		7.72 (s, N=CH–, 2H); 2.90 (br, NCH, 2H); 1.05–1.60 (br, CH_2, 20H)
$PtMe_3Cl$(*c*-HxN=CHCH=NHx-*c*)]	0.25 (s, *Me*, *J*(*Pt-H*)= 74 *Hz*; *trans* to Cl) 1.05 (s, 2Me, *J*(Pt-H)= 72 Hz; *trans* to N)	8.35 (s, N=CH, 2H, J(Pt-H) =27.7 Hz 3.85 (br, NCH, 2H); 1.10–2.10 (br, m, CH_2, 20H)
$PtMe_3Br$(*c*-HxN=CHCH=NHx-*c*)]	0.38 (s, Me, J(Pt-H)= 74 Hz; *trans* to Br) 1.14 (s, 2Me, J(Pt-H)= 69.6 Hz; *trans* to N)	8.41 (s, N=CH, 2H, J(Pt-H) =27.7 Hz 3.90 (br, >NCH, 2H); 1.20–2.25 (br, m, CH_2, 20H)
$PtMe_3I$(*c*-HxN=CHCH=NHx-*c*)]	0.49 (s, Me, J(Pt-H)= 72 Hz; *trans* to I) 1.26 (s, 2Me, J(Pt-H)= 70 Hz; *trans* to N)	8.41 (s, N=CH, 2H, J(Pt-H)= 28 Hz) 4.00 (br, >NCH, 2H); 1.20–2.20 (br, m, CH_2, 20H)

=singlet, d=doublet, t=triplet, m=multiplet, br=broad.

TABLE III

$^{13}C\{^1H\}$ NMR data for $[PtMe_3X(R\text{-dim})]$ in $CDCl_3$.

Complex	Pt-Me carbons*	Ligand carbons
PtMe$_3$I(Pr^{i}N=CHCH=NPr^i)]	−6.4 (*trans* to N) 6.3 (*trans* to I)	N=CH 159.2 =NCH— 57.6 [J(Pt-C)=18 Hz] CH_3 23.5, 22.8
PtMe$_3$I(Bu^{i}N=CHCH=NBu^i)]	−7.1 (*trans* to N) (651) 6.2 (*trans* to I)	N=CH 161.8 N=CH 68.3 [J(Pt-C)=17 Hz] —CH_2 27.6 —CH_3 20.2
PtMe$_3$Cl(Bu^{t}N=CHCH=NBu^t)]	−2.2 (*trans* to N) (692) −5.7 (*trans* to Cl) (706)	N=CH 159.1 =NC 66.4 [J(Pt-C)=14 Hz] CH_3 29.3
PtMe$_3$Br(Bu^{t}N=CHCH=NBu^t)]	−2.5 (*trans* to N) (685) −0.9 (*trans* to Br) (691)	N=CH 159.1 =NC 66.8 [J(Pt-C)=14 Hz] —CH_3 29.6
PtMe$_3$I(Bu^{t}N=CHCH=NBu^t)]	−3.2 (*trans* to N) (678) 7.2 (*trans* to I) (681)	N=CH 159.5 =NC 67.3 [J(Pt-C)=14 Hz] —CH_3 30.1
PtMe$_3$I(*c*-HxN=CHCH=NHx-*c*)]	−6.5 (*trans* to N) (655) 6.1 (*trans* to I)	N=CH 159.5 =NCH 65.5 [J(Pt-C)=17 Hz] 2, 6 CH_2 34.1, 33.7 3–5 CH_2 25.4

Values in parenthesis are $^1J(^{195}Pt\text{-}^{13}C)$.

satellites, $^2J(^{195}Pt\text{-}^{13}C)$ ~15 Hz. The spectrum of $[PtMe_3I(Pr^iN{=}CHCH{=}NPr^i)]$ displayed two signals for methyl carbons of the Pr^i-dim ligand. However, the methyl groups of Bu^i-dim in $[PtMe_3I(Bu^iN{=}CHCH{=}NBu^i)]$ appeared as a singlet, although two doublets were observed for the methyl protons in the ^1H NMR spectrum; this is simply due to accidental chemical shift degeneracy.

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