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PREPARATION AND CHARACTERIZATION OF O,O′-DIALKYLDITHIOPHOSPHATE COMPLEXES OF METHYLPLATINUM(II)

VIMAL K. JAIN*

Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay-400085, India

and

SATYAJEET CHAUDHURY

Fuel Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay-400085, India

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Abstract—The reaction of [PtMe(X)(COD)] (X = Cl, I) with 1 mole equivalent of $\mathrm{NH_4SSP(OR')_2}$ gave $[\{\mathrm{Pt(Me)SSP(OR')_2}\}_2\mathrm{COD}]$ (R′ = Et or $\mathrm{Pr^i}$). The latter complexes on treatment with tertiary phosphines afforded $[\mathrm{Pt(Me)}\{\mathrm{SSP(OR')_2}\}(\mathrm{PR_3})]$ (R = $4\text{-}\mathrm{MeC_6H_4}$, $2\text{-}\mathrm{MeC_6H_4}$ or $(2,4,6\text{-}\mathrm{MeO})_3\mathrm{C_6H_2}$). All the complexes were characterized by elemental analysis, and NMR data.

During the last two decades or so classical coordination complexes of platinum(II) with dithio ligands, $\mathrm{R_2NCS_2}$, $\mathrm{ROCS_2}$, $\mathrm{RCS_2}$, $\mathrm{R_2PS_2}$, $\mathrm{(RO)_2PS_2}$, have been extensively studied.[1–6] However, the chemistry of organometallic platinum complexes with such ligands has not received much attention.[7–9] Recently, we have isolated methylplatinum complexes of the type $[\mathrm{PtMe}\{\mathrm{SSP(OR')_2L}]$ by the reaction of [PtMeX(COD)] with 1 mole equivalent of $\mathrm{NH_4SSP(OR')_2}$ in the presence of Group 15 donor ligands.[9] We carried out this reaction in the absence of a Group 15 donor ligand with the hope to isolate the intermediate cyclooctadiene complex which would be a useful precursor for a variety of organoplatinum dithiolate derivatives. The results of this work are reported in this paper.

RESULTS AND DISCUSSION

The reaction of [PtMe(X)COD] (X = Cl or I) with 1 mole equivalent of $\mathrm{NH_4SSP(OR')_2}$ in benzene readily afforded complexes having the composition $[\{\mathrm{Pt(Me)SSP(OR')_2}\}_2\mathrm{COD}]$. The latter complexes on treatment with tertiary phosphines gave mononuclear $[\mathrm{PtMe}\{\mathrm{SSP(OR')_2}\}(\mathrm{PR_3})]$ and 1,5-cyclooctadiene (Scheme 1).

$$2[\mathrm{PtMe(X)COD}] + 2\mathrm{NH_4SSP(OR')_2} \longrightarrow$$

$$[\{\mathrm{Pt(Me)SSP(OR')_2}\}_2\mathrm{COD}] + \mathrm{COD} + 2\mathrm{NH_4X}$$

I

R′ = Et **Ia**
$\mathrm{Pr^i}$ **Ib**

$\downarrow$ $2\mathrm{PR_3}$

$$2[\mathrm{PtMe}\{\mathrm{SSP(OR')_2}\}(\mathrm{PR_3})] + \mathrm{COD}$$

II

R′	R	
Et	$4\text{-}\mathrm{MeC_6H_4}$	**IIa**
$\mathrm{Pr^i}$	$4\text{-}\mathrm{MeC_6H_4}$	**IIb**
Et	$2\text{-}\mathrm{MeC_6H_4}$	**IIc**
$\mathrm{Pr^i}$	$2\text{-}\mathrm{MeC_6H_4}$	**IId**
Et	$(2,4,6\text{-}\mathrm{MeO})_3\mathrm{C_6H_2}$	**IIe**
$\mathrm{Pr^i}$	$(2,4,6\text{-}\mathrm{MeO})_3\mathrm{C_6H_2}$	**IIf**

Scheme 1

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* Author to whom correspondence should be addressed.

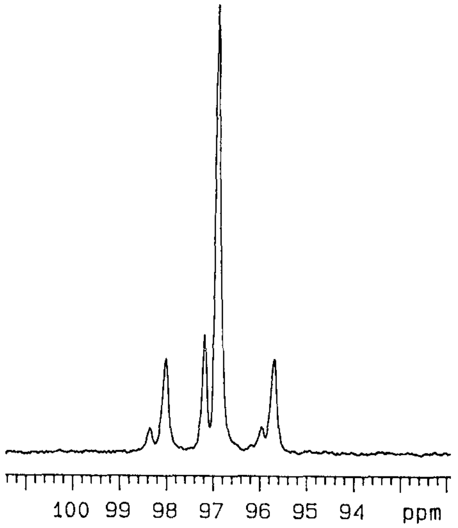
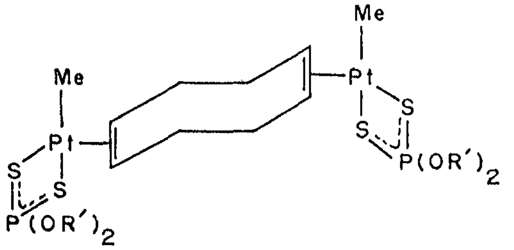
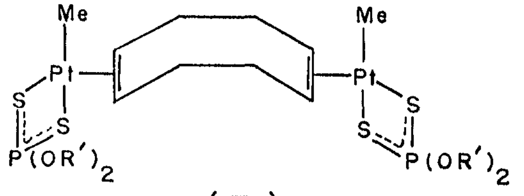


Fig. 1. $^{31}P\{^{1}H\}$ NMR spectrum of $[\{Pt(Me)SSP(OPr^{i})_2\}_2COD]$ in $CDCl_3$.

The ^{31}P NMR spectra of $[\{Pt(Me)SSP(OR)_2\}_2COD]$ (**I**) displayed two closely spaced singlets with platinum couplings (Fig. 1), the downfield signal being 10–15% in abundance with higher ^{2}J(Pt—P). The variable temperature ^{31}P NMR spectra of **Ib** were recorded in $CDCl_3$ in the temperature range 45 to −45°C. The chemical shifts showed temperature dependence and deshielded gradually on lowering the temperature [at 45°C $\delta = 96.4$ (major), 96.7 (minor) ppm and at −45°C $\delta = 98.1$ (major), 98.3 (minor) ppm]. Although the signal intensity of the less abundant isomer increased with increasing the temperature, complete transformation of one form into another was not noticed in the temperature range 45 to −45°C. Like the ^{31}P NMR spectra, the ^{195}Pt NMR spectra of **Ib** displayed two doublets [$^{195}Pt\{^{1}H\}$ in $CDCl_3$: $\delta = -3913.8$ (d, $^{2}J(^{195}Pt—^{31}P) = 259$ Hz, major); -3909.7 (d, $^{2}J(^{195}Pt—^{31}P) = 279$ Hz, minor]. Similarly, the ^{1}H NMR spectra showed two Pt—Me resonances for **Ib** at 500 MHz, however, only one signal was observed using lower field NMR spectrometers. The mass spectrum of **Ib** displayed a molecular ion peak at m/z 955. Based on analytical data and also integration in ^{1}H NMR spectra, **I** appears to contain a bridging cyclooctadiene ligand. A bridging cyclooctadiene group has been reported in analogous complexes $[\{PtX(SSCNEt_2)\}_2COD]$ (X = Cl,[10] Me[11]). However, no NMR data have been reported for these complexes due to their insolubility in common organic solvents.[10,11] The observed two sets of resonances in the ^{31}P NMR spectra of **I** can be assigned to structures **A** and **B** which differ in the conformation of cyclooctadiene.



(A)



(B)

The ^{1}H NMR spectra of **II** exhibited the expected multiplicities and integration. The Pt—Me resonance appeared as a triplet of doublets due to Pt—H and P—H couplings. The methyl groups of OPr^{i} moiety are anisochronous as two doublets were observed. The ^{31}P NMR spectra showed a triplet of the doublets each for the dithio and the neutral phosphine ligands. However, the doublet pattern [^{3}J(P—P)] could not be resolved in cases of **IIc** and **IId** due to broadening of the signals. The spectra of (^{1}H and ^{31}P) of **IIa** and **IIb** were identical to those reported recently by us.[9]

EXPERIMENTAL

The compounds [PtMe(X)COD] (X = Cl or I)[12] and $NH_4SSP(OR')_2$[13,14] were prepared by the published methods. The tertiary phospines were obtained from Strem Chemicals. NMR spectra were recorded on a Varian XL-300 or Bruker AX-500 spectrometer in 5 mm NMR tubes in $CDCl_3$. Chemical shifts are relative to internal chloroform peak ($\delta = 7.26$ ppm) for ^{1}H and external 85% H_3PO_4 for ^{31}P. Variable temperature ^{31}P, ^{13}C and ^{195}Pt NMR spectra were reported in 5 mm tube on a Varian XL-300 NMR spectrometer. The $^{195}Pt\{^{1}H\}$ NMR shifts are relative to external Na_2PtCl_6 in D_2O. Elemental analyses were performed by the Analytical Chemistry Division of the Bhabha Atomic Research Centre.

Preparation of $[\{Pt(Me)SSP(OPr^{i})_2\}_2COD]$

To an isopropanol solution (5 cm^3) of $NH_4SSP(OPr^{i})_2$ (68 mg, 0.29 mmol), a benzene solution (10 cm^3) of [PtMe(Cl)COD] (101 mg, 0.29 mmol) was added with stirring at room temperature. The whole was stirred at room temperature for 6 h. The solvents were stripped off *in vacuo* and the residue

Table 1. NMR data for methylplatinum dialkyldithiophosphate complexes in $CDCl_3$

	^{31}P NMR data				
	Phosphine ligand		Dithio ligand		
Complex	δ in ppm	*J* in Hz	δ in ppm	*J* in Hz	^1H NMR data
Ia	—	—	100.7 101.1(minor)	^2J(Pt—P) = 282 ^2J(Pt—P) = 292	0.50(t, ^2J(Pt—H) = 78 Hz, PtMe); 1.40(t, 7 Hz, $OCCH_3$); 4.18(m, OCH_2-); 2.05(br), 2.55(br), 4.35(br, ^2J(Pt—H) = 77 Hz, COD)
Ib	—	—	96.9 97.2(minor)	^2J(Pt—P) = 281 ^2J(Pt—P) = 291	0.48[t, ^2J(Pt—H) = 78 Hz, Pt—Me(major)]; 0.50[t, ^2J(Pt—H) = 79 Hz, Pt—Me-(minor]; 1.38, 1.39(d, each 6 Hz, $OCMe_2$); 4.80(m, OCH); 2.00(br), 2.50(br), 4.35(br ^2J(Pt—H) = 73 Hz, COD)
IIa	18.7(d)	^1J(Pt—P) = 4509 ^3J(P—P) = 9	98.0(d)	^2J(Pt—P) = 216 ^3J(P—P) = 9	0.47(d, t, ^2J(Pt—H) = 80 Hz, ^3J(P—H) = 4.5 Hz, PtMe); 1.30(t, 7 Hz, $OCCH_3$); 2.35(s, tol-Me) : 4.15(m, OCH_2-); 7.10–7.65(m, C_6H_4-)
IIb$_2$	18.7(d)	^1J(Pt—P) = 4468 ^3J(P—P) = 8	93.8(d)	^2J(Pt—P) = 215 ^3J(P—P) = 8	0.48(d, t, ^2J(Pt—H) = 80 Hz, ^3J(P—H) = 4.5 Hz, PtMe); 1.32(d), 1.37(d) (each 6 Hz, $OCHMe_2$); 2.38(s, tol-Me); 4.90(m, OCH <); 7.10–7.60(m, C_6H_4-)
IIc	16.3	^1J(Pt—P) = 4450	100.1	^2J(Pt—P) = 223	0.37(d, t, ^2J(Pt—H) = 80 Hz, ^3J(P—H) = 4 Hz, PtMe); 1.34(t, 7 Hz, $OCCH_3$); 2.08(br, 2Me, tolMe); 3.06(br, 1Me, tol-Me); 4.16(br, OCH_2); 7.18(br), 7.34(br) [C_6H_4]
Iid	16.6	^1J(Pt—P) = 4421	96.6	^2J(Pt—P) = 224	0.35(d, t, ^2J(Pt—H) = 79 Hz, ^3J(P—H) = 3 Hz, PtMe); 1.29(d), 1.36(d) (each 6 Hz, $OCHMe_2$); 2.08(br, 2Me, tol-Me); 3.02(br, 1Me, tol-Me); 4.78(br, OCH <) 7.18(br), 7.33(br)[C_6H_4]
IIe	−34.4(d)	^1J(Pt—P) = 4951 ^3J(P—P) = 9	99.5(d)	^2J(Pt—P) = 209 ^3J(P—P) = 9	0.38(d, t, ^2J(Pt—H) = 84 Hz, ^3J(P—H) = 4.5 Hz, PtMe); 1.29(t, 7 Hz, $OCCH_3$); 3.56(s, 2, 6-OMe); 3.78(s, 4-OMe); 4.10(m, OCH_2-); 5.96(C_6H_2)
IIf	−34.0(d)	^1J(Pt—P) = 4915 ^2J(P—P) = 8	98.1(br)	^2J(Pt—P) = 212	0.37(d, t, ^2J(Pt—H) = 84 Hz, ^3J(P—H) = 5 Hz; PtMe); 1.23(d), 1.34(d) (each 6 Hz, $OCHMe_2$); 3.55(s, 2,6-OMe); 3.78(s, 4-OMe); 4.75(m, OCH <); 5.96(C_6H_2)

Table 2. Physical and analytical data for methylplatinum dialkyldithiophosphate complexes

Complex		Recrystallization solvent (% Yield)	m.p. (°C)	Found (Calcd) % C	H
$[\{Pt(Me)SSP(OEt)_2\}_2COD]$	**(Ia)**	Benzene–hexane (40)	122	24.6 (24.1)	4.3 (4.3)
$[\{Pt(Me)SSP(OPr^i)_2\}_2COD]$	**(Ib)**	CH_2Cl_2–hexane (50)	145	27.4 (27.7)	4.8 (4.8)
$[PtMe\{SSP(OEt)_2\}\{P(4\text{-}MeC_6H_4)_3\}]$	**(IIa)**	Hexane (66)	110	44.2 (44.6)	4.8 (4.9)
$[PtMe\{SSP(OPr^i)_2\}\{P(4\text{-}MeC_6H_4)_3\}]$	**(IIb)**	Hexane (60)	80	46.7 (46.2)	5.1 (5.2)
$[PtMe\{SSP(OEt)_2\}\{P(2\text{-}MeC_6H_4)_3\}]$	**(IIc)**	CH_2Cl_2–hexane	170–172	45.2 (44.6)	5.0 (4.9)
$[PtMe\{SSP(OPr^i)_2\}\{P(2\text{-}MeC_6H_4)_3\}]$	**(IId)**	CH_2Cl_2–hexane	154–156	45.5 (46.2)	4.7 (5.2)
$[PtMe\{SSP(OEt)_2\}\{P(2,4,6\text{-}(MeO)_3C_6H_2)_3\}]$	**(IIe)**	CH_2Cl_2–hexane (70)	135–138	41.4 (41.4)	5.3 (5.0)
$[PtMe\{SSP(OPr^i)_2\}\{P(2,4,6\text{-}(MeO)_3C_6H_2)_3\}]$	**(IIf)**	CH_2Cl_2–hexane (55)	138–140	43.1 (42.7)	5.0 (5.3)

was extracted with benzene–hexane (60 : 40, v/v) mixture and filtered. The filtrate was dried under reduced pressure to give a white solid which was recrystallized from benzene (1 cm^3)–hexane (4 cm^3) mixture at 0°C as a colourless crystalline solid (76 mg, 50%). $^{13}C\{^1H\}$ in $CDCl_3$: $\delta = -6.5$ (s, $^1J(^{195}Pt—^{13}C) = 670$ Hz, PtMe, major): -6.7 (s, PtMe, minor); 23.6 (br s, $OC\underline{Me}_2$); 31.4 ($^2J(^{195}Pt—^{13}C) = 73.5$ Hz), 31.5 (COD, CH_2); 73.5 (d, $^2J(P—C) = 4.2$ Hz, OCH<); 81.8 (s, $^1J(^{195}Pt—^{13}C) = 205$ Hz, COD, CH).

Similarly, $[\{Pt(Me)SSP(OEt)_2\}_2COD]$ was prepared but ethanol was used in place of isopropanol to avoid any exchange of the alkoxy group on phosphorus.

Preparation of $[Pt(Me)\{SSP(OEt)_2\}P\{(2,4,6\text{-}MeO)_3C_6H_2\}_3]$

To a benzene solution of $[\{Pt(Me)SSP(OEt)_2\}_2COD]$ (73 mg, 0.081 mmol), a solution of $P\{(2,4,6\text{-}MeO)_3C_6H_2\}_3$ (87 mg, 0.163 mmol) was added dropwise with stirring for 2 h at room temperature. The solvent was removed *in vacuo* and the residue was washed with hexane to remove the cyclooctadiene and further dried. The resulting white solid was recrystallized from dichloromethane–hexane as a colourless crystalline solid (105 mg, 70%). Similarly, all other complexes **(II)** were prepared.

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