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PREPARATION AND CHARACTERISATION OF SOME THIOL COMPOUNDS OF TRIMETHYLPLATINUM(IV), $[(Pt(CH_3)_3SR)_4]$

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Summary

An efficient, clean synthesis of $[Pt(CH_3)_3SR]$, R = CH_3, C_2H_5, iso-C_3H_7, $CH_2C_6H_5$ and C_6H_5, from $[(Pt(CH_3)_3OH)_4]$ is reported. Mass spectroscopy indicates a tetrameric structure for the first four compounds. The complexes have been further characterised by ^1H NMR and vibrational spectroscopy. A striking feature of the tetramers is their total unreactivity towards donor ligands.

Introduction

Trimethylplatinum(IV) readily forms stable complexes with both neutral [1] and anionic [2,3] sulphur donor ligands. It is therefore surprising that of the monodentate thiol ligands RS^-, only the complexes $[(PtMe_3SR)_4]$, R = H [4] Me, Ph and CF_3 [5], have been reported; yields of below 60% are recorded.

We describe here a generally applicable method based on $[(PtMe_3OH)_4]$ which gives the complexes in high yield and purity.

Results and discussion

The compounds were all made by treating $[(PtMe_3OH)_4]$ with excess of the thiol in a sealed tube at room temperature. On standing for several days the hydroxide dissolved, and the formation of water was noted. The product was obtained either by removal of excess thiol and recrystallisation of the residue (R = Me and Et) or by precipitation of the complex from solution and recrystallisation (R = ^{i}Pr, Bz, and Ph). Complexes having R = Me, Et and Ph were all obtained pure and in quantitative yield. The products are all air-stable, crystalline solids, which do not have sharp melting points but decompose over a wide temperature range above 175°C. The compounds with R = Me, Et, ^{i}Pr and Bz are soluble in non-polar solvents, the phenyl complex being markedly less soluble. Analytical data are recorded in Table 1.

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TABLE 1

ANALYTICAL AND ^{1}H NMR DATA FOR THE COMPLEXES [(PtMe$_3$SR)$_4$]

Complex	Colour	M.p. (°C)	Analysis [a] (%)		δ(Pt—Me)	^{1}H NMR Data [b]		
			C	H		^2J(Pt—Me)	δ(Pt—S—C—H)	^3J(Pt—S—C—H)
[(PtMe$_3$SMe)$_4$]	White	225—250 (dec)	16.47 (16.73)	4.09 (4.18)	0.96	70.5	2.27	15.3
[(PtMe$_3$SEt)$_4$]	White	205—242 (dec)	20.13 (19.93)	4.57 (4.65)	1.11	70.6	3.12	14.8 [c]
[(PtMe$_3$S^{i}Pr)$_4$]	White	239—240	23.00 (22.85)	4.62 (5.08)	complex spectrum		3.00	16.0 [c]
[(PtMe$_3$SPh)$_4$]	Orange	175—240 (dec)	31.00 (30.93)	3.94 (4.01)	1.33	71.3	—	—
[(PtMe$_3$SBz)$_4$]	White	240	32.81 (33.06)	4.41 (4.41)	1.00	70.8	4.23	13.2

[a] Calculated values in parentheses. [b] Chemical shifts in ppm measured relative to Me$_4$Si; Coupling constants are in Hz; Solvent was CDCl$_3$. [c] Average value.

TABLE 2

INFRARED AND RAMAN DATA FOR THE COMPLEXES [(PtMe$_3$SR)$_4$] [a]

R	C—H(str)	C—H(def)	Pt—C(str)	[Pt—S]$_4$ (skeletal bending)	Anion frequencies
Me	2960s, 2920w, 2900vs	2810m, 1425m, 1260s, 1226s	565w		1305w, 953s, 850vw(br), 718vw
(Me)	2932w, 2913m	1260vw, 1227m	566vs	84s, 66w	730vw, 265m(br), 252m(br), 150m, 126m, 97w

Et	2960s, 2920w, 2900s	2800w, (1450, 1425)m(db), 1265vs, 1223vs	560m		1375m, 1076w(br), (1053, 1030)m(db), 978s, 840w(sh), 800m, 757m
(Et)	3015vw(br)	1280vw(br), 1222w	558vs	82s, 55s	570vw(br), 260w(br), 206w(br), 120m
^{i}Pr	2960s, 2900vs	2810m, 1452w 1260s, (1235, 1225)m(db)	560m		1150w, 1090w, 1050m, 850w(br), 730w(br), 610vw(br), 440w
(^{i}Pr)	2910m(vbr), 2876vw(br)	1272w, 1220m	558vs		1052w(br), 1028vw(br), 725vw(br), 220vw(br), 180m(br), 123m, 120vw, 105w
Ph	2970s, 2900vs	2810w, 1260m, 1230s	555w(br)		3060s, 1580s, 1480vs, 1440vs, (1080, 1070)m(db), 1028s, 1003m, 740vs, 690vs, 618vw, 485s, 440vw
(Ph)	2980w(br), 2921s	2832vw, 1275w(br), 1230m(br)	567vs, 550vw(sh)	82s, 62—58w(db), 52—50w(sh), 45vw, 40vw	3086m, 3040w, 1588s, 1570vvw, 1483vw(br), 1446vw(br), 1190vw(br), 1169vw(br), 1148vw(br), 1084s, 1030m, 1007s, 700m, 620w, 489vw, 466m, 117m
Bz	2960m, 2900vs	2810w, 1425m(br), 1260s, 1230w(sh), 1225s	565m		(3050, 3040, 3030, 3015)w, 1500m, 1456m, 1170m, 1030w, 1005vw, 915w, 860m(br), 810vw, 770m, 700vs, 675m, 480m
(Bz)	2980vw(br), 2940w, 2917m, 2906(sh)	1275w, 1235w, 1220m	558vs	77s, 55m	3080w, 3060w, 1607m, 1592vw, 1433vvw(br), 1200vw(br), 1160w, 1032w, 1005m, 767w, 705vw, 680m, 624vw, 475vw, 275w(br), 190w(br), 170w(br), 120m, 96(sh)

v = very, w = weak, m = medium, s = strong, br = broad, sh = shoulder, db = doublet.

[a] Raman data in parentheses.

Hall et al. [5] showed that the methyl compound $[(PtMe_3SMe)_4]$ was a tetramer both in the vapour phase and in chloroform solution, and concluded that the most likely structure was that already established by X-ray crystallography for the compounds $[(PtMe_3X)_4]$, X = Cl [6], I [7], OH [8], N_3 [9] and ClO_4 [10]; and also proposed on the basis of spectroscopic studies for the compounds X = OMe [11], Br [12] and SCN [13]. We suggest the same structure for all members of the series reported here. Peaks corresponding to the tetrameric molecular ion were present in the mass spectra of the compounds having R = Me, Et, ^{i}Pr and Bz, and the isotope patterns exactly matched those of the computer simulation. In each case a similar fragmentation pattern was seen, with a set of peaks corresponding to the successive loss of each of the twelve platinum methyl groups. The phenyl complex did not give a molecular ion.

Further support for the tetrameric structure comes from the synthesis of mixed methyl/ethyl tetramers $[(PtMe_3SMe)_n(PtMe_3SEt)_{4-n}]$, n = 0—4, by treating $[PtMe_3OH]_4$ with a large excess of EtSH containing a little MeSH. Mass spectrometry showed the presence of approximately equal amounts of all five possible products, but attempts to separate them by solution chromatography failed.

^{1}H NMR spectra

Evidence that the tetrameric structure persists in solution is provided by the ^{1}H NMR spectra of the complexes (Table 1). Hall et al. showed [5] that $[(PtMe_3SMe)_4]$ was tetrameric in $CHCl_3$ solution by osmometry, and the ^{1}H NMR spectrum in the same solvent showed only one platinum-methyl signal at low frequency, confirming the expected equivalence of all twelve groups. This same feature is found in the spectra of the R = Et, Bz and Ph complexes (Table 1). The Pt-methyl region of the spectrum of the R = ^{i}Pr complex is by contrast very complicated. We attribute this to a non-equivalence among the platinum-methyl protons caused by the conformational demands of the ^{i}Pr groups. Molecular models indicate that it is impossible to maintain an equivalence among the platinum-methyl groups in this particular compound. A comparison of the $^2J(Pt—CH_3)$ coupling constants (Hz) with recorded data for analogous tetramers shows that the SR groups have the strongest *trans*-influence [14,15] of all reported ligands, the order being.-

SMe (70.5) < SEt (70.6) < SBz (70.8) < SPh (71.3) < SH (73.4) [4]
< *N*CS (74.2) [13] < N_3 (74.4) [16] < *S*CN (75.0) [13]
< ClO_4 (76.0) [10] < I (78.4) [17] < OH (78.8) [18] < Br (80.1) [17]
< Cl (81.7) [17].

Morgan et al. [18] showed that the compound $[(PtMe_3OH)_4]$ was tetrameric in solution by a consideration of the ^{1}H NMR spectrum of the hydroxide proton. A comparable argument can be applied to the SMe signal in $[(PtMe_3SMe)_4]$. Each tetramer may have from zero to four spin active ^{195}Pt nuclei. All four SMe groups are equivalent in the tetramer, and each methyl group will be expected to show coupling to any of the three platinum atoms bonded to its sulphur atom which have spin active nuclei. It is possible to estimate binomially what is the relative probability of each SMe group being coupled to 0, 1, 2 or 3 nuclei of ^{195}Pt ($I = \frac{1}{2}$, 33.7%), and the resultant methyl proton signal is predicted to be a seven line multiplet with intensity ratios 1.0:11.8:49.0:83.6:49.0:11.8:1.0. The observation of just this theoretical pattern in the spectra is consistent only with a tetrameric species in solution.

Interestingly, a value of 15.3 Hz for ^3J(Pt—S—C—H) in [$(PtMe_3SMe)_4$] is similar to the ^2J(Pt—X—H) values reported for the SH (15.2 Hz) and OH (11.2 Hz) tetramers. The α-proton signals for the complexes with R = Et, ^{i}Pr, and Bz are complex multiplets from which ^3J(Pt—S—C—H) can be measured (Table 1). It is further of interest that the values lie in the same range (ca. 12—15 Hz) as ^3J for the mononuclear thioether complexes [$PtMe_3X\{MeS(CH_2)_2SMe\}$] (X = Cl, Br and I) in which the neutral sulphur donor acts as a bidentate ligand [1]. In view of the marked similarity between the ^2J(Pt—X—H) and ^3J(Pt—S—C—H) values, it is perhaps surprising that no ^3J(Pt—H) coupling is observed in the spectra of the R = Et, ^{i}Pr and Bz complexes.

Vibrational spectra

Infra red and Raman spectroscopic data are presented in Table 2. The spectra consist essentially of features typical of the $PtMe_3$ [4,19] and SR [20,21] groups, with additional stretching and bending modes for the cage atoms. Very strong Raman lines between 550 and 600 cm^{-1} are assigned to Pt—C stretches. Some coincident bands are observed between the Raman and infrared spectra, but all have very low intensity, consistent with a centrosymmetric structure.

Reactivity

The ^2J(Pt—CH_3) values indicate that the compounds [$(PtMe_3SR)_3$] are the most strongly bonded of any [$(PtMe_3X)_4$] species so far reported. The robustness of the cage is confirmed by attempts to make adducts with neutral donor ligands of the type that are readily formed by the halides [1]. Refluxing [$(PtMe_3SMe)_4$] in organic solvents with pyridine, 2,2′-bipyridyl, 1,2-diaminoethane, 1,2-bis(diphenylphosphine)ethane and dimethyldisulphide gave only the starting materials in each case. A further contributory factor to the inertness of the SR tetramer is the lack of a site available for nucleophilic attack, since all the valence shell orbitals on the sulphur atom are occupied. Moreover, the Pt—S bond is extensively shielded by numerous methyl and alkythio groups in such a structure.

Experimental

Preparation of [$(PtMe_3SMe)_4$]

An excess of methane thiol was added to [$(PtMe_3OH)_4$] in a heavy walled glass tube which was evacuated at —100°C and sealed. After warming to room temperature and standing for 24 hours the solid had dissolved, and the presence of water was noticed. After 3 days a mass of small crystals had formed. The tube was opened and the excess thiol decanted at 0°C. Dry nitrogen was passed over the lemon yellow crystals. Treatment of the crystals with activated charcoal in chloroform, followed by recrystallisation from chloroform/ethanol gave a white crystalline product (Table 1).

Preparation of $[(PtMe_3SEt)_4]$

An excess of ethane thiol was added to $[(PtMe_3OH)_4]$. The solid dissolved readily. After seven days excess thiol was removed, and recrystallisation from chloroform/acetone gave the product as shining white crystals (Table 1).

Preparation of $[(PtMe_3SPh)_4]$

A yellow solution was obtained on adding an excess of phenyl thiol to $[(PtMe_3OH)_4]$. Over a period of three days the solution turned orange, with the deposition of rhombic orange crystals which were removed. Further product was obtained on adding hexane to the solution. Recrystallisation from benzene/hexane gave a quantitative yield of a pale orange powder (Table 1).

Preparation of $[(PtMe_3S^iPr)_4]$

An excess of iso-propane thiol was added to $[(PtMe_3OH)_4]$. The hydroxide dissolved slowly, giving a colourless solution which turned yellow on standing for five days. Addition of ethanol precipitated a white powder, which was recrystallised from hexane to give white crystals (16% yield) (Table 1). From the solution polymeric material was obtained which was shown by infrared spectroscopy to contain hydroxide, isopropyl and platinum-methyl groups.

Preparation of $[(PtMe_3SBz)_4]$

This was prepared by the method used for $[(PtMe_3S^iPr)_4]$. Recrystallisation from chloroform/acetone gave the product as fine white crystals in 36% yield (Table 1).

Infrared spectra were recorded on a Perkin-Elmer 357 spectrophotometer as KBr discs. Raman spectra were recorded on solid samples on a Spex Ramalog instrument at the Department of Chemistry, University of Glasgow. Mass spectra were recorded on a single focusing VG-Micromass MM-30 spectrometer at 70 eV with a source temperature of 200°C. 100 MHz NMR spectra were recorded on either a JEOL MH-100 spectrometer operating in the continuous-wave mode under internal field-frequency lock conditions, or a JEOL PS/PFT-100 spectrometer operating in the Fourier transform mode.

Melting points (uncorrected) were determined using an electrothermal melting point apparatus.

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