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2,5-DISELENA-3,3,4,4-TETRAFLUOROHEXANE AND 2,5-DISELENA-1,1,1,6,6,6-HEXAFLUOROHEXANE AND THEIR PLATINUM AND PALLADIUM CHLORIDE COMPLEXES

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SUMMARY

The diselenoethers, $\text{CH}_3\text{SeCF}_2\text{CF}_2\text{SeCH}_3$ and $\text{CF}_3\text{SeCH}_2\text{CH}_2\text{SeCF}_3$ are described. 1:1 Complexes are formed between these ligands and platinum(II) and palladium(II) chloride.

INTRODUCTION

Diselenoethers containing fluorine do not appear to have been described in the literature although many non-fluorine-containing analogues are known [1] together with the formation of their complexes through chelation by the selenium atoms [2]. We now report the preparation of two 2,5-diselenahexanes, $\text{CH}_3\text{SeCF}_2\text{CF}_2\text{SeCH}_3$ and $\text{CF}_3\text{SeCH}_2\text{CH}_2\text{SeCF}_3$, together with the formation of platinum and palladium chloride complexes. Corresponding dithioethers are known [3,4,5] together with many complexes including platinum derivatives of many of the fluorinated species [6].

RESULTS AND DISCUSSION

2,5-Diselena-3,3,4,4-tetrafluorohexane, $\text{CH}_3\text{SeCF}_2\text{CF}_2\text{SeCH}_3$ (A), is prepared from sodium methaneselenol, NaSeCH_3 , and 1,2-dibromotetrafluoroethane. 2,5-Diselena-1,1,1,-

6,6,6-hexafluorohexane, $\text{CF}_3\text{SeCH}_2\text{CH}_2\text{SeCF}_3$ (B), is prepared from bis(trifluoromethyl)diselenide, $\text{CF}_3\text{SeSeCF}_3$, and ethene under u.v. irradiation. The diselenoethers react with solutions of platinum(II) and palladium(II) chloride species to give 1:1 complexes LMCl_2 (L = A or B). The ease of formation of palladium complexes is noteworthy as the dithio analogue of (B) forms only platinum complexes whilst no metal complexes have yet been isolated with the thio analogue of (A) [6]. This suggests considerably greater complexing ability of selenium in these fluorinated species as compared to sulphur.

The spectroscopic properties of the present complexes strongly suggest the presence of molecular species with square planar co-ordination about the metals. The ^{19}F n.m.r. spectrum of $[(\text{CF}_3\text{SeCH}_2\text{CH}_2\text{SeCF}_3)\text{PtCl}_2]$ shows the presence of the two syn- and anti-isomers expected for such a geometry with each selenium having a lone pair and a trifluoromethyl substituent. The ^{19}F n.m.r. spectrum of the palladium chloride complex is very broad (400 Hz) at -21 p.p.m. It does not vary with temperature.

The ^1H n.m.r. spectra of $[(\text{CH}_3\text{SeCF}_2\text{CF}_2\text{SeCH}_3)\text{MCl}_2]$ (M = Pt and Pd) also show the presence of two isomers. The ^{19}F n.m.r. spectra of these complexes are complex and consist of two AA'BB' spectra (with ^{195}Pt satellites in the case of the platinum complex) arising because of slow inversion at selenium and fast ring inversion on the n.m.r. time scale (compare the spectrum of the methylene protons in $[(\text{PrSeCH}_2\text{CH}_2\text{SePr})\text{PdCl}_2]$ [7]). The spectrum could be simulated [8] with the parameters in the Table and the isomer ratios are approximately 60:40. The absolute signs of the coupling are based on the $^2J_{\text{FF}}$ values being positive; the analysis does not give the assignment of $J_{\text{AA}'}$ and $J_{\text{BB}'}$.

From the relative values of the shifts and coupling constants of the platinum and palladium species it is probable that the more abundant isomer for each metal has the same configuration. It has not proved possible to identify these isomers.

The infrared spectra of the complexes are virtually identical to those of the free ligands except that two extra bands assigned to metal-chlorine stretching modes [9] are seen near to 300 cm^{-1} .

EXPERIMENTAL

Synthesis of 2,5-diselena-3,3,4,4-tetrafluorohexane, $\text{CH}_3\text{SeCF}_2\text{CF}_2\text{SeCH}_3$, and its complexes

Dimethyldiselenide [10] (18.8 g, 0.1 mole) was converted to NaSeCH_3 in liquid ammonia at -78°C and 1,2-dibromo-tetrafluoroethane (26.2 g, 0.1 mole) was added dropwise over a period of 1 hour. The mixture was stirred for 72 hours, ammonia allowed to evaporate, the mixture treated with water and extracted with chloroform. After distillation under reduced pressure 2,5-diselena-3,3,4,4-tetrafluorohexane was obtained as a vile-smelling pale yellow oil, b.p. 31°C at 0.01 mm: (yield 20.3 g, 70%). Found: C, 16.6; H, 2.2; F, 26.0; $\text{C}_4\text{H}_6\text{F}_4\text{Se}_2$ requires C, 16.7; H, 2.1; F, 26.4%. Mass spectral data (m/e (relative intensity) assignment) 290 (100) M; 275 (15) M- CH_3 ; 190 (50) $\text{CH}_3\text{SeSeCH}_3$; 175 (70) CH_3Se_2 ; 145 (50) CH_3SeCF_2 ; 126(15) CH_3SeCF ; 100 (15) CF_2CF_2 ; 95 (70) CH_3Se . Infrared data: 3030w, 2950w, 2840w, 1425m, 1321w, 1280s, 1260m, 1210s, 1105s(sh), 1085vs, 1000s, 918s, 810s, 870s, 790m(br), 750vs, 580m(br). (s strong, m medium, w weak, sh shoulder, br broad). The ^1H n.m.r. spectrum shows a singlet at +2.33 p.p.m. and the ^{19}F n.m.r. spectrum a singlet at -99.7 p.p.m.

2,5-diselena-3,3,4,4-tetrafluorohexane reacts with an aqueous ethanolic solution of K_2PtCl_4 to form a 1:1 orange-yellow PtCl_2 complex recrystallised from ethanol. Found: C, 8.4; H, 1.0; Cl, 12.6; F, 13.6. $\text{C}_4\text{H}_6\text{Cl}_2\text{F}_4\text{PtSe}_2$ requires C, 8.6; H, 1.1; Cl, 12.8; F, 13.7%.

The diselenoether reacts with an aqueous acetone solution of K_2PdCl_4 to form a brick-red 1:1 PdCl_2 complex. Found: C, 10.2; H, 1.2; Cl, 15.2; F, 16.2. $\text{C}_4\text{H}_6\text{Cl}_2\text{F}_4\text{PdSe}_2$ requires C, 10.3; H, 1.3; Cl, 15.2; F, 16.3%.

Synthesis of 2,5-diselena-1,1,1,6,6,6-hexafluorohexane, $CF_3SeCH_2CH_2SeCF_3$ and its complexes

Bis(trifluoromethyl)diselenide [11]) (0.296 g, 1 mmole) and ethene (0.042 g, 1.5 mmole) were condensed into a reaction flask so that at room temperature the total pressure of the reactants was ca. 1 atm. The flask was irradiated for 30 hours (Hanovia medium pressure mercury lamp) and the contents were then fractionated and characterised by standard vacuum line techniques. The fraction left after removal of unreacted $CF_3SeSeCF_3$ and ethene was 2,5-diselena-1,1,1,6,6,6-hexafluorohexane (0.194 g, 80%). B.p. 75 - 76°C at atmospheric pressure. Found: C, 14.7; H, 1.4; F, 35.1. $C_4H_4F_6Se_2$ requires C, 14.8; H, 1.2; F, 35.2%. Mass spectral data 326 (100) M; 298 (20) $CF_3SeSeCF_3$; 280 (10) $CF_3SeSeCF_2$; 257 (70) $CF_3SeCH_2CH_2Se$; 229 (15) CF_3Se_2 ; 161 (65) CF_3Se . Infrared data: 2960w, 2950w, 2860w, 1520w, 1425s, 1280s, 1250s, 1190vs, 900sh, 800m(sh), 740vs, 710m, 580s, 530m. The 1H n.m.r. spectrum of the diselenoether shows a singlet at +3.36 p.p.m. (w.r.t Me_4Si), the ^{19}F n.m.r. spectrum shows a singlet at -37.98 p.p.m. (w.r.t. CCl_3F).

The 2,5-diselena-1,1,1,6,6,6-hexafluorohexane reacts in aqueous-acetone solution with K_2PtCl_4 to give an orange-yellow 1:1 adduct on cooling (80% yield). Found: C, 7.9; H, 0.8; Cl, 11.9; F, 19.1. $C_4H_4Cl_2F_6PtSe_2$ requires C, 8.1; H, 0.7; Cl, 12.0; F, 19.3%. The 1H n.m.r. spectrum of the complex in $CDCl_3$ shows a broad resonance at +4.2 p.p.m. which changes to a very complex spectrum on cooling. The ^{19}F n.m.r. spectrum shows two isomers

	Shift	$^3J_{Pt-Se-C-F}$	Ratio
Isomer A	-38.43	55.4	21
Isomer B	-39.82	53.9	79

The brick red 1:1 2,5-diselena-1,1,1,6,6,6-hexafluorohexane palladium(II) chloride complex was prepared similarly. Found: C, 9.4; H, 0.7; Cl, 14.0; F, 22.7. $C_4H_4Cl_2F_6PdSe_2$ requires C, 9.6; H, 0.8; Cl, 14.1; F, 22.7%.

TABLE 1

^{19}F n.m.r. data for $[(\text{CH}_3\text{SeCF}_2\text{CF}_2\text{SeCH}_3)\text{MCl}_2]$ (M = Pt, Pd)

Isomer	Compound	δ_A	δ_B	$^2J_{AB}$	$^3J_{AA'}$	$^3J_{BB'}$	$^3J_{AB'}$	$^3J_{Pt-A}$	$^3J_{Pt-B}$
Major	Pt	-102.4	-94.5	+221.0	-14.9	-17.2	-9.8	+74	+112
	Pd	-98.1	-90.4	+220.9	-14.1	-18.2	-10.9		
Minor	Pt	-100.8	-97.5	+217.5	-9.1	-11.1	-15.9	+128	+56
	Pd	-96.0	-93.3	+217.0	-10.5	-12.6	-16.0		

Chemical shifts are in p.p.m., positive to low field of external CFCl_3 ; coupling constants are in Hz.

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