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SOME NEW σ-BONDED ARYL–PLATINUM COMPLEXES

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SUMMARY

The preparations are described of some new complexes *trans*-[PtL_2RX] and *cis*- and *trans*-[PtL_2R_2] (where $L=S(C_2H_5)_2$ or $Se(C_2H_5)_2$, R=phenyl, *o*-tolyl or mesityl and X=halogen). The *trans*-[PtL_2(mesityl)$_2$] complexes are the first σ-bonded demesityl derivatives of Pt^{II}.

The factors determining the stability of these complexes and the IR stretching frequencies ν(Pt–Cl) and ν(Pt–C) are discussed.

INTRODUCTION

Chatt and Shaw[1,2] reported the preparation of complexes with Pt–C and Ni–C bonds stabilized by phosphine and arsine ligands. Analogous Pd^{II} complexes have also been prepared[3]

We now describe the preparation of some new complexes *trans*-[PtL_2RX] and *cis*- and *trans*-[PtL_2R_2], (where $L=S(C_2H_5)_2$ or $Se(C_2H_5)_2$, R=phenyl, *o*-tolyl or mesityl and X=Cl, Br, or I).

EXPERIMENTAL

Apparatus

IR spectra (nujol mull) were recorded on a Perkin–Elmer 457 grating spectrophotometer. Dielectric constants were measured with a WTW Multidekameter DK 06, and dipole moments were evaluated by the method of Everard, Hill and Sutton[4].

Reactions

All reactions were carried out under nitrogen.

trans-Bis(diethylselenide)halogeno(phenyl)platinum, $Pt[Se(C_2H_5)_2]_2(C_6H_5)X$. *trans*-Bis(diethylselenide)dichloroplatinum (2.00 g; 3.36 mmoles) in dry ether (30 ml) was added to an ethereal solution of phenyllithium (8.8 mmoles). After 5 h the mixture was hydrolysed, and the organic layer separated and evaporated to dryness. The residue was chromatographed on alumina, and elution with chloroform gave *trans*-bis(diethylselenide)chloro(phenyl)platinum as colourless needles from methyl alcohol. Yield 40%. m.p. 64°. (Found: C, 28.23; H, 4.50; Cl, 6.00. $C_{14}H_{25}ClPtSe_2$ calcd.: C, 28.94; H, 4.34; Cl, 6.26%.)

trans-Bis(diethylselenide)bromo- and -iodo(phenyl)platinum were prepared by metathetical replacement from the *trans*-bis(diethylselenide)chloro(phenyl)platinum with LiX salts in methyl alcohol.

trans- and cis-Bis(diethylsulphide)diphenylplatinum, $Pt[S(C_2H_5)_2]_2(C_6H_5)_2$ *trans*-Bis(diethylsulphide)dichloroplatinum (2.5 g; 5.6 mmoles) was similarly treated with an ethereal solution of phenyllithium (15 mmoles) for 4 h. Working-up as above gave *trans*-$Pt[S(C_2H_5)_2]_2(C_6H_5)_2$ as colourless needles from ether. Yield 20%, m.p. 99–101°. (Found: C, 45.0; H, 5.73. $C_{20}H_{30}PtS_2$ calcd.: C, 45.11; H, 5.68%) *cis*-$\{Pt[S(C_2H_5)_2]_2(C_6H_5)_2\}$ was obtained as colourless needles from chloroform. Yield 60%, m.p.165° with decompn. (Found: C, 45.3; H, 5.6. $C_{20}H_{30}PtS_2$ calcd.: C, 45.11; H, 5.68%.)

trans-Bis(diethylselenide)chloro(o-tolyl)platinum, $Pt[Se(C_2H_5)_2]_2(o\text{-}Tol)Cl$. An ethereal solution of *trans*-$Pt[Se(C_2H_5)_2]_2Cl_2$ (2.0 g, 3.36 mmoles) was added to *o*-tolyllithium (9 mmoles) in ether. After 2 h working-up as above gave *trans*-$Pt[Se(C_2H_5)_2]_2(o\text{-}Tol)Cl$ as needles from ether. Yield 50%, m.p. 63–65°. (Found: C, 30.12; H, 4.50; Cl, 5.90. $C_{15}H_{27}ClPtSe_2$ calcd.: C, 30.18; H, 4.57; Cl, 5.97%.)

trans-Bis(diethylsulphide)di-o-tolylplatinum, $Pt[S(C_2H_5)_2]_2(o\text{-}Tol)_2$ and trans-bis(diethylsulphide)chloro(o-tolyl)platinum, $Pt[S(C_2H_5)_2]_2(o\text{-}Tol)Cl$. 0.5 g (1.12 mmoles) of *trans*-$Pt[S(C_2H_5)_2]_2Cl_2$ in ether was similarly treated with *o*-tolyllithium in ether (3 mmoles). After 2 h the usual working-up gave a crude product which was recrystallized several times from ether to give first *trans*-$Pt[S(C_2H_5)_2]_2(o\text{-}Tol)_2$. Yield 50%, m.p. 118–122°. (Found: C, 47.49; H, 6.09. $C_{22}H_{34}PtS_2$ calcd.: C, 47.30; H, 6.10%); second *trans*-$Pt[S(C_2H_5)_2]_2(o\text{-}Tol)Cl$ was obtained. Yield 20%, m.p. 103°. (Found: C, 35.90; H, 5.40; Cl, 7.00. $C_{15}H_{27}ClPtS_2$ calcd.: C, 35.88; H, 5.43; Cl, 6.97%.)

trans-Bis(diethylselenide)dimesitylplatinum, $Pt[Se(C_2H_5)_2]_2(mesityl)_2$. An ethereal solution of *trans*-$Pt[Se(C_2H_5)_2]_2Cl_2$ (1.4 g; 2.56 mmoles) was added to mesityllithium (6.6 mmoles) in ether. After 2 h working-up gave a crude product which was recrystallized from methanol to give *trans*-$Pt[Se(C_2H_5)_2]_2(mesityl)_2$. Yield 50%, m.p. 192° with decompn. (Found: C, 44.13; H, 5.95. $C_{26}H_{42}PtSe_2$ calcd.: C, 44.10; H, 5.90%.)

trans-Bis(diethylsulphide)dimesitylplatinum, $Pt[S(C_2H_5)_2]_2(mesityl)_2$. 1.0 g (2.24 mmoles) of *trans*-$Pt[S(C_2H_5)_2]_2Cl_2$ in ether was added to mesityllithium (5 mmoles) in ether. After 2 h the usual working-up followed by recrystallization from methyl alcohol gave *trans*-$Pt[S(C_2H_5)_2]_2(mesityl)_2$. Yield 50% m.p. 180° with decompn. (Found: C, 50.95; H, 6.86. $C_{26}H_{42}PtS_2$ calcd.: C, 50.95; H, 6.89%.)

Attempts to prepare complexes with a Pt–CH_3 bond. An ethereal solution of *trans*-$[PtL_2X_2]$ ($L = S(C_2H_5)_2$, $Se(C_2H_5)_2$) was added to CH_3Li in ether. Hydrolysis with ice, at 0°, afforded metallic platinum.

DISCUSSION

The stability of σ-bonded organo-derivatives of platinum(II) complexes is generally attributed to the energy difference (ΔE) between the d_{x-y} non bonding metal orbital and $d^*_{x^2-y^2}$ antibonding orbital. The ligands such as the phosphines and arsines may cause an increase in ΔE and so contribute to a greater kinetic stability of the M–C bond[1,2].

Arylplatinum compounds show a greater resistance to thermal decomposition and cleavage reactions than their alkyl analogues[5]. This can be attributed to overlap between the platinum filled 5*d* orbitals and the π-orbitals of the aromatic system. The results of NMR measurements on *trans*-[Pt(PEt$_3$)$_2$(*m*- or *p*-FC$_6$H$_4$)X] complexes confirm that there is a general drift of electrons from platinum to the aromatic group by both inductive and π-bonding effects[6]. On the other hand S(C$_2$H$_5$)$_2$ and Se(C$_2$H$_5$)$_2$ ligands exert their influence mainly by inductive electron release to Pt[7]. The stability of the Pt–C bonds in *trans*-[PtL$_2$RX] and *cis*- and *trans*-[PtL$_2$R$_2$] [L=S(C$_2$H$_5$)$_2$, Se(C$_2$H$_5$)$_2$; R=phenyl, *o*-tolyl, mesityl] could thus be due to the simultaneous presence of L and aryl ligands. It is noteworthy that analogous complexes containing a Pt–methyl bond have not been prepared, neither have Ni^{II} σ-bonded methyl derivatives been obtained[2].

In Table 1 are shown values of dipole moments and ν(Pt–C) and ν(Pt–Cl).

TABLE 1

DIPOLE MOMENTS AND IR FREQUENCIES

Complex	μ (D)	ν(Pt–C) (cm^{-1})	ν(Pt–Cl) (cm^{-1})
trans-Pt[Se(C$_2$H$_5$)$_2$]$_2$(C$_6$H$_5$)Cl		505 vw	266 s
trans-Pt[Se(C$_2$H$_5$)$_2$]$_2$(C$_6$H$_5$)Br		496 vw	
trans-Pt[Se(C$_2$H$_5$)$_2$]$_2$(C$_6$H$_5$)I	3.2	490 vw	
trans-Pt[Se(C$_2$H$_5$)$_2$]$_2$(o-Tol)Cl	2.9	442 m	262 s
trans-Pt[Se(C$_2$H$_5$)$_2$]$_2$(mesityl)$_2$	1.42		
trans-Pt[S(C$_2$H$_5$)$_2$]$_2$(C$_6$H$_5$)$_2$	1.8	502 s	
cis-Pt[S(C$_2$H$_5$)$_2$]$_2$(C$_6$H$_5$)$_2$		495 m 478 m	
trans-Pt[S(C$_2$H$_5$)$_2$]$_2$(o-Tol)Cl	2.78	442 m	265 s
trans-Pt[S(C$_2$H$_5$)$_2$]$_2$(o-Tol)$_2$	2.1	446 m	
trans-Pt[S(C$_2$H$_5$)$_2$]$_2$(mesityl)$_2$	1.94		

The ν(Pt–C) frequencies have been assigned on the basis of values reported in the literature[8,9]. No bands arising from the neutral coordinated ligands were observed in the region 550–400 cm^{-1}.

The configurations of the complexes were established by means of dipole moment measurements and confirmed by IR data. The monosubstituted [PtL$_2$(C$_6$H$_5$)X] exhibits a very low value for ν(Pt–Cl) as expected for a complex in which a halogen ligand is in *trans* position to a strong "*trans*-activating" group.

The ν(Pt–Cl) value is insensitive to change in the aryl ligands. In the complexes *trans*-Pt[Se(C$_2$H$_5$)$_2$]$_2$(C$_6$H$_5$)X, the ν(Pt–C) values are in the order $\mathrm{Cl} > \mathrm{Br} > \mathrm{I}$.

It is noteworthy that *trans*-[PtL$_2$(mesityl)$_2$] [L=S(C$_2$H$_5$)$_2$, Se(C$_2$H$_5$)$_2$] are the only known σ-bonded dimesityl derivatives of Pt^{II}, but analogous Ni^{II} complexes have been obtained[2]. X-ray measurements are in progress to confirm the structures of the mesityl complexes.

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