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Preliminary communication

ALKYL- AND ARYL-PLATINUM(II) COMPLEXES FROM $K_2[PtCl_4]$ AND TETRAORGANOTIN COMPOUNDS IN DIMETHYLSULPHOXIDE. PREPARATION AND REACTIONS OF COMPLEXES $[PtR_2(DMSO)_2]$ AND $[PtR(C)(DMSO)_2]$ [‡]

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Summary

The reaction between $K_2[PtCl_4]$ and a variety of tetraorganotin compounds $SnMe_3R$ (R = Me, aryl) in DMSO gives the complexes *cis*-$[PtR_2(DMSO)_2]$ and *trans*-$[PtR(Cl)(DMSO)_2]$ in which the DMSO ligands are bound to Pt through S in the solid state. The DMSO ligands are easily displaced by a variety of N, P, As and Sb donors.

The introduction of alkyl or aryl ligands into platinum(II) complexes normally requires the conversion of the usual starting material $K_2[PtCl_4]$ into an uncharged complex $[PtCl_2L_2]$ [where, for example, L = PR_3 or ½ COD (COD = cycloocta-1,5-diene)], which is usually isolated and purified before treatment with an organometallic reagent. Work in this laboratory has shown that the tin compounds $SnMe_3R$ are convenient reagents for conversion of Pt—Cl into Pt—R, especially when the Pt—Cl bond is activated as in $[PtCl_2(COD)]$ [1]. We now report that the tin compounds react with *cis*-$[PtCl_2(DMSO)_2]$ (DMSO = dimethylsulphoxide) which can be obtained in situ from $K_2[PtCl_4]$ in DMSO.

Typically, $K_2[PtCl_4]$ (2 mmol) was dissolved in DMSO (8 cm^3) at room temperature, an excess of $SnMe_3R$ (R = Me, aryl; 4—10 mmol) added, and the mixture stirred for several hours at 70—90°C. After removal of DMSO under vacuum at 70°C, the complex was isolated by stirring with diethyl ether and recrystallising the solid thus obtained from dichloromethane/ether. This procedure gave the pure complexes *cis*-$[PtR_2(DMSO)_2]$ in good yields (Table 1); experiments in which the products were examined before recrystallisation or in which they were converted into phosphine complexes showed that the diaryl complexes

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[‡] No reprints available.

TABLE 1

COMPLEXES OBTAINED FROM K$_2$[PtCl$_4$] AND SnMe$_3$R IN DMSO[a]

Complex	Conditions[b] (°C/h)	Yield (%)	Colour	M.p. (°C)[c]
cis-[PtMe$_2$(DMSO)$_2$]	70/20	14	white	122
cis-[PtPh$_2$(DMSO)$_2$]	70/4	63	white	136
cis-[Pt(C$_6$H$_4$Me-*p*)$_2$(DMSO)$_2$]	80/20	58	off-white	146
cis-[Pt(C$_6$H$_4$OMe-*p*)$_2$(DMSO)$_2$]	70/6	80	off-white	142
cis-[Pt(C$_6$H$_4$Cl-*p*)$_2$(DMSO)$_2$]	90/10	52	white	154
cis-[Pt(C$_4$H$_3$O-2)$_2$(DMSO)$_2$][d]	25/12	14	yellow	142
trans-[PtMe(Cl)(DMSO)$_2$]	70/20	26	white	120[e]
trans-[PtPh(Cl)(DMSO)$_2$]	70/4	39	yellow	162[e]
trans-[Pt(C$_6$H$_4$Me-*p*)Cl(DMSO)$_2$]	80/5	19	yellow	164
trans-[Pt(C$_6$H$_4$Cl-*p*)Cl(DMSO)$_2$]	80/6	33	yellow	162

[a] Satisfactory C and H analyses were obtained for all complexes. [b] Temperature (°C) and duration of reaction, see text. [c] Complexes blacken at stated temperature; melting occurs at ca. 20° higher temperature. [d] C$_4$H$_3$O-2 = 2-furyl. [e] Complex melts with decomposition.

are formed virtually quantitatively, and that the lower yields shown in Table 1 result from losses in recrystallisation.

The solid complexes were shown to have the *cis*-configuration with Pt—S bonds by the presence in the IR spectra of two bands from ν(Pt—S) between 433 and 412 cm^{-1} and two bands from ν(S—O) between 1135 and 1070 cm^{-1}. That the configuration is the same in deuterochloroform solution can be inferred from the coupling constants ^3J(PtSCH) (ca. 15 Hz) in the ^{1}H NMR spectra. The observation of this coupling indicates the presence of *S*-bonded DMSO ligands [2], and its magnitude, which is substantially smaller than in *cis*-[PtCl$_2$(DMSO)$_2$] (23 Hz), shows that the ligand is *trans* to the high *trans* influence R ligands.

The complexes [PtR(Cl)(DMSO)$_2$] were obtained by use of K$_2$[PtCl$_4$] and SnMe$_3$R in equimolar proportions. These complexes have single bands in the IR spectra corresponding to ν(Pt—S) (420—418 cm^{-1}), ν(S—O) (1130—1120 cm^{-1}) and ν(Pt—Cl) (300—275 cm^{-1}), so they have *trans* configurations with Pt—S bonded DMSO ligands in the solid state. The ^{1}H NMR spectra in deuterochloroform are somewhat more complicated than those of the diorganoplatinum(II) complexes; the methyl protons of the DMSO ligands give rise to a broadened line split by ^{195}Pt (^3J(PtSCH) ca. 26 Hz) characteristic of *S*-bonded DMSO *trans* to a ligand of low *trans* influence, but less intense broad lines are also present in this region. It is evident that exchange processes, possibly involving *O*-bonded DMSO ligands [2], are occurring in these solutions, and we are investigating the phenomenon further.

The synthetic utility of reactions 1—3, which are involved in our procedures, is enhanced by the ease of displacement of the DMSO ligands by, for example,

$$\mathrm{K_2[PtCl_4]} + 2\,\mathrm{DMSO} \rightarrow cis\text{-}\mathrm{[PtCl_2(DMSO)_2]} + 2\mathrm{KCl} \qquad (1)$$

$$cis\text{-}\mathrm{[PtCl_2(DMSO)_2]} + \mathrm{SnMe_3R} \rightarrow trans\text{-}\mathrm{[PtR(Cl)(DMSO)_2]} + \mathrm{SnMe_3Cl} \qquad (2)$$

$$\mathrm{[PtR(Cl)(DMSO)_2]} + \mathrm{SnMe_3R} \rightarrow cis\text{-}\mathrm{[PtR_2(DMSO)_2]} + \mathrm{SnMe_3Cl} \qquad (3)$$

2,2′-bipyridyl, PPh_3, 1,2-bis(diphenylphosphino)ethane, $P(OPh)_3$, $AsPh_3$, and $SbPh_3$ to form the corresponding organoplatinum complexes of these ligands. These displacements may be carried out after isolation of the DMSO complex or directly on the mixture obtained from $K_2[PtCl_4]$ after removal of the excess of DMSO.

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