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THE REACTION BETWEEN $[Pt(cod)Cl(PMe_2Ph)]BF_4$ AND ARYLTRIMETHYLTIN COMPOUNDS *

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Summary

The complex $[Pt(cod)Cl(PMe_2Ph)]BF_4$ reacts in dichloromethane with $SnArMe_3$ compounds having Ar = 2-thienyl, 2-benzo[*b*]thienyl, or 2-benzo-[*b*]furyl to give air-stable cationic aryl complexes $[Pt(cod)Ar(PMe_2Ph)]BF_4$. No reaction takes place when Ar = Ph. The cod ligand in the new complexes can be readily replaced by ligands such as PMe_2Ph, dppe, or 4-dimethylaminopyridine. The ^1H and $^{31}P\text{-}\{^1H\}$ NMR parameters of the various complexes are reported.

Introduction

We recently described the reactions between aryltrimethyltin compounds and the complex $[Pt(cod)Cl_2]$ to give $[Pt(cod)(Ar)Cl]$ or $[Pt(cod)Ar_2]$, depending on the mol ratio of reagents used [1]. We showed that the rate of reaction increased with the ease of electrophilic substitution at the corresponding Ar—H bond, so that 2-thienyl- and 2-furyl-tin compounds, for example, were especially reactive. We have now examined the interaction of some aryltrimethyltin compounds with the cationic complex $[Pt(cod)Cl(PMe_2Ph)]BF_4$.

Results and discussion

The complex $[Pt(cod)Cl(PMe_2Ph)]BF_4$ reacted during a few hours' reflux in dichloromethane with $SnArMe_3$ compounds having Ar = 2-thienyl, 2-benzo[*b*]furyl, or 2-benzo[*b*]thienyl, to give the new complexes $[Pt(cod)Ar[PMe_2Ph)]BF_4$ (eq. 1). A small quantity of $Sn(BF_4)Me_3$ was obtained as a white precipi-

$$[Pt(cod)Cl(PMe_2Ph)]BF_4 + SnArMe_3 \rightarrow [Pt(cod)Ar(PMe_2Ph)]BF_4 + SnClMe_3 \quad (1)$$

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* No reprints available.

TABLE 1

$^1H^a$ AND $^{31}P\text{-}\{^1H\}$ NMR DATA FOR THE COMPLEXES $[PtR(PMe_2Ph)(cod)]X$

R	X	^1J(Pt—P) (Hz)	δ^b (ppm)	Olefin protons					Methylene protons τ (ppm)	Alkyl phosphorus protons			Aryl protons τ (ppm)
				trans-PR_3			*trans*-R			^3J-(Pt—PCH) (Hz)	^2J-(P—CH)^c (Hz)	τ-(P—CH_3) (ppm)	
				^3J-(P—PtCH) (Hz)	^2J-(Pt—CH) (Hz)	τ (Pt—CH) (ppm)	^2J-(Pt—CH) (Hz)	τ (Pt—CH) (ppm)					
2-C_4H_3S	BF_4	3459	145.9	2.5	51	4.20	40	4.59	7.0—7.6	42	12	8.20	2.2—3.5
2-C_8H_5O	BF_4	3450	145.3	2.5	48	4.22	41	4.64	7.1—7.6	42	12	8.10	2.2—3.8
2-C_8H_5S	BF_4	3440	146.3	2.5	49	4.19	41	4.57	7.1—7.6	42	12	8.05	2.2—3.5
2-C_8H_5S	ClO_4	3469	145.9	2.5	50	4.19	40	4.59	7.1—7.6	42	12	8.10	2.2—3.5
Cl	BF_4	2961	138.9	3.0	44.5	3.80	65	4.60	7.0—8.0	43	12	8.23	2.3—3.0

[a] Recorded in $CDCl_3$, except for R = Cl, for which CD_2Cl_2 was used. [b] Positive shifts are to high field of $(MeO)_3P$ in C_6D_6. Resolution 2.44 Hz. [c] Doublet separation. strictly $|^2J(P—CH) + ^4J(PPt—PCH)|$.

tate, indicating that some exchange occurs between the tetrafluoroborate complex and the chlorotrimethyltin formed, and in order to obtain analytically pure samples of the cationic complexes an excess of sodium tetrafluoroborate was added.

The $[Pt(cod)Ar(PMe_2Ph)]BF_4$ complexes are air-stable white solids, very soluble in polar organic solvents; the conductivities in nitromethane are as expected for 1/1 electrolytes. The one perchlorate salt isolated has similar properties. There is no band in the 340—250 cm^{-1} region of the IR spectra, confirming the absence of Pt—Cl bonds, but the characteristic bands of the counterions BF_4^- (1050s and 525ms cm^{-1}) and ClO_4^- (1100vs, 620s cm^{-1}) are present. The NMR parameters are listed in Table 1. In the ^1H NMR spectrum the olefin protons give two distinct resonances with platinum satellites, and the low field peak is further split by coupling to the phosphorus nucleus [^3J(PPt—CH 2.5 Hz)], and thus comes from the olefin protons *trans* to the phosphine ligand. The coupling constant ^2J(Pt—CH) is larger for the low field peak, which is consistent with the lower *trans* influence of a triorganophosphine than of an aryl ligand. The coupling constants ^1J(Pt—P) of the $[Pt(cod)Ar(PMe_2Ph)]BF_4$ complexes, viz. 3440—3460 Hz, are substantially larger than that for the $[Pt(cod)Cl(PMe_2Ph)]BF_4$ complex (2961 Hz); since the triorganophosphine ligand is *trans* to the olefin in all cases, the aryl groups clearly exert fairly large *cis*-influences.

Some reactions of the complexes $[Pt(cod)(2\text{-}C_4H_3S)(PMe_2Ph)]BF_4$ were studied by monitoring the changes in the $^{31}P\text{-}\{^1H\}$ NMR spectrum. It was found that the cod ligand can be readily displaced by other neutral or anionic ligands. Thus two molar proportions of PMe_2Ph reacted immediately in CD_2Cl_2 with $[Pt(cod)(2\text{-}C_4H_3S)(PMe_2Ph)]BF_4$ to give $[Pt(2\text{-}C_4H_3S)(PMe_2Ph)_3]BF_4$, the NMR spectrum of which shows the characteristic doublet and triplet sets of resonances. Similar use of dppe gave a complex central resonance of multiplicity 12 associated with an ABX spin system, and an intricate arrangement of platinum satellites consistent with the structure $[Pt(2\text{-}C_4H_3S)(dppe)(PMe_2Ph)]BF_4$. Even 4-dimethylaminopyridine readily effected the displacement at room temperature, to give $[Pt(2\text{-}C_4H_3S)(4\text{-}Me_2NC_5H_5N)_2(PMe_2Ph)]BF_4$. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of the solution obtained by treatment of $[Pt(cod)(2\text{-}C_4H_3S)(PMe_2Ph)]BF_4$ with an excess of Et_4NI in methanol containing a little water showed that the final products were $Et_4N[Pt(2\text{-}C_4H_3S)I_2(PMe_2Ph)]$, δ 157.0 ppm, ^1J(Pt—P) 4023 Hz and *trans*-$[Pt(C_4H_3S)I(PMe_2Ph)_2]$, δ 151.4 ppm, ^1J(Pt—P) 2583 Hz. In the reaction with Et_4NCl, *cis*-, δ 153.9 ppm, ^1J(Pt—P) 4507 Hz, and *trans*-$[Pt_2(2\text{-}C_4H_3S)_2Cl_2(PMe_2Ph_2)]$ δ 153.9 ppm, ^1J(Pt—P) 4578 Hz, were initially produced, but further reaction took place to give $Et_4N[Pt(2\text{-}C_4H_3S)Cl_2(PMe_2Ph)]$, δ 157.2 ppm, ^1J(Pt—P) 4263 Hz, and *trans*-$[Pt(2\text{-}C_4H_3S)Cl(PMe_2Ph)_2]$, δ 145.6 ppm, ^1J(Pt—P) 2651 Hz.

No detectable reaction took place when $[Pt(cod)Cl(PMe_2Ph)]BF_4$ was treated with the markedly less reactive tin compound $SnPhMe_3$, the complex being recovered almost quantitatively after prolonged refluxing in dichloromethane. When reaction of 100°C in *sym*-tetrachloroethane (which was very satisfactory for reactions between $[Pt(cod)Cl_2]$ and the less reactive $SnArMe_3$ compounds) was used, extensive decomposition occurred, and a little $[PtCl_2(PMe_2Ph)_2]$ was the only product isolated. The cationic complex $[Pt(cod)Cl(PMe_2Ph)]BF_4$ is thus markedly less reactive than the neutral $[Pt(cod)Cl_2]$ towards aryltin compounds. Since both reactions seem to involve electrophilic attack at the aryl—tin bond, the low reactivity of the cationic complex would not necessarily be expected, but it is consistent with the low reactivity of the olefin ligand in [Pt-(cod)Cl(PMe_2Ph)]BF_4 towards nucleophiles [2], and can be associated with the presence of a triorganophosphine ligand on platinum.

Experimental

Reactions of [Pt(cod)Cl(PMe_2Ph)]BF_4 with $ArSnMe_3$ compounds

2-Thienyltrimethyltin (0.57 g, 2.3 mmol) was added to a solution of [Pt(cod)-Cl(PMe_2Ph)]BF_4 (1.13 g, 2.0 mmol) (prepared as described in ref. 2) in dichloromethane (4.0 cm^3). The mixture was stirred for 14 h at room temperature, during which the solution went yellow and a white solid separated. The precipitate was filtered off, washed with benzene, and identified as Sn(BF_4)Me_3 (0.08 g). The filtrate was evaporated under vacuum, and the residual oil was washed with pentane (15 cm^3) to remove some $SnClMe_3$. The residue was recrystallized twice from $CHCl_3/Et_2O$ to give pale-yellow crystals of 2-thienyl(cycloctadiene)-(dimethylphenylphosphine)platinum(II) tetrafluoroborate (0.84 g, 69%), m.p. 150—152°C (decomp.), $\nu(BF_4)$ 1050vs, 530m cm^{-1}, molar conductance, Λ, in $MeNO_2$ (measured on ca. 10^{-3} *M* solution) 104 ohm^{-1} cm^2 mol^{-1} (Found: C, 39.0; H, 4.2. $C_{20}H_{26}BF_4PPtS$ calcd.: C, 39.3; H, 4.3%).

A similar procedure gave the other [Pt(cod)Ar(PMe_2Ph)]BF_4 complexes, with properties as follows: (a) Ar = 2-benzo[*b*]furyl, m.p. 179—183°C (decomp.), Λ 109 ohm^{-1} cm^2 mol^{-1} (Found: C, 44.7; H, 4.3. $C_{24}H_{28}BF_4OPPt$ calcd.: C, 44.7; H, 4.4%). (b) Ar = 2-benzo[*b*]thienyl, m.p. 152—160°C (decomp.), Λ 100 ohm^{-1} cm^2 mol^{-1} (Found: C, 43.1; H, 4.0. $C_{24}H_{28}BF_4PPtS$ calcd.: 43.1; H, 4.3%).

Preparation of [Pt(cod)(2-thienyl)(PMe_2Ph)]ClO_4

A suspension of [Pt(cod)(2-thienyl)(PMe_2Ph)]BF_4 (0.1 g, 0.16 mmol) and sodium perchlorate (0.3 g, 2.4 mmol) in acetone (15 cm^3) was stirred overnight at room temperature then filtered. The solvent was removed under vacuum, and the residual oil dissolved in chloroform. Addition of ether gave [Pt(cod)(2-thienyl)-(PMe_2Ph)]ClO_4 (0.095 g, 93%), m.p. 131°C (decomp.); $\nu(ClO_4)$ 1100vs, 620s, cm^{-1}; Λ 94 ohm^{-1} cm^2 mol^{-1} (Found: C, 38.5; H, 4.2. $C_{20}H_{26}ClO_4PPtS$ calcd.: C, 38.5; H, 4.2%).

Displacement of (cod) from [Pt(cod)(2-thienyl)(PMe_2Ph)]BF_4

When 2 molar proportions of PMe_2Ph were added to [Pt(cod)(C_4H_3S-2)-(PMe_2Ph)]BF_4 in CD_2Cl_2 the ^{31}P-{^1H} NMR spectrum showed clean conversion into [Pt(C_4H_3S-2)$(PMe_2Ph)_2$]BF_4: δ (relative to $(MeO)_3P$) 157.3 ppm, ^1J(Pt—P) 2036 Hz (P *trans* to Ar); 147.9 ppm, ^1J(Pt—P) 2461, ^2J(Pt—P) 22 Hz (P *trans* to PMe_2Ph).

Similarly, one molar proportion of $Ph_2PCH_2CH_2PPh_2$(dppe) gave [Pt(C_4H_3S-2)-(PMe_2Ph)(dppe)]BF_4 (see main text) while an excess of 4-dimethylaminopyridine gave [Pt(C_4H_3S-2)$(4\text{-}Me_2NC_5H_4N)_2$($PMe_2Ph$)]$BF_4$, δ 158.8 ppm, ^1J(Pt—P) 3658 Hz.

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References

1 C. Eaborn, K.J. Odell and A. Pidcock, J. Organometal. Chem., 96 (1975) C38; J. Chem. Soc. Dalton, in press.
2 C. Eaborn, N. Farrell and A. Pidcock, J. Chem. Soc. Dalton, (1976) 289.