The Reaction between *cis*-Bis(trifluoroacetato)bis(triorganophosphine)-platinum(II) and Tetraorganotin Compounds †

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The complex *cis*-[$Pt(O_2CCF_3)_2L_2$] (L = PMe_2Ph) reacts with $SnRMe_3$ compounds (R = aryl) to give *trans*-[$PtR(O_2CCF_3)L_2$] and *cis*-[PtR_2L_2], except for the sterically hindered mesityltrimethyltin which gives mainly *trans*-[$PtMe(O_2CCF_3)L_2$]. The latter is also the main product from $SnMe_3(CH_2Ph)$. For L = PPh_3, $SnMe_3Ph$, and $SnMe_3(C_6H_4Me$-*p*) give mainly *cis*-[$PtMe(O_2CCF_3)L_2$]. For L = PMe_2Ph, $SnMe_4$ gives only *trans*-[$PtMe(O_2CCF_3)L_2$], but, for L = PPh_3, *cis*-[$PtMe_2L_2$] is also formed. The most reactive tin compound used, trimethyl-(2-thienyl)tin, readily reacts with *cis*-[$Pt(O_2CCF_3)_2L_2$] (L = PMe_2Ph or PEt_2Ph) or [$Pt(cod)(O_2CCF_3)_2$] to give exclusively *cis*-[$Pt(C_4H_3S$-$2)_2L_2$] or [Pt(cod)(C_4H_3S-$2)_2$]. ^{31}P-{^1H} N.m.r. parameters are given.

We have previously described the reactions of some organotin compounds, notably aryltrimethyltins, with the chloroplatinum(II) complexes (L = triorganophosphine; cod = cyclo-octa-1,5-diene) [$Pt(cod)Cl_2$],[1,2] *cis*-[$Pt(C_2H_4)Cl_2L$],[3] *cis*-[$Pt(CO)Cl_2L$],[3] *trans*-[$Pt(CO)(Cl)L_2$][ClO_4],[4] and [$Pt(cod)Cl(PMe_2Ph)$][BF_4].[5] We now present the results of a study of the reaction between the tetraorganotin compounds and the trifluoroacetato-complexes *cis*-[$Pt(O_2CCF_3)_2L_2$], which, in contrast with *cis*-[$PtCl_2L_2$] complexes,[2] are readily converted by the organotin compounds into organoplatinum species.

RESULTS AND DISCUSSION

Heating a suspension of *cis*-[$Pt(O_2CCF_3)_2(PMe_2Ph)_2$] under reflux in benzene containing an excess of tetramethyltin for 4 h gave a 90% yield of *trans*-[$PtMe(O_2CCF_3)(PMe_2Ph)_2$]. The presence of only one signal (with satellites) in the ^{31}P-{^1H} n.m.r. spectrum of the product indicated a *trans* configuration, and this was confirmed by the appearance of a triplet for the PMe protons at τ 8.33 in the ^1H n.m.r. spectrum. [A 1 : 2 : 1 triplet at τ 9.82 is assigned to PtMe, the multiplicity arising from equal coupling to both *trans* ^{31}P nuclei; the value of the coupling constant ^2J(PtCH), *viz.* 85 Hz, is consistent with the presence of a ligand of low *trans* influence *trans* to the methyl group.] The i.r. spectrum contains bands at 1 690 and 1 417 cm^{-1} characteristic of the unidentate trifluoroacetate ligand.[6]

In the reactions of other $SnRMe_3$ compounds the products were not isolated, but were identified in the reaction mixture by means of ^{31}P-{^1H} n.m.r. spectroscopy. In each case, *cis*-[$Pt(O_2CCF_3)_2L_2$] (*ca.* 0.05 g) was treated with a large excess (*ca.* 0.3 cm^3) of the $SnRMe_3$ compound, usually in dichloromethane (1 cm^3) but sometimes in benzene (1 cm^3). Reaction times are shown in Table 1, but disappearance of the *cis*-[$Pt(O_2CCF_3)_2L_2$] may have been complete in a shorter time. The approximate compositions of the product mixtures shown in Table 1 reflect the peak heights of the relevant lines in the ^{31}P-{^1H} n.m.r. spectrum. The products *cis*-[PtR_2L_2] (R = Me or aryl) were identified by comparison of the ^{31}P-{^1H} n.m.r. spectra with those of authentic samples obtained from the [$Pt(cod)R_2$] complexes by addition of the phosphine L.[2] The products *trans*-[$PtR(O_2CCF_3)L_2$] (R = Me, aryl, or CH_2Ph) were identified by adding lithium chloride or tetraethylammonium chloride to the product solution to give the corresponding chlorides *trans*-[$PtR(Cl)L_2$], and comparing the resulting ^{31}P-{^1H} n.m.r. spectral parameters with those of authentic samples obtained from [Pt(cod)R(Cl)] [2] by addition of the phosphine L.

TABLE 1

Products from the interaction of *cis*-[$Pt(O_2CCF_3)_2L_2$] (1) and $SnRMe_3$ compounds: *trans*-[$PtMe(O_2CCF_3)L_2$] (2), *cis*-[$PtMe_2L_2$] (3), *trans*-[$PtR(O_2CCF_3)L_2$] (4), *cis*-[PtR_2L_2] (5)

		Conditions [a]		Product composition (%) [b]				
L	R	θ_c/°C	*t*/h	(1)	(2)	(3)	(4)	(5)
PMe_2Ph	Ph	20	9				38	62
	C_6H_4OMe-*o*	20	12				35	65
	C_6H_4F-*m*	80 [c]	4				49	51
	C_6H_4OMe-*p*	80 [c]	2				78	12
	C_4H_3S-2	20	2					100
	$C_6H_2Me_3$-2,4,6	20	100	6	77		17	
	Me	80 [c]	10		100			
	CH_2Ph	20	15		100			
	CH_2Ph	80 [c]	24		60		40	
PEt_2Ph	C_4H_3S-2	20	2					100
PPh_3	Ph	20	9	83	17			
	C_6H_4Me-*p*	20	23		85		15	
	Me	20	18		70	30		
½ cod	C_6H_4OMe-*p*	20	3					100 [d]

[a] In CH_2Cl_2 unless otherwise stated. [b] Composition derived from peak heights in ^{31}P-{^1H} n.m.r. spectra. [c] In benzene under reflux. [d] Spectrum recorded after addition of dppe.

In reactions with *cis*-[$Pt(O_2CCF_3)_2L_2$] complexes (L = PMe_2Ph or PEt_2Ph), the most reactive aryltin compound used, trimethyl(2-thienyl)tin gave the diaryl complex *cis*-[$Pt(C_4H_3S$-$2)_2L_2$] as the sole phosphine-containing species in <2 h at room temperature. Less active $SnRMe_3$ (R = aryl) compounds gave mixtures of mono- and di-aryl complexes, *trans*-[$PtR(O_2CCF_3)L_2$] and *cis*-[PtR_2L_2] (Table 1), except that the sterically hindered mesityltin compound gave mainly the methyl complex *trans*-[$PtMe(O_2CCF_3)L_2$] together with some of the aryl complex *trans*-[$Pt(C_6H_2Me_3$-2,4,6)($O_2CCF_3)L_2$]. Benzyltrimethyltin in dichloromethane at room temperature gave exclusively the methyl complex *cis*-[$PtMe(O_2CCF_3)L_2$], but in refluxing benzene this and the

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TABLE 2

^{31}P-{^{1}H} N.m.r. parameters for *trans*-[PtR(O_2CCF_3)L_2] and *cis*-[PtR_2L_2] complexes [a]

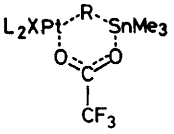
Complex	R	L	δ/ p.p.m. [b]	^1J (Pt–P)/ Hz
trans-[PtR(O_2CCF_3)L_2]				
	Me	PMe_2Ph	139.3	2 988
	CH_2Ph		142.6 [c]	2 956 [c]
	Et		139.2	3 179
	C_4H_3S-2		152.8	2 888
	Ph		142.7	2 954
	C_6H_4OMe-*p*		142.7 [c]	2 942 [c]
	C_6H_4OMe-*o*		143.7	2 915
	C_6H_4F-*m*		145.7 [c]	2 817 [c]
	Me	PPh_3	110.9	3 230
	C_6H_4Me-*p*		117.6	3 224
cis-[PtR_2L_2]				
	Ph	PMe_2Ph	155.6	1 751
	C_6H_4OMe-*o*		156.1	1 951
	C_6H_4F-*m*		155.9	1 809
	C_6H_4OMe-*p*		155.1	1 762
	C_4H_3S-2	PEt_2Ph	138.2	2 024
	Me	PPh_3	112.7	1 899
	C_6H_4OMe-*p*	½ dppe	99.3	1 721

[a] In $CHCl_2$ except where indicated. [b] Relative to external $P(OMe)_3$ in CH_2Cl_2; positive values are to high field of the reference. [c] In PhH.

benzyl complex *cis*-[Pt(CH_2Ph)(O_2CCF_3)L_2] were found in 3 : 2 ratio.

Aryl transfer from tin to platinum is markedly less effective for L = PPh_3; treatment of *cis*-[Pt(O_2CCF_3)$_2$(PPh_3)$_2$] with $SnMe_3Ph$ at room temperature for 9 h gives solely the monomethyl complex *trans*-[PtMe(O_2CCF_3)(PPh_3)$_2$] (in 17% yield), whereas under the same conditions *cis*-[Pt(O_2CCF_3)$_2$(PMe_2Ph)$_2$] undergoes complete conversion into *cis*-[PtPh(O_2CCF_3)(PMe_2Ph)$_2$] and *trans*-[PtPh_2(PMe_2Ph)$_2$]. Even trimethyl(*p*-tolyl)tin gives mainly *trans*-[PtMe(O_2CCF_3)(PPh_3)$_2$] together with some *trans*-[Pt(C_6H_4Me-*p*)(O_2CCF_3)(PPh_3)$_2$]. In contrast, towards tetramethyltin the triphenylphosphine complex *cis*-[Pt(O_2CCF_3)$_2$(PPh_3)$_2$] is more reactive than the corresponding PMe_2Ph complex in the sense that it gives the dimethyl complex *cis*-[PtMe_2(PPh_3)$_2$] together with *trans*-[PtMe(O_2CCF_3)(PPh_3)$_2$]. The low reactivity of the triphenylphosphine complexes towards aryltin compounds and their preference for accepting Me rather than aryl groups can reasonably be attributed to steric hindrance.

The sequence of ease of transfer of R groups from $SnRMe_3$ compounds to platinum in reactions with *cis*-[Pt(O_2CCF_3)$_2$(PMe_2Ph)$_2$], *viz.* (R =) C_4H_3S-2 > C_6H_4X > Me, and CH_2Ph, is consistent with regarding the reaction as involving electrophilic attack on the carbon atom of the Sn–R bond, as suggested for the reaction between $SnRMe_3$ (R = aryl) compounds and [Pt(cod)Cl_2]. However, the much greater reactivity of *cis*-[Pt(O_2CCF_3)$_2L_2$] than of *cis*-[PtCl_2L_2] complexes (L = PMe_2Ph) suggests that there may be a cyclic transition state of the type (A); the bond makings and breakings need not be fully synchronous, and so there could still be substantial Wheland-intermediate character for R = aryl. The results in Table 1 indicate that replacement of the first trifluoroacetate ligand of *cis*-[Pt(O_2CCF_3)$_2L_2$] by the R group is normally substantially faster than that of the second. We tentatively suggest that *cis*-[PtR(O_2CCF_3)L_2] is initially produced, and can either (*a*) react with further $SnRMe_3$ to give *cis*-[PtR_2L_2] or (*b*) isomerize to *trans*-[PtR(O_2CCF_3)L_2], which then reacts only very slowly with $SnRMe_3$. Further work would be needed to establish this.



(A)

The reaction of tetraethyltin with *cis*-[Pt(O_2CCF_3)$_2L_2$] (L = PMe_2Ph) in dichloromethane was also examined. After 24 h at room temperature the ^{31}P-{^{1}H} n.m.r. spectra showed the presence of only one phosphine-containing species, with δ 139.2 p.p.m., ^1J(Pt–P) 3 179 Hz. This was identified as *trans*-[PtEt(O_2CCF_3)L_2] by (*i*) comparison of the spectrum with that of a solution obtained by treatment of *trans*-[PtEt(Cl)L_2] [2] with silver(I) trifluoroacetate,[7] and (*ii*) by addition of [NEt_4]Cl to the product solution to give a spectrum [δ 142.3 p.p.m., ^1J(Pt–P) 3 071 Hz] identical with that of *trans*-[PtEt(Cl)L_2]. Because of its high solubility in the common organic solvents the product could not be isolated crystalline.

As expected, the cod complex [Pt(cod)(O_2CCF_3)$_2$] was found to be very reactive towards organotin compounds, and thus treatment with $SnMe_3$(C_6H_4OMe-*p*) in dichloromethane at room temperature for 3 h gave the diaryl complex [Pt(cod)(C_6H_4OMe-*p*)$_2$] in 100% yield; formation of this product from [Pt(cod)Cl_2] required refluxing in this solvent for several hours.[2]

The high reactivity of *cis*-[Pt(cod)(O_2CCF_3)] led us to hope that it might react usefully with tetraorganosilanes, so the complex was treated with $SiMe_3$(C_6H_4OMe-*p*) in *sym*-dichloromethane for 10 h, and with $SiMe_3$(C_4H_3S-2) in chloroform for 0.5 h. In each case the only product isolated was [Pt(cod)Cl_2], and addition of 1,2-bis(diphenylphosphino)ethane (dppe) to the product solution and examination of the ^{31}P-{^{1}H} n.m.r. spectrum [δ 98.7 p.p.m., ^1J(Pt–P) 3 621 Hz] showed [PtCl_2(dppe)] to be the only phosphine-containing product present. The chloride ligands must have come from the solvent, and reactions in non-chlorinated solvents have yet to be examined.

Sodium tetraphenylborate was found to be more effective than aryltrimethyltin compounds in arylating platinum in *cis*-[Pt(O_2CCF_3)$_2L_2$] (L = PPh_3). When the complex was treated with a large excess of Na[BPh_4] in dichloromethane–tetrahydrofuran for 12 h at 25 °C the ^{31}P-{^{1}H} n.m.r. spectrum of the solution indicated that *ca.* 90% of *trans*-[PtPh(O_2CCF_3)L_2] [δ 117.0 p.p.m., ^1J(Pt–P) 3 213 Hz] had been formed together with *ca.* 10% of *trans*-[PtPh(Cl)L_2] [δ 115.6 p.p.m., ^1J(Pt–P) 3 157 Hz]. The spectrum did not change after another

2 d, but addition of sodium chloride caused conversion of all the *trans*-$[PtPh(O_2CCF_3)L_2]$ into *trans*-$[PtPh(Cl)L_2]$. The formation of the complex $[PtPh(Cl)L_2]$ in the reaction mixture can be accounted for by assuming that the commercial sample of $Na[BPh_4]$ used contained $\geqslant 1\%$ of NaCl.

EXPERIMENTAL

Dried deoxygenated solvents were used, and reactions were carried out under dry nitrogen.

Preparation of Complexes cis-$[Pt(O_2CCF_3)_2L_2]$.[8]—(*i*) An excess of trifluoroacetic acid (1.5 cm³) was added to a solution of $[Pt(CO_3)(PMe_2Ph)_2]$ (2.5 g, 4.7 mmol) in dichloromethane (60 cm³). The mixture was boiled under reflux for 2.5 h, then set aside at room temperature overnight. The solvent was removed, and diethyl ether (10 cm³) added to give a white solid, which was filtered off, washed with diethyl ether, dried *in vacuo*, and shown to be cis-*bis*(*dimethylphenylphosphine*)*bis*(*trifluoroacetato*)*platinum*(II) (3.1 g, 95%).

TABLE 3

Yields, analyses, and physical constants for complexes $[Pt(O_2CCF_3)_2L_2]$

			Analysis(%)								
			Found		Calc.		$\nu(OCO)/cm^{-1}$ [a]		^{31}P-{^1H} n.m.r. [b]		
Complex	Yield(%)	M.p. (θ_c/°C)	C	H	C	H	asym	sym	δ/p.p.m.	$^1J(Pt{-}P)$/ Hz	Notes
cis-$[Pt(O_2CCF_3)_2(PMe_2Ph)_2]$	95	168—172	34.6	3.4	34.4	3.2	1 692	1 412	161.5	3 770	*c*
cis-$[Pt(O_2CCF_3)_2(PEt_2Ph)_2]$	85	162	38.3	4.0	38.3	4.0	1 694	1 408	143.3	3 765	
cis-$[Pt(O_2CCF_3)_2(PPh_3)_2]$	90	*d*	50.4	4.1	50.8	3.2	1 692	1 412	136.1	3 938	*e*
trans-$[Pt(O_2CCF_3)_2(PPh_3)_2]$	80	190—230	50.2	3.0	50.8	3.2	1 724	1 405	126.3	2 815	
cis-$[Pt(cod)(O_2CCF_3)_2]$	70	135—155	26.8	2.7	27.2	2.3	1 700	1 406			*f*

[a] In Nujol. [b] In CH_2Cl_2 relative to external $P(OMe)_3$. [c] ^1H N.m.r., τ 8.45 [d, PMe, $^2J(PCH)$ 11.5, $^3J(PtPCH)$ 35 Hz]. [d] Lit.,[8] m.p. 230—235 °C. [e] Product contained some *cis*-isomer. [f] ^1H N.m.r., τ 7.3 (m, CH_2CH_2), 4.33 [t, CH=CH, $^2J(PCH)$ 67.5 Hz]. Weak $\nu(OCO)_{asym}$ bands at 1 570 and 1 710 cm⁻¹ and weak $\nu(OCO)_{sym}$ bands at 1 387 and 1 230 cm⁻¹ are attributed to $[Pt_2(O_2CCF_3)_2(C_8H_{12}{\cdot}CO_2CF_3)_2]$ impurity, which also gives rise to a weak ^1H n.m.r. multiplet at τ 7.7—8.7.

(*ii*) The corresponding complexes with L = PPh_3 and PEt_2Ph were prepared analogously. Analyses and physical constants for all three complexes are given in Table 3, which also gives data for *trans*-$[Pt(O_2CCF_3)_2(PPh_3)_2]$, which was obtained, contaminated with a little of the *cis* isomer, by refluxing a dichloromethane solution of *cis*-$[PtCl_2(PPh_3)_2]$ for 6 h with a small excess of silver(I) trifluoroacetate.

(*iii*) A mixture of $Ag[O_2CCF_3]$ (1.4 g, 6.5 mmol), $[Pt(cod)Cl_2]$ (1.1 g, 2.9 mmol), and dichloromethane (20 cm³) was boiled under reflux for 6 h with protection from light. The mixture was filtered, and the filtrate reduced in volume to *ca.* 5 cm³. Addition of diethyl ether gave colourless needles of (*cyclo-octa*-1,5-*diene*)*bis*(*trifluoroacetato*)*platinum*(II) (1.05 g, 68%). The i.r. and ^1H n.m.r. spectra indicated that a small quantity of $[Pt_2(O_2CCF_3)_2(C_8H_{12}{\cdot}CO_2CF_3)_2]$ was also present (see Table 3), having been formed by attack of the carboxylate ion at the olefinic bond.[9]

Preparation of trans-$[PtMe(O_2CCF_3)(PMe_2Ph)_2]$.—A suspension of *cis*-$[Pt(O_2CCF_3)_2(PMe_2Ph)_2]$ (0.25 g, 0.36 mmol) in benzene (10 cm³) containing an excess of tetramethyltin (0.5 cm³) was heated under reflux for 5 h then set aside overnight. The solvent was removed *in vacuo*, and the residual waxy solid dissolved in warm diethyl ether (7 cm³). Addition of pentane followed by cooling gave white plates of *bis*(*dimethylphenylphosphine*)*methyl*(*trifluoroacetato*)*platinum*(II) (0.195 g, 90%), m.p. 103—108 °C; $\nu(OCO)_{asym}$ at 1 690 cm⁻¹, $\nu(OCO)_{sym}$ at 1 417 cm⁻¹; τ($CDCl_3$) 9.81 [t, PtMe, $^2J(PtCH)$ 83, $^3J(PPtCH)$ 7.0 Hz], 8.33 [t, PMe, $|^2J(PCH) + {}^4J(PPtPCH)|$ 6.9, $^3J(PPtCH)$ 29.5 Hz], 2.38—2.68 (m, C_6H_5) (Found: C, 37.6; H, 4.2. $C_{19}H_{25}F_3O_2P_2Pt$ requires C, 38.1; H, 4.2%). The ^{31}P-^{1}{H} n.m.r. data are given in Table 2.

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