Reactions of Pentafluorophenyl(ylide)-silver(I) or -gold(I) Complexes with Chlorobis(pentafluorophenyl)thallium(III)

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Chlorobis(pentafluorophenyl)thallium(III) reacts with silver–ylide complexes $[Ag(C_6F_5)(CH_2ER_3)]$ ($ER_3 = PPh_3$, PPh_2Me, $PPhMe_2$, or $AsPh_3$) to give AgCl and $[Tl(C_6F_5)_3(CH_2ER_3)]$, whereas the reactions with gold–ylide complexes, $[Au(C_6F_5)(CH_2PR_3)]$, lead to gold(III) complexes of the types *trans*-$[Au(C_6F_5)_2Cl(CH_2PR_3)]$ and $[Au(CH_2PR_3)_2][Au(C_6F_5)_4]$ which have been isolated and characterized.

We have recently reported the first observed phosphorus ylide transfer reactions from one gold(I) centre to another gold(I) or gold(III) centre.[1] Furthermore, we have studied ylide transfer reactions from a silver centre to other silver or gold centres.[2] Therefore, these previously unprecedented ylide transfer reactions seem to be more general than was anticipated. In the present paper, we report more ylide (phosphorus or arsenic) transfer reactions between different metal centres, namely, from a silver centre, $[Ag(C_6F_5)(CH_2ER_3)]$ ($ER_3 = PPh_3$, PPh_2Me, $PPhMe_2$, or $AsPh_3$), to a thallium one, $[Tl(C_6F_5)_2Cl]$, accompanied by the simultaneous transfer of the C_6F_5 group.

The analogous ylide complexes of gold(I), $[Au(C_6F_5)(CH_2PR_3)]$, behave differently: they undergo oxidation to $[Au(C_6F_5)_2Cl(CH_2PR_3)]$ and partial oxidation along with ligand rearrangement to give $[Au(CH_2PR_3)_2][Au(C_6F_5)_4]$.

The only previously known ylide complexes of thallium were $[TlMe_3(CH_2PMe_3)]$,[3] $[\overline{TlMe_2(CH_2PMe_2NPMe_2C}H_2)]$,[4] and $[Me_2P(CH_2TlMe_2CH_2)_2PMe_2]$.[5]

Results and Discussion

The room temperature reaction between $[Tl(C_6F_5)_2Cl]$ and $[Ag(C_6F_5)(CH_2ER_3)]$ in diethyl ether or chloroform solution takes place readily, AgCl being precipitated [equation (1)]

$$[Tl(C_6F_5)_2Cl] + [Ag(C_6F_5)(CH_2ER_3)] \longrightarrow AgCl + \underset{(1)-(4)}{[Tl(C_6F_5)_3(CH_2ER_3)]} \quad (1)$$

[$ER_3 = PPh_3$ (**1**), PPh_2Me (**2**), $PPhMe_2$ (**3**), or $AsPh_3$ (**4**)]. Complexes (**1**)—(**4**) are air- and moisture-stable white solids. They are soluble in acetone (non-conducting), dichloromethane, chloroform (monomeric, isopiestic method), and diethyl ether and insoluble in aliphatic hydrocarbons. Their i.r. spectra show a band at 636—603 cm^{-1} (Table 1) which we assign to ν(Tl–C, ylidic), by analogy with previous observations on gold–ylide complexes.[6,7]

Table 2 gives the ^1H and ^{31}P n.m.r. ($CDCl_3$) data. The chemical shifts and J(P–H) values are similar to those found[1] for $[Au(C_6F_5)_3(CH_2PR_3)]$. The coupling constants J(Tl–P) are similar to those published for thallium–ylide complexes,[3–5] but the values of J(P–H) are noticeably larger.

Complex (**1**) can also be prepared by a similar process to that previously used in the preparation[6] of gold–ylide complexes [equation (2)], albeit in lower yield (60%) with the need for a longer reaction time (3 d). Reaction of $Q[Tl(C_6F_5)_3I]$ ($Q = PPh_2Me_2$ or $PPhMe_3$) with NaH leads to intractable mixtures which do not include complexes (**2**) or (**3**) as can be concluded from the ^1H n.m.r. spectra. The organothallate starting material, $Q[Tl(C_6F_5)_3X]$ [$Q = PPh_3Me$, $X = Br$ (**5**); $Q = PPh_2Me_2$, $X = I$ (**6**), or $Q = PPhMe_3$, $X = I$ (**7**)], can be prepared by reaction of the 1,4-dioxane adduct $[Tl(C_6F_5)_3(diox)]$ with the corresponding QX. Complexes (**5**)—(**7**) are white solids which behave as 1:1 electrolytes in acetone solution.

$$[PPh_3Me][Tl(C_6F_5)_3Br] + NaH \longrightarrow [Tl(C_6F_5)_3(CH_2PPh_3)] + NaBr + H_2 \quad (2)$$

The reactions of gold–ylide complexes with $[Tl(C_6F_5)_2Cl]$ follow a different pattern to those of silver [equation (3)] [$PR_3 = PPh_3$ for (**8**) and (**11**), PPh_2Me for (**9**) and (**12**), or $PPhMe_2$ for (**10**) and (**13**)], which also differs from the commonly observed oxidative addition to the gold(I) centre by transfer of the two C_6F_5 groups and precipitation of TlCl.[8,9] In the present case [equation (3)], part of the thallium reagent appears as soluble $[Tl(C_6F_5)_3]$, which can be recovered in the form of the dioxane adduct $[Tl(C_6F_5)_3(diox)]$ after removal by filtration of the precipitated TlCl and subsequent crystallization of the two major reaction products, the neutral complex and the ionic salt.

$$[Tl(C_6F_5)_2Cl] + [Au(C_6F_5)(CH_2PR_3)] \longrightarrow TlCl + [Tl(C_6F_5)_3] + \underset{(8)-(10)}{trans\text{-}[Au(C_6F_5)_2Cl(CH_2PR_3)]} + \underset{(11)-(13)}{[Au(CH_2PR_3)_2][Au(C_6F_5)_4]} \quad (3)$$

The different reaction paths observed for the gold or silver complexes respectively [equations (1) and (3)] could be due to the greater difficulty in oxidizing silver(I) to higher oxidation states and/or the ready precipitation of silver chloride.

Complexes (**8**)—(**10**) can be isolated (see Experimental section) as white solids, which are slightly soluble or insoluble in chloroform and diethyl ether and soluble in acetone (non-conducting). Only complex (**9**) is sufficiently soluble in chloroform for molecular weight determination (monomeric). The ^{19}F n.m.r. spectra of complexes (**8**)—(**10**) show in, each case, only three resonances (Table 2), therefore the two C_6F_5 groups are mutually *trans*. In the ^1H n.m.r. spectra the protons of the methylene group resonate as doublets at lower field [3.18 (**8**), 2.94 (**9**), and 2.95 p.p.m. (**10**)] than in the corresponding *cis* isomers (2.61, 2.21, and 1.9, respectively) recently reported by us.[1] The observation that the *cis* resonance appears at lower field when the CH_2 group is *trans* to chlorine rather than to C_6F_5 has also been made in the gold(I) derivatives $[AuCl(CH_2PPh_3)]$ and $[Au(C_6F_5)(CH_2PPh_3)]$.[6,7]

The i.r. spectra of complexes (**8**)—(**10**) show a strong band at *ca.* 310 cm^{-1} assignable to ν(Au–Cl) as well as another

Table 1. Physical data for the complexes

Complex	Yield (%)	Analysis^a/%			$\Lambda_M{}^b$/ ohm^{-1} cm^2 mol^{-1}	$M^{a,c}$	M.p./ °C	I.r./cm^{-1}	
		C	H	Au				ν(M–C)	ν(Au–Cl)
(**1**) $[Tl(C_6F_5)_3(CH_2PPh_3)]$	75	45.4 (45.3)	1.9 (1.75)		3	1 020 (982)	242 (decomp.)	625	
(**2**) $[Tl(C_6F_5)_3(CH_2PPh_2Me)]$	74	42.0 (41.8)	1.6 (1.6)		1	898 (920)	151	636	
(**3**) $[Tl(C_6F_5)_3(CH_2PPhMe_2)]$	80	38.2 (37.8)	1.65 (1.5)		0	878 (858)	117	620	
(**4**) $[Tl(C_6F_5)_3(CH_2AsPh_3)]$	82	43.5 (43.3)	1.9 (1.7)		1	1 057 (1 026)	189	603	
(**5**) $[PPh_3Me][Tl(C_6F_5)_3Br]$	90	41.8 (41.8)	1.7 (1.7)		91		117		
(**6**) $[PPh_2Me_2][Tl(C_6F_5)_3I]$	87	36.8 (36.7)	1.6 (1.55)		96		99		
(**7**) $[PPhMe_3][Tl(C_6F_5)_3I]$	92	32.75 (32.9)	1.6 (1.45)		96		92		
(**8**) $[Au(C_6F_5)_2Cl(CH_2PPh_3)]$	46	43.9 (44.2)	2.3 (2.2)	23.7 (23.4)	0	*d*	239 (decomp.)	600	318
(**9**) $[Au(C_6F_5)_2Cl(CH_2PPh_2Me)]$	38	39.75 (40.0)	2.1 (1.95)	24.9 (25.2)	1	816 (781)	217 (decomp.)	592	309
(**10**) $[Au(C_6F_5)_2Cl(CH_2PPhMe_2)]\cdot Me_2CO$	49	37.3 (37.1)	2.8 (2.45)	25.7 (25.35)	2	*d*	308 (decomp.)	563	305br
(**11**) $[Au(CH_2PPh_3)_2][Au(C_6F_5)_4]$	42	46.0 (46.1)	2.3 (2.1)	24.35 (24.4)	81		158	580, 562	
(**12**) $[Au(CH_2PPh_2Me)_2][Au(C_6F_5)_4]$	33	41.6 (41.9)	2.2 (2.05)	26.55 (26.4)	73		120	542, 552	
(**13**) $[Au(CH_2PPhMe_2)_2][Au(C_6F_5)_4]$	32	36.65 (36.9)	2.0 (1.9)	28.5 (28.85)	90		193 (decomp.)	560	

[a] Calculated values in parentheses. [b] In acetone. [c] In chloroform. [d] Not soluble enough for molecular weight determination.

Table 2. N.m.r. data for the complexes (δ in p.p.m., *J* in Hz, solvent $CDCl_3$ unless otherwise stated)

Complex	^1H						^{31}P		^{19}F			
	δ(CH_2)	^2J(TlH)	^2J(PH)	δ(Me)	^2J(PH)	^4J(TlH)	δ	^2J(TlP)	$\delta_{ortho}{}^a$	$\delta_{meta}{}^a$	$\delta_{para}{}^b$	*J*(FF)
(**1**) $[Tl(C_6F_5)_3(CH_2PPh_3)]$	2.33	320.6	13.3				35.93	312.0				
(**2**) $[Tl(C_6F_5)_3(CH_2PPh_2Me)]$	2.14	310.4	13.3	2.17	13.2		28.04	286.2				
(**3**) $[Tl(C_6F_5)_3(CH_2PPhMe_2)]$	1.84	319.0	13.3	1.88	13.1	5.9	27.78	313.1				
(**4**) $[Tl(C_6F_5)_3(CH_2AsPh_3)]$	2.47	278.0										
(**8**) $[Au(C_6F_5)_2Cl(CH_2PPh_3)]$	3.18		11.6				29.07		−122.75	−168.83	−159.70	19.9
(**9**) $[Au(C_6F_5)_2Cl(CH_2PPh_2Me)]$	2.94		11.53	2.38	13.4		24.50		−123.03	−162.18	−159.02	19.7
(**10**) $[Au(C_6F_5)_2Cl(CH_2PPhMe_2)]^c$	2.95		12.48	2.23	14.05		29.14		−121.15	−162.38	−159.82	19.6
(**11**) $[Au(CH_2PPh_3)_2][Au(C_6F_5)_4]$	1.70		12.94				32.12		−122.09	−164.78	−162.19	19.8
(**12**) $[Au(CH_2PPh_2Me)_2][Au(C_6F_5)_4]$	1.42		12.7	2.00	12.94		28.09		−122.12	−164.56	−161.86	19.8
(**13**) $[Au(CH_2PPhMe_2)_2][Au(C_6F_5)_4]$	1.22		12.69	1.89	13.0		27.35		−122.18	−164.45	−161.61	20.0

[a] Multiplet. [b] Triplet. [c] In $(CD_3)_2CO$.

absorption at *ca.* 585m cm^{-1} tentatively assigned to ν(Au–C), as has been observed in other gold–ylide complexes.[6,7] Complex (**10**) shows an absorption at 1 712vs cm^{-1} due to acetone (Table 1).

Complexes (**11**)—(**13**) are white solids, soluble in diethyl ether, acetone (1:1 electrolytes), and chloroform and insoluble in n-hexane. Their ^1H n.m.r. spectra show resonances at 1.70, 1.42, and 1.22 p.p.m., respectively, due to Au–CH_2 protons. These values are very similar to those observed in the $[Au(CH_2PR_3)_2]Cl$ complexes[10,11] containing the same cation. The ^{19}F n.m.r. spectra show three resonances, the values being very similar for the three complexes (**11**)—(**13**) and to those observed for $[N(PPh_3)_2][Au(C_6F_5)_4]$[12] [at −122.10 (m), −164.78 (m), and −162.15 p.p.m. (t) (*J* 20.0 Hz)] which contains the same anion.

Experimental

Instrumentation and general experimental techniques were as described earlier.[7] Nuclear magnetic resonance spectra were recorded on a Varian XL 200 spectrometer in $CDCl_3$. Chemical shifts are quoted relative to $SiMe_4$ (^1H), 85% H_3PO_4 (external, ^{31}P), and $CFCl_3$ (external, ^{19}F). The yields, melting points, C and H analyses, conductivities, and molecular weights of the novel complexes are listed in Table 1.

Preparation of the Complexes.—$[Tl(C_6F_5)_3(CH_2ER_3)]$ [ER_3 = PPh_3 (**1**), PPh_2Me (**2**), $PPhMe_2$ (**3**), *or* $AsPh_3$ (**4**)]. *To* a diethyl ether solution (30 cm^3) of $[Tl(C_6F_5)_2Cl]$[13] (0.287 g, 0.5 mmol) was added $[Ag(C_6F_5)(CH_2ER_3)]$[2] [ER_3 = PPh_3 (0.276 g, 0.5 mmol), PPh_2Me (0.245 g, 0.5 mmol), $PPhMe_2$ (0.214 g, 0.5 mmol), or $AsPh_3$ (0.298 g, 0.5 mmol)]. The respective mixtures were stirred at room temperature for 3 h. The precipitated AgCl was filtered off and washed with diethyl ether (2 × 5 cm^3). The filtrate was vacuum evaporated to *ca.* 5 cm^3 and, upon addition of n-hexane (20 cm^3), complexes (**1**)—(**4**) respectively precipitated.

$[Tl(C_6F_5)_3(CH_2PPh_3)]$ (**1**). This complex can also be obtained by the following procedure. To a diethyl ether (25 cm^3) suspension of NaH (0.25 g, in 20% paraffin) was added complex (**5**) (0.319 g, 0.3 mmol) and the mixture was stirred at room temperature for 3 d. The excess of NaH and the precipitated NaBr were filtered off and washed with diethyl ether (2 × 5 cm^3). The filtrate was vacuum evaporated to *ca.* 5 cm^3 and upon addition of n-hexane (20 cm^3) the white complex (**1**) precipitated.

$Q[Tl(C_6F_5)_3X]$ [Q = PPh_3Me, X = Br (**5**); Q = PPh_2Me_2, X = I (**6**), *or* Q = $PPhMe_3$, X = I (**7**)]. To a diethyl ether (25 cm^3) suspension of $[Tl(C_6F_5)_3(diox)]$ [14] (0.238 g, 0.3 mmol) was added $[PPh_3Me]Br$ (0.107 g, 0.3 mmol), $[PPh_2Me_2]I$ (0.103 g, 0.3 mmol), or $[PPhMe_3]I$ (0.084 g, 0.3 mmol), and the mixtures were stirred at room temperature for 45 min. Evaporation to dryness gave complexes (**5**)—(**7**), which were washed with n-hexane (2 × 5 cm^3).

$[Au(C_6F_5)_2Cl(CH_2PR_3)]$ [PR_3 = PPh_3 (**8**), PPh_2Me (**9**), *or* $PPhMe_2$ (**10**)] *and* $[Au(CH_2PR_3)_2][Au(C_6F_5)_4]$ [PR_3 = PPh_3 (**11**), PPh_2Me (**12**), *or* $PPhMe_2$ (**13**)]. To a chloroform solution (30 cm^3) containing $[Au(C_6F_5)(CH_2PR_3)]$ (0.4 mmol) (PR_3 = PPh_3, 0.256 g; PPh_2Me, 0.23 g; or $PPhMe_2$, 0.206 g) [6] was added $[Tl(C_6F_5)_2Cl]$ [13] (0.4 mmol, 0.230 g) and the mixture was refluxed for 3 h. The white precipitate was filtered off and identified as TlCl, except in the reaction with PR_3 = $PPhMe_2$ where it also contained $[Au(C_6F_5)_2Cl(CH_2PPhMe_2)]$ (**10**) which was isolated by extraction with acetone (2 × 10 cm^3), partial evaporation to 5 cm^3, and addition of diethyl ether (20 cm^3) (yield 0.152 g, 49%). In all cases, the filtered chloroform solutions were evaporated to dryness and the residues extracted with diethyl ether (2 × 20 cm^3). The insoluble white solids were recrystallized from CH_2Cl_2–diethyl ether and identified as (**8**) (0.155 g, 46%) or (**9**) (0.118 g, 38%). The diethyl ether extracts were concentrated to 3 cm^3 and upon addition of n-hexane the white (**11**) (0.134 g, 42%), (**12**) (0.098 g, 33%), or (**13**) (0.087 g, 32%) were isolated. Addition of dioxane (1 cm^3) to the mother-liquors led to precipitation of the white complex $[Tl(C_6F_5)_3(diox)]$ (3, 10, or 12% respectively). The yields are referred to total gold or thallium, respectively.

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