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METAL—METAL BONDED COMPOUNDS

III *. NOVEL COMPLEXES CONTAINING IRIDIUM(II)—THALLIUM(II) BONDS

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Summary

Reaction of $[L_2(CO)IrX]$ ($L = Ph_3P, PhMe_2P, Ph_3As$; $X = Cl, O_2CR$) with $Tl(O_2CR)_3$ ($R = CH_3, C_2H_5, CH(CH_3)_2, CF_3$) afforded $[L_2(CO)X(O_2CR)IrTl(O_2CR)_2]$ containing an Ir—Tl bond and monodentate carboxylato groups. Reaction of $[L_2(CO)(O_2CR)_2IrTl(O_2CR)_2]$ with H_2O and HCl resulted in the formation of $[L_2(CO)(OH)(O_2CR)IrTl(O_2CR)_2]$ and $[L_2(CO)Cl_2IrTlCl_2]$, while with HO_2CR exchange of the carboxylato groups bonded to Tl occurred, which, together with other chemical properties, shows a remarkable stability of the iridium(II)—thallium(II) bond. Analogous complexes of Rh could not be prepared; instead a catalytic reduction of thallium(III) to thallium(I) was found.

Introduction

Recent work has shown that in the $Rh^I(Ir)^I$-to-$Cu^I(Ag^I)$ bonded compounds $[L_2(CO)MM'(RN_3R')X]$ ($L = Ph_3P, Ph_3As$; $M = Rh, Ir$; $M' = Ag^I, Cu^I$; $X = Cl, Br, I$) the M-to-M' donor bond can be stabilised by bridging triazenido groups. Furthermore it appeared, that amidino, carboxylato and even perchlorato groups were also able to act as bridging ligands between the M and M' atoms in this type of compound [1—5]. On the other hand in the case of the $Rh^{II}(Ir^{II})$—Hg^I bonded compounds $[(Ph_3P)_2(CO)Cl(O_2CR)MHg(O_2CR)]$, for which the proposed structure was recently confirmed by an X-ray study of the analogous $[(Ph_3P)_2(CO)ClXIrHgX]$ ($X = Cl, Br$) compound [6], the carboxylato groups are monodentate. Reaction of $[(Ph_3P)_2(CO)MX]$ ($M = Rh^I, Ir^I$; $X = Cl, O_2CCF_3$) with $[X'Hg(RN_3R')]$ ($X' = Cl, I$; $R = CH_3$; $R' = CH_3$, *p*-tolyl) afforded a great variety of

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* For Part II, see ref. 7.

compounds in which, depending critically on X, X' and R', the triazenido group sometimes bridges the M—Hg bond, but mainly appears to form an acyltriazenido group with the CO group [7]. The chelate form of the triazenido group was observed for $[(Ph_3P)(CORN_3R')RN_3R'MHgX]$ (M = Rh, Ir; R = CH_3, R' = CH_3, *p*-tolyl; X = Cl, O_2CCF_3) [7]. In no case does the triazenido group act as a monodentate, in contrast to the carboxylato group, although this mode of bonding is mentioned in the literature [8—10]. The analogies and differences between the triazenido and carboxylato groups led us to investigate the influence of these groups on the formation and stabilization of bonds between transition metals and post-transition metals. We describe below our work on Ir—Tl bonds, for which it was possible to prepare carboxylato derivatives, but not the triazenido derivatives since $Tl(RN_3R)_nCl_{3-n}$ (n = 1, 2, 3) is not stable.

Experimental

All preparations were carried out under dry, oxygen free nitrogen.

Preparations of $Tl(prop)_3$ and $Tl(IB)_3$ *

Although the preparation of these compounds has been described earlier [11], a modified method is given. To a suspension of $Tl(OAc)_3$ (20 mmol) in dry benzene (100 ml) was added propanioc or isobutyric acid (40 ml). The mixture was boiled for 5 h under a slow stream of nitrogen. After cooling the clear solution was concentrated and dry ether was added. White crystals were obtained in 90% yield at —25°C.

Reaction of $TlCl_3$ with n $Ag(RN_3R')$ ($n = 1, 2, 3$); R = p-tolyl, R' = CH_3, p-tolyl

These reactions in CH_2Cl_2, C_6H_6 or ether gave a quantitative yield of AgCl, and a red solution from which no thallium triazenido compound could be obtained, because of decomposition of the triazenido group. Efforts to obtain thallium compounds in other ways also failed [12].

Preparation of $[L_2(CO)(O_2CR)_2IrTl(O_2CR)_2]$ (L = Ph_3P, Ph_3As, $PhMe_2P$; R = CH_3, CF_3, C_2H_5, $CH(CH_3)_2$

To a mixture of $[L_2(CO)IrCl[$ (1 mmol), $Ag(O_2CR)$ (1 mmol) and $Tl(O_2CR)_3$ (1 mmol) CH_2Cl_2 was added (10 ml) with rapid stirring. The suspension immediately became deep red, and turned yellow after about 30—45 s. After 10 min the AgCl was removed by filtration, the solution was concentrated, 50 ml of hexane was added; a precipitate sometimes yellow or orange, but usually white, was formed. The product was recrystallised from CH_2Cl_2/ether/hexane (yield 70—90%).

Preparation of $[L_2(CO)Cl(OAc)IrTl(OAc)_2]$ (L = Ph_3P, Ph_3As)

To a suspension of $[L_2(CO)IrCl]$ (1 mmol) in CH_2Cl_2 (10 ml) $Tl(OAc)_3$ (1 mmol) was added with rapid stirring. The yellow suspension turned deep red, and after 30—45 s a clear yellow solution was obtained. The procedure used

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* prop = propanoic acid; IB = isobutyric acid.

in the precedings preparation was then followed. Each reaction gave a white solid containing two different isomers (yield 90%), as shown spectroscopically.

Reaction of [$L_2(CO)Rh(O_2CR)$] with $Tl(O_2CR)_3$ ($L = Ph_3P$, Ph_3As; $R = CH_3$, CF_3)

To a suspension of [$L_2(CO)Rh(O_2CR)$] (1 mmol) in CH_2Cl_2 or C_6H_6 (10 ml) was added $Tl(O_2CR)_3$ (in a range from 1 to 6 mmol) with rapid stirring. The yellow suspension slowly turned to orange, with evolution of CO_2. After 30

TABLE 1

ANALYTICAL DATA

Compound [a]	Molecular weight [b]	Analysis Found (calcd.) (%))		Colour
		C	H	
[$(Ph_3P)_2(CO)(OAc)_2IrTl(OAc)_2$]	1251 (1185)	45.35 (45.46)	3.57 (3.57)	white
[$(Ph_3P)_2(CO)(O_2CCF_3)_2IrTl(O_2CCF_3)_2$]		39.17 (38.57)	2.35 (2.16)	orange
[$Ph_3P)_2(CO)(prop)_2IrTl(prop)_2$]		46.84 (47.41)	4.09 (4.06)	white
[$(Ph_3P)_2(CO)(IB)_2IrTl(IB)_2$]	1345 (1442)	45.03 (44.16)	4.67 (4.06)	white
[$(Ph_3P)_2(CO)(IB)(OAc)IrTl(OAc)_2$] [c]		45.89 (46.37)	4.04 (3.82)	pink
[$(Ph_3P)_2(CO)Cl(OAc)IrTl(OAc)_2$] [d]	1236 (1162)	44.19 (44.45)	3.76 (3.38)	white
[$(Ph_4P)_2(CO)(OH)(prop)IrTl(prop)_2$]		46.21 (46.61)	3.96 (3.91)	white
[$(Ph_3P)_2(CO)Cl_2IrTlCl_2$] [e]		39.96 (40.73)	2.91 (2.77)	yellow
[$(PhMe_2P)_2(CO)(OAc)_2IrTl(OAc)_2$]		32.05 (32.04)	4.15 (3.66)	white
[$(PhMe_2P)_2(CO)(O_2CCF_3)_2IrTl(O_2CCF_3)_2$]		25.85 (26.04)	2.34 (1.92)	yellow
[$(Ph_3As)_2(CO)(OAc)_2IrTl(OAc)_2$]	1310 (1273)	41.24 (42.45)	3.62 (3.32)	yellow
[$(Ph_3As)_2(CO)(O_2CCF_3)_2IrTl(O_2CCF_3)_2$]	1548 (1489)	35.73 (36.30)	2.24 (2.03)	white
[$(Ph_3As)_2(CO)(prop)_2IrTl(prop)_2$]		43.30 (44.27)	3.77 (3.79)	white
[$(Ph_3As)_2(CO)(IB)_2IrTl(IB)_2$]		41.85 (41.62)	4.24 (3.82)	white
[$(Ph_3As)_2(CO)Cl(OAc)IrTl(OAc)_2$] [f]	1235 (1250)	41.11 (41.33)	3.37 (3.15)	yellow
[$(Ph_3As)_2(CO)(OH)(IB)IrTl(IB)_2$]	1302 (1315)	44.43 (44.74)	4.21 (3.98)	white
[$(Ph_3P)_2(CO)Rh(OAc)$]		64.62 (65.55)	4.68 (4.66)	yellow
[$(Ph_3P)_2(CO)Rh(O_2CCF_3)$]	856 (768)	60.49 (60.95)	3.45 (3.93)	orange
[$(Ph_3As)_2(CO)Rh(OAc)$]		58.48 (58.37)	4.43 (4.15)	orange

[a] $OAc = O_2CCH_3$; $prop = O_2CC_2H_5$; $IB = O_2CCH(CH_3)_2$. [b] The experimental error is ±10% in $CHCl_3$. [c] This compound has three isomers. [d] These compounds have two isomers. [e] Cl 12.80 (13.00).

TABLE 2

^{1}H NMR DATA IN $CDCl_3$ (ppm relative to TMS)

Compound[a]	Resonances of OAc; prop; IB						Resonances of L (Ph_3P; Ph_3As; $PhMe_2P$)	$J(CH_2—CH_3)$ or $J(CH—CH_3)$ in H_2
	CH_3 resonances			CH_2 or CH resonances				
	Bonded to Tl	Bonded to Ir, Rh		Bonded to Tl	Bonded to Ir			
		trans to CO	*cis* to CO		*trans* to CO	*cis* to CO		
$[Tl(prop)_3]$	1,17(t)			2,43(q)				7
$[Tl(IB)_3]$	1,27(d)			2,73(sept)				7
$[(Ph_3P)_2(CO)(OAc)_2IrTl(OAc)_2]$	1,63	1,40	0,77				7,40(m); 7,63(m)	
$[(Ph_3P)_2(CO)(O_2CCF_3)_2IrTl(O_2CCF_3)_2]$							7,53(m)	
$[(Ph_3P)_2(CO)(prop)_2IrTl(prop)_2]$	0,92(t)	0,67(t)	0,47(t)	1,97(q)	1.70(q)	1,23(q)	7,43(m); 7,66(m)	7
$[(Ph_3P)_2(CO)(IB)_2IrTl(IB)_2]$	0,95(d)	0,77(d)	0,48(d)	2,03(sept)	f	f	7,42(m); 7,66(m)	7
$[(Ph_3P)_2(CO)(IB)(OAc)IrTl(OAc)_2]$[b]	1,60; 0,93(d)	1,40; 0,76(d)	0,80; 0,67(d)	2,16(sept)	f	f	7,46(m); 7,71(m)	7
$[(Ph_3P)_2(CO)Cl(OAc)IrTl(OAc)_2]$[c]	1,66	1,40	0,83				7,43(m); 7,67(m)	
$[(Ph_3P)_2(CO((OH)(prop)IrTl(prop)_2]$[d]	0,86(t)	0,67(t)		1,93(q)	1.47(q)		7,47(m); 7,66(m)	7
$[(PhMe_2P)_2(CO)(OAc)_2IrTl(OAc)_2]$[g]	1,67	h	h				7,50(m); 1,93(t)	
$[(PhMe_2P)_2(CO)(O_2CCF_3)_2IrTl(O_2CCF_3)_2]$[g]							7,46(m); 1,80(t)	
$[(Ph_3As)_2(CO)(OAc)_2IrTl(OAc)_2]$	1,76	1,53	0,93				7,43(m)	
$[(Ph_3As)_2(CO)(O_2CCF_3)_2IrTl(O_2CCF_3)_2]$							7,33(m)	
$[(Ph_3As)_2(CO)(prop)_2IrTl(prop)_2]$	0,97(t)	0,68(t)	0,64(t)	2,07(q)	1.80(q)	1,63(q)	7,43(m)	7
$[(Ph_3As)_2(CO)(IB)_2IrTl(IB)_2]$	0,93(d)	0,73(d)	0,66(d)	2,03(sept)	1.50(setp)	1,26(sept)	7,40(m); 7,60(m)	7
$[(Ph_3As)_2(CO)Cl(OAc)IrTl(OAc)_2]$[c]	1,53	1,35	0,90				7,40(m); 7,61(m)	
$[(Ph_3As)_2(CO)(OH)(IB)IrTl(IB)_2]$[e]	0,94(d)	0,72(d)		2,00(sept)	1.53(sept)		7,48(m); 7,61(m)	7
$[(Ph_3P)_2(CO)Rh(OAc)]$		1,41					7,40(m); 7,66(m)	
$[(Ph_3P)_2(OO)Rh(O_2CCF_3)]$							7,46(m); 7,66(m)	
$[(Ph_3As)_2(CO)Rh(OAc)]$		1,73					7,33(m)	

[a] See note a Table 1. [b] This compound has three isomers. [c] These compounds have two isomers. [d] Also an OH resonance was found at 3.04 ppm. [e] Also an OH resonance was found at 3.16 ppm. [f] No assignment could be made; due to broadening and coalescence of the signals, but three isomers are present (see Table 3; ^{31}P NMR). [g] The resonances of L at 1.93 and 1.80 ppm are triplets; due to coupling with ^{31}P. [h] No assignment could be made; due to broadning and coalescence of the signals.

min the solid was filtered off, shown to be $Tl(O_2CR)$ in quantitative yield. The procedure used in the previous preparations then gave 80% of unchanged $[L_2(CO)Rh(O_2CR)]$. Treatment of $TlCl_3$, $RTlX_2$ and R_2TlX ($R = CH_3$, C_6H_5; $X = Cl$, O_2CR) with $[L_2(CO)MX]$ ($L = Ph_3P$, Ph_3As; $M = Rh$, Ir; $X = Cl$, O_2CR) in C_6H_6, CH_2Cl_2 or THF did not five any observable reaction, and this was confirmed by ^1H NMR.

Preparation of $[L_2(CO)Cl_2IrTlCl_2]$ ($L = Ph_3P$, Ph_3As)

Gaseous HCl (5 mmol) was bubbled through a solution of $[L_2(CO)(O_2CR)_2IrTl(O_2CR)_2]$ (1 mmol) in CH_2Cl_2 (10 ml) with rapid stirring. After 1 h the yellow precipitate was filtered off, washed with ether, and dried in vacuo (yield 90%).

Preparation of $[L_2(CO)(OH)(O_2CR)IrTl(O_2CR)_2]$ ($L = Ph_3P$, Ph_3As; $R = CH_3$, C_2H_5, $CH(CH_3)_2$

For this preparation all solvents used were saturated with H_2O. To a solution of $[L_2(CO)(O_2CR)_2IrTl(O_2CR)_2]$ in CH_2Cl_2 (10 ml) was added H_2O (0.1 ml) with rapid stirring. After 1 h the clear yellow solution was concentrated and the usual procedure was followed to give a white compound in 70% yield.

Elemental analysis (C and H were carried out in the Organic Chemistry Laboratory (TNO) in Utrecht), colours and some Molecular Weights are listed in Table 1. ^1H NMR spectra (Table 2) were recorded with Varian XL-100, T-60A and A-60D spectrometers and ^{31}P NMR spectra (Table 3) with a Varian XL-100 spectrometer. IR spectra (Table 4) were measured with a Beckman IR 4250 spectrometer and molecular weights with a Hewlett—Packard vapour pressure osmometer Model 302 B.

Results

Structural characterisation of the metal—metal bonded Ir—Tl compounds

Reactions of $[L_2(CO)IrCl]$ ($L = Ph_3P$, Ph_3As, $PhMe_2P$) with $Ag(O_2CR)$ and $Tl(O_2CR')_3$ ($R = R' = CH_3$, CF_3, C_2H_5, $CH(CH_3)_2$) resulted in the rapid and quantitative precipitation of AgCl and the formation of metal—metal bonded compound containing four carboxylato groups, as in equation 1.

$$L_2(CO)IrCl + Ag(O_2CR) + Tl(O_2CR)_3 \rightarrow L_2(CO)(O_2CR)_2IrTl(O_2CR)_2 + AgCl\downarrow \quad (1)$$

The ^{31}P NMR data (Table 3) show that the phosphines are equivalent, with in all cases, a ^{31}P—$^{203,205}Tl$ coupling constant of about 1140 Hz. The phosphine groups are therefore *trans* to each other and bonded to the iridium atom *cis* to the thallium atom [7,13]. It should be noted that there is no significant difference between the ^{31}P—^{203}Tl and ^{31}P—^{205}Tl coupling constants *, as is shown in Fig. 1.

From the available IR data (Table 4) it is clear that all the carboxylato groups are monodentate [3,7,14]. The stretching frequency of the CO group lies at

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* Magnetic moments: $\mu(^{203}Tl)$ 1.5960; $\mu(^{205}Tl)$ 1.6114.

TABLE 3

^{31}P NMR DATA (ppm relative to 85% H_3PO_4 in C_6D_6)

Compound [a]	P atoms bonded to Ir, Rh	J(P—Tl) [b] or J(P—Rh) [f] (Hz)
$[Ph_3P]$	4.95 [e]	
$[PhMe_2P]$	46.29 [e]	
$[(Ph_3P)_2(CO)IrCl]$	—24.43	
$[(PhMe_2P)_2(CO)IrCl]$	5.44	
$[(Ph_3P)_2(CO)(OAc)_2IrTl(OAc)_2]$	—0.67(d)	1134
$[(Ph_3P)_2(CO)(O_2CCF_3)_2IrTl(O_2CCF_3)_2]$	2.43(d)	1081
$[(Ph_3P)_2(CO)(prop)_2IrTl(prop)_2]$	—0.34(d)	1119
$[(Ph_3P)_2(CO)(IB)_2IrTl(IB)_2]$	2.88(d)	1112
$[(Ph_3P)_2(CO)(IB((OAc)IrTl(OAc)_2]$ [c]	—0.95(d); 2.48(d); 4.54(d)	1131; 1113; 1056
$[(Ph_3P)_2(CO)Cl(OAc)IrTl(OAc)_2]$ [d]	—0.76(d); 3.23(d)	1148. 1099
$[(Ph_3P)_2(CO)(OH)(prop)IrTl(prop)_2]$	—0.65(d)	1121
$[(PhMe_2P)_2(CO)(OAc)_2IrTl(OAc)_2]$	22.71(d)	1202
$[(PhMe_2P)_2(CO)(O_2CCF_3)_2IrTl(O_2CCF_3)_2]$	25.57(d)	1140
$[(Ph_3P)_2(CO)Rh(Cl)]$	—29.58(d)	129 [f]
$[(Ph_3P)_2(CO)Rh(O_2CCF_3)]$	—37.89(d)	137 [f]
$[(Ph_3P)_2(CO)Rh(OAc)]$	—31.22(d)	132 [f]

[a] See note *a* Table 1. [b] Coupling of ^{31}P with ^{203}Tl and ^{205}Tl (natural abundance 29.52 and 70.48%). [c] Three isomers were found for this compound. [d] Two isomers were found for this compound. [e] Not bonded to Ir or Rh. [f] Coupling of ^{31}P with ^{103}Rh (natural abundance 100%).

about 2050 cm^{-1}, as expected for this type of metal—metal bonded compound, with the CO group *cis* to the metal bonded to iridium [6,7,15].

^{1}H NMR data (Table 2) show the presence of three different kinds of carboxylato groups: two equivalent groups bonded to the thallium atom and two

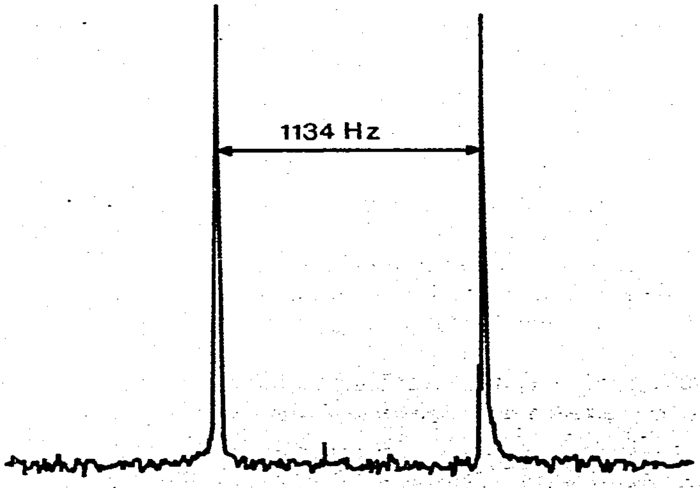

Fig. 1. ^{31}P NMR spectrum of $[(Ph_3P)_2(CO)(OAc)_2IrTl(OAc)_2]$.

TABLE 4

IR DATA (KBr, cm^{-1})

Compound [a]	ν(CO)	ν_{as}(OAc, O_2CCF_3, prop, IB) [b]
$[(Ph_3P)_2(CO)(OAc)_2IrTl(OAc)_2]$	2051	1629, 1583(br)
$[(Ph_3P)_2(CO)(O_2CCF_3)_2IrTl(O_2CCF_3)_2]$	2061	1688(br)
$[(Ph_3P)_2(CO)(prop)_2IrTl(prop)_2]$	2043	1631, 1568(br)
$[(Ph_3P)_2(CO)(IB)_2IrTl(IB)_2]$	2041	1621, 1557(br)
$[(Ph_3P)_2(CO)(IB)(OAc)IrTl(OAc)_2]$ [c]	2053(br)	1622, 1572(br)
$[(Ph_3P)_2(CO)Cl(OAc)IrCl(OAc)_2]$ [d]	2043, 2038(sh)	1619, 1577(br)
$[(Ph_3P)_2(CO)(OH)(prop)IrTl(prop)_2]$ [e]	2033	1632, 1566(br)
$[(Ph_3P)_2(CO)Cl_2IrTlCl_2]$ [g]	2063	
$[(PhMe_2P)_2(CO)(OAc)_2IrTl(OAc)_2]$	2038	1587(br)
$[(PMe_2P)_2(CO)(O_2CCF_3)_2IrTl(O_2CCF_3)_2]$	2059	1688(br)
$[(Ph_3As)_2(CO)(OAc)_2IrTl(OAc)_2]$	2042	1623, 1584(br)
$[(Ph_3As)_2(CO)(O_2CCF_3)_2IrTl(O_2CCF_3)_2]$	2061	1689(br)
$[(Ph_3As)_2(CO)(prop)_2IrTl(prop)_2]$	2056	1623, 1569(br)
$[(Ph_3As)_2(CO)(IB)_2IrTl(IB)_2]$	2045	1629, 1562(br)
$[(Ph_3As)_2(CO)Cl(OAc)IrTl(OAc)_2]$ [d]	2041, 2022	1571(br)
$[(Ph_3As)_2(CO)(OH)(IB)IrTl(IB)_2]$ [f]	2042	1627, 1572(br)
$[(Ph_3P)_2(CO)Rh(OAc)]$	1989	1598(br)
$[(Ph_3P)_2(CO)Rh(O_2CCF_3)]$	1989	1685(br)
$[(Ph_3As)_2(CO)Rh(OAc)]$	1971	1628, 1567(br)

[a] See note *a* Table 1. [b] These vibrations indicate that all carboxylato groups are monodentate, especially those of the O_2CCF_3 group at about 1688 cm^{-1} [3,7,14]. [c] This compound has three isomers. [d] These compounds have two isomers with Ir—Cl stretching frequencies at 271; 303 and 274; 315 cm^{-1} (Nujoll mull). [e] Also an OH stretching frequency at 3257 cm^{-1} was found (Nujol mull). [f] Also an OH stretching frequency at 3261 cm^{-1} was found (Nujol mull). [e] This compound has a Tl—Cl stretching frequency at 184 cm^{-1} (broad) and two Ir—Cl stretching frequencies at 317 and 254 cm^{-1} (Nujol mull).

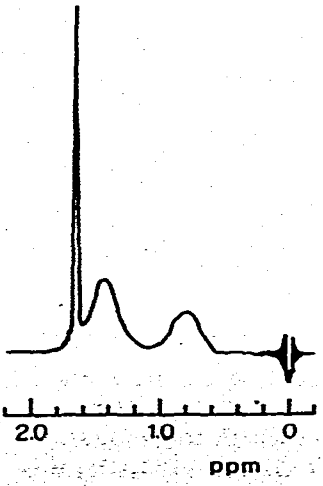

Fig. 2. ^{1}H NMR spectrum of the methyl resonances of $[(Ph_3P)_2(CO)(OAc)_2IrTl(OAc)_2]$.

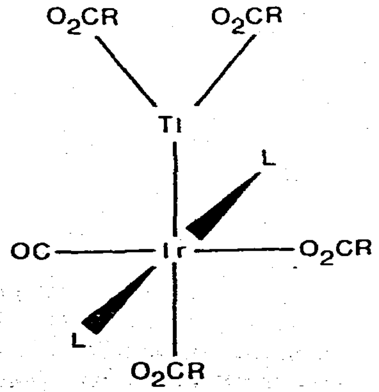

Fig. 3. Proposed structure of $[L_2(CO)(O_2CR)_2IrTl(O_2CR)_2]$ (L = Ph_3P, Ph_3As, $PhMe_2P$; R = CH_3, CF_3, C_2H_5, $CH(CH_3)_2$).

inequivalent groups bonded to the iridium atom. The resonances of the carboxylato groups bonded to the iridium atom are very broad, as shown in Fig. 2.

Temperature dependent ^{1}H NMR measurements show greater broadening at lower temperature, but there is no change of the chemical shift and no exchange with free O_2CR^- for the two carboxylato groups bonded to the iridium atom. Since there is no intra- and/or inter-molecular exchange to account for the broadening, we assume that there is a mixture of rotamers, arising from steric interactions.

The only possible structure is thus one analogous to that described earlier for $[(Ph_3P)_2(CO)Cl(O_2CR)IrHg(O_2CR)]$ ($R = CH_3, CF_3, CH(CH_3)_2$) [7] and $[(Ph_3P)(CO)_2XClIrHgX]$ (X = Cl, Br) [6]; it is shown in Fig. 3. Reaction of $[L_2(CO)IrCl]$ ($L = Ph_3P, Ph_3As$) with $Tl(OAc)_3$ gave a mixture of two geometrical isomers according to equation 2.

$$L_2(CO)IrCl + Tl(OAc)_3 \rightarrow L_2(CO)Cl(OAc)IrTl(OAc)_2 \qquad (2)$$

^{1}H NMR data (Table 2) show a methyl resonance with a relative intensity of two at about 1.66 ppm which belongs to two equivalent carboxylato groups bonded to thallium and two methyl resonances at about 1.40 ppm and about 0.83 ppm which have together a relative intensity of one. For $L = Ph_3P$, ^{31}P NMR data (Table 3) show two doublets with a chemical shift of −0.76 and 3.23 ppm. Furthermore IR data (Table 4) show two different CO frequencies and two different Ir—Cl frequencies. Combination of the NMR data and IR data indicates clearly that in both isomers the chlorine atom is bonded to iridium; in the first isomer *trans* to thallium and in the second isomer *cis* to thallium while in both isomers the phosphine groups are *trans* to each other.

Reaction of $[L_2(CO)IrCl]$, AgO_2CR and $Tl(O_2CR')_3$ with $R \neq R'$ resulted in a mixture of three isomers, as indicated by ^{31}P NMR and ^{1}H NMR. In this case the O_2CR group can be bonded to the thallium atom or to the iridium atom *cis* or *trans* to thallium. For this type of compound only one example, $[(Ph_3P)_2(CO)(O_2CCH(CH_3)_2)(OAc)IrTl(OAc)_2]$, is given (see Tables 1—4).

Reaction of [L₂(CO)Rh(O₂CR)] with Tl(O₂CR)₃

These reactions resulted in the formation of $Tl(O_2CR)$ and CO_2, probably according to equations 3 and 4.

$$L_2(CO)Rh(O_2CR) + Tl(O_2CR)_3 \rightarrow L_2(CO)Rh(O_2CR) + 2\,{}^{\cdot}O_2CR \qquad (3)$$

$$^{\cdot}O_2CR \rightarrow {}^{\cdot}R + CO_2 \qquad (4)$$

($L = Ph_3P, Ph_3As$; $R = CH_3, CF_3$)

The ^{1}H NMR, ^{31}P NMR and IR data (Tables 2—4) show that the Rh compound remains unchanged and only catalytic reduction of thallium(III) to thallium(I) occurs; this was confirmed by experiments in which the concentrations of the reactants were varied. The formation of CO_2 and $Tl(O_2CR)$ was confirmed by IR spectroscopy. The $R^{\cdot}$ radicals probably react directly with the solvent (CH_2Cl_2 and C_6H_6), since no traces of R_2 were observed in the ^{1}H NMR or IR spectra.

Reaction of [$L_2(CO)(O_2CR)_2IrTl(O_2CR)_2$] with Lewis acids and bases

Reaction with acids. Different reactions were observed, depending on the acid strength. Independent of the quantity of water used (more than 1 equivalent) the reaction with H_2O afforded a compound in which only one carboxylato group, was replaced by on OH group (eq. 5).

$$L_2(CO)(O_2CR)_2IrTl(O_2CR)_2 + H_2O \rightarrow L_2(CO)(O_2CR)(OH)IrTl(O_2CR)_2 + HO_2CR \qquad (5)$$

^{31}P NMR data (Table 3) indicate that the phosphine groups are bonded to iridium and *trans* to each other. ^1H NMR data show the presence of two equivalent carboxylato groups bonded to thallium and one carboxylato group bonded to iridium. In contrast to the analogous compound with two carboxylato groups bonded to iridium (eq. 1), no broadening of the resonances of the carboxylato groups is observed. This confirms the existence of different rotamers, arising from steric interaction when two carboxylato groups are bonded to iridium. The available IR data (Table 4) show that all carboxylato groups are monodentate. Furthermore the CO stretching frequency lies at about 2038 cm^{-1} and in view of the small difference (6 cm^{-1}) of the analogous compounds with two carboxylato groups bonded to iridium it is clear that the carboxylato group bonded to iridium must be *trans* to CO and *cis* to the OH group. From this and by comparison of the chemical shifts of the carboxylato groups of [$L_2(CO)$-$(O_2CR)_2IrTl(O_2CR)_2$] and [$L_2(CO)(OH)(O_2CR)IrTl(O_2CR)_2$] it is possible to assign the absorptions of the carboxylato groups *cis* and *trans* to thallium in the first compound.

Reaction with weak acids, HO_2CR, show a concentration-dependent change of the chemical shift od the carboxylato groups bonded to thallium, but no change of the chemical shift of the carboxylato groups bonded to iridium; thus only the carboxylato groups bonded to thallium exhange with O_2CR^-. Reaction with triazenes $R(H)N_3R'$ and $Ag(RN_3R')$ ($R = CH_3$, *p*-tolyl; $R' =$ *p*-tolyl) gave a mixture of unidentified products in which the iridium—thallium bond was still present, since the ^{31}P—$^{203,205}Tl$ coupling was retained.

Reaction with a strong acid such as HCl gives, depending on the quantity used, an insoluble yellow product and the original metal—metal bonded carboxylato compound. If a stoichiometric amount or excess of HCl is used an almost quantitative yield of the insoluble yellow compound is obtained according to equation 6.

$$L_2(CO)(O_2CR)_2IrTl(O_2CR)_2 + 4HCl \rightarrow L_2(CO)Cl_2IrTlCl_2 + 4HO_2CR \qquad (6)$$

IR data (Table 4) show the presence of one CO stretching frequency at 2063 cm^{-1}, while the absorptions of the carboxylato groups are absent. Furthermore, three metal—chlorine frequencies are found; one at 314 cm^{-1} belonging to the Cl-atom *trans* to the CO group [7,16]; one at 254 cm^{-1} probably belonging to the Cl-atom *trans* to thallium [7] and one probably belonging to the Cl-atoms bonded to thallium at about 284 cm^{-1} [17].

Reactions with iodine and chlorine gave a mixture of products which could not be identified.

Reaction with bases. The metal—metal bonded carboxylato compounds do not react with donor ligands such as Ph_3P and Ph_3As. However, treatment with NH_3 or $N(C_2H_5)_3$ gives a mixture of products in which, in all cases, the Ir—Tl bond remains unaffected, the ^{31}P—$^{203,205}Tl$ coupling being retained. Furthermore, the reaction with CO gives a mixture of product in which the Ir—Tl bond is broken, no ^{31}P—$^{203,205}Tl$ coupling being observed.

Discussion

Although many metal—transition metal bonded compounds, containing a Group IIB or a Group IVA element [7,15,18—24] are known, little work has been carried out in the field of metal—transition metal bonded compounds containing a Group IIIA element [25,26].

The compounds described here have, in general, a structures analogous to those of $[L_2(CO)ClXIrHgX]$ ($X = Cl, Br, O_2CCH_3, O_2CCF_3, O_2CCH(CH_3)_2$) [6,7,15]; (i) all carboxylato groups are monodentate; (ii) the CO group is bonded *cis* to thallium; (iii) the phosphine groups are equivalent and *trans* to each other A remarkable difference is that in all cases the mercury—metal bonded compounds in the previously described compounds occur only in one isomeric form with the Cl-atom *trans* to the CO group [6,7], while for the analogous thallium—iridium bonded complexes $[L_2(CO)(O_2CR)ClIrTl(O_2CR)_2]$ two isomers are observed in all cases, with the chlorine atom bonded *cis* or *trans* to the CO group. No similarities in chemical properties are found. In contrast to the Ir—Hg, the Ir—Tl bond is not cleaved by reagents such as HCl and Ph_3P. Very little is understood of the reaction with the acids used (HCl, HO_2CR, H_2O) which depending on the acid strength give markedly different types of reactions.

It is of interest to compare the behaviour of the Ir—Tl bonded complexes with formally similar $RTlX_2$ ($X = Cl, O_2CR$) compounds. For example the susceptibility towards hydrolysis decreases strongly in the series $Tl(O_2CR)_3 > MeTl(O_2CR)_2 > [L_2(CO)(O_2CR)_2IrTl(O_2CR)_2]$ [27,28]. It appears therefore that the strongly covalent It—Tl bond has a great stabilizing influence on the Tl—O bond towards hydrolysis [27—31]. The strength of the metal—metal bond may be compared with, e.g., the aryl—Tl bond in $(aryl)Tl(O_2CR)_2$, since neither is attacked by strong acids [29—31].

In previous publications, compounds were described [1—3,7,15] in which in all cases the metal—rhodium bond is significantly less stable than the analogous metal—iridium bond. In the reactions described in this paper this difference is so great that no stable rhodium—thallium bond is formed. Instead a catalytic reduction of thallium(III) to thallium(I) is observed.

Finally, the mechanism by which the compounds described are formed is not completely understood. Of interest is the formation of a deep red colour at the start of the reaction which indicates an intermediate. The structure of this intermediate is probably five-coordinate, with an iridium-to-thallium donor bond analogous to other known metal-to-metal donor bonds [1—3, 32—35]. In this intermediate Berry Pseudorotations and exchange of groups from Tl to Ir and vice versa may occur, which would provide an explanation for the formation of the compounds described.

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