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SYNTHESIS, RAMAN AND NMR SPECTROSCOPY OF THE TRIMETALLIC COMPLEXES $[IrCl(SnCl_3)(HgCl)(CO)(PR_3)_2]$

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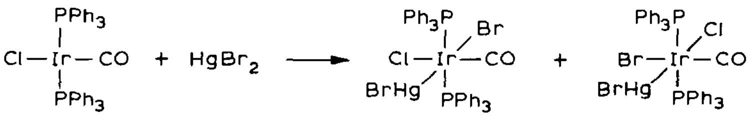
Summary

Synthesis, Raman and NMR studies are presented for the new octahedral trimetallic complexes with composition $[IrCl(SnCl_3)(HgCl)(CO)(PR_3)_2]$, R = *p*-$XC_6H_4$; X = H, CH_3O, F, Cl. Only the isomer containing the Cl_3Sn–Ir–Hg–Cl fragment and *trans* phosphine ligands is observed. Force constants for the Ir–Sn and Ir–Hg bonds as well as ^{31}P, ^{119}Sn and ^{199}Hg NMR data are reported. The presence of a spin–spin coupling constant of more than 40,000 Hz between the ^{199}Hg and ^{119}Sn atoms is shown to originate from a two-bond and not a one-bond interaction.

Introduction

Vaska's complex *trans*-$[IrClCO(PPh_3)_2]$ (I) [1] oxidatively adds to mercury halides [2] forming six-coordinated Ir^{III} complexes with HgX and X as the additional ligands. The crystal structure of the $HgBr_2$ adduct $[IrClHgBr_2(CO)(PPh_3)_2]$ (II) shows that the addition is 85% *trans* [3] (eq. 1). Addition of HCl produces the well



(1)

(I) (IIa, 85%) (IIb, 15%)

known *trans*-$[IrHCl_2(CO)(PPh_3)_2]$ (III), in which H is *trans* to Cl [1,4]. Further, reaction of III with $SnCl_2$ gives $[IrH(SnCl_3)Cl(CO)(PPh_3)_2]$ (IV), for which ^1H and ^{119}Sn NMR spectroscopy have shown that H and $SnCl_3$ occupy *trans* positions in the coordination sphere of iridium [5a]. As part of our study of chemistry of trichlorostannate complexes [5] we have synthesized and isolated trimetallic complexes of composition $[IrCl(HgCl_2)(CO)(SnCl_2)(PR_3)_2]$ (V). These may be prepared by reac-

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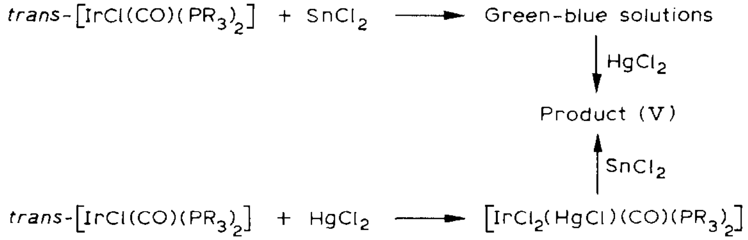
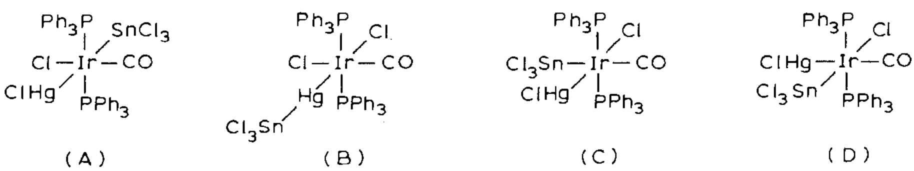
tion of I with $SnCl_2$, followed by addition of $HgCl_2$, or by using the reverse sequence, in which the Ir^{III} complex II (all chlorine atoms) is first formed (eq. 2).



(2)

There is considerable NMR spectroscopic support for the view that the product contains an $SnCl_3^-$ ligand (see Table 1), and for the continued presence of two equivalent tertiary aryl phosphine ligands. However, the exact configuration of the coordination sphere of V is not known. Some possible structures are shown in Scheme 1. In this paper we report the NMR and Raman spectra of several trimetallic complexes, and suggest that V has structure A and is formally the product of oxidative addition of $ClHgSnCl_3$. In addition we report force constants for the Ir–Sn and Ir–Hg bonds as well as ^{31}P, ^{119}Sn and ^{199}Hg NMR data.

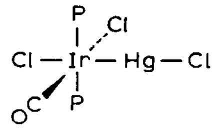
SCHEME 1

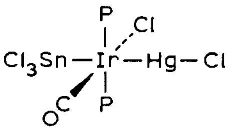


NMR spectra

Distinction between the isomers A–D should be possible, in principle, using NMR spectroscopy. The ^{31}P, ^{119}Sn and ^{199}Hg NMR data (see Table 1) do indeed, provide useful information. The triplet multiplicities in the ^{119}Sn and ^{199}Hg spectra confirm the presence of equivalent phosphine atoms. The magnitude of this interaction for $^2J(^{119}Sn, ^{31}P)$ is consistent with a *cis* orientation of these two spins [5] but is not sufficiently unambiguous to permit us to exclude a three-bond coupling such as that expected for isomer B. Moreover, the coupling between the mercury and tin spins, 39,294–42,688 Hz, is quite large and suggestive of a one-bond interaction, in which case B would be correct. However, we have recently demonstrated that two-bond coupling constants involving ^{119}Sn, e.g., $^2J(^{119}Sn, ^{117}Sn)$ can exceed 35,000 Hz [5b]. Consequently, although such a large value would be inconsistent with either C or D (the *cis* orientation routinely gives ^2J values < 5 KHz [5b,5g]) both A, in which the two spins are *trans*, and B require further consideration.

The ^{119}Sn and ^{199}Hg chemical shifts should also be revealing. Indeed, in retrospect we can say that $\delta(^{119}Sn)$ at -176 to -197 is certainly consistent with our previous measurements on $Ir–SnCl_3$ complexes [5a]; however, the ^{199}Hg data present a difficulty, in that on changing from a structure such as VI to one of the


(VI)


(VA)

isomers of V, induces a 619 ppm shift to lower field of the ^{199}Hg resonance. Consequently, further information was required.

Raman spectra

The Raman bands for $[IrCl(SnCl_3)(HgCl)(CO)(PR_3)_2]$ with frequency shift lower than 650 cm^{-1} are compiled in Table 2, along with additional data for some model derivatives. Figure 1 shows the Raman spectra of $[IrCl_2(HgCl)(CO)(PPh_3)_2]$ (VI), $[IrClBr(HgBr)(CO)(PPh_3)_2]$ (II) and $[IrBr_2(HgBr)(CO)(PPh_3)_2]$. Figure 2 compares the spectra of $[IrCl_3(CO)(PPh_3)_2]$ and $[IrCl_2(HgCl)(CO)(PPh_3)_2]$ with the tin chloride adducts $[IrHCl(SnCl_3)(CO)(PPh_3)_2]$ (IV) and $[IrCl(HgCl)(SnCl_3)(CO)(PPh_3)_2]$ (V). The spectra show many Raman bands due to low frequency vibrations of PPh_3; consequently, the first step of the interpretation requires the assignment of these bands, which we base on a comparison with the spectra of free PPh_3 [6] and related complexes of PPh_3 [7]. The weak Raman band between 190 and 200 cm^{-1} is tentatively assigned to the symmetric P–Ir–P vibration. This assignment is based on the fact that this band is present in the spectra of all the complexes. Shobotake and Nakamoto [7] identified the Ni–P vibration in $[NiCl_2(PPh_3)_2]$ at 189 cm^{-1} and the Pd–P vibration in $[PdCl_2(PPh_3)_2]$ at 191 cm^{-1}. The other bands indicated by footnote a in Table 2 are due to vibrations within the planar IrXYZ(CO) moiety of the oxidative addition products. To get some indication of the arrangement of the four ligands in the plane and the charge distribution in these complexes, an approximate normal coordinate analysis of the stretching vibrations within this structural element was carried out. The structural parameters used in the calculation are listed in Table 3. The following approximations have been made: (i) only the stretching vibrations are considered (with exception of the δ(Ir–H) vibration in IV); (ii) all the interaction force constants f_{rr} are set to 0; (iii) the force constants are independent of the other ligands with exception of the different *trans* effects of C≡O, Cl and HgCl [8]; (iv) C≡O is treated as a point mass. The set of force constants in Table 4 is chosen to reproduce the Raman frequencies of known complexes which contain either Ir–Hg or Ir–Sn bonds. In Table 5 the observed and calculated frequencies and the normal coordinates (potential energy distribution) are listed. As expected, the vibrations of the two rectangular fragments X–Ir–CO and Y–Ir–Z are separated in this approximation. In complex VI, the ν(Ir–Cl) [8,9] and ν(Hg–Cl) [10] vibrations of the linear Cl–Ir–Hg–Cl fragment have similar energies. However, due to their separation by the heavy metal nuclei their coupling is small, and it is reasonable to associate the normal coordinates with localized vibrations. Consequently the assignment of the observed bands ν(Ir–Cl) at 324 ν(Hg–Cl) at 300 and ν(Ir–Hg) at 179 cm^{-1} is straightforward. In the oxidative addition products from $HgBr_2$ and HgI_2 the three stretching vibrations of the X–Hg–Ir–X (X = Br, I) moieties are strongly coupled and so it is not possible to discuss these spectra in

(Continued on p. 22)

TABLE 1

NMR DATA FOR THE COMPLEXES [a]

Complex	Chemical shift [b] (ppm)			Two-bond coupling constant (Hz)		
	^{31}P	^{119}Sn	^{199}Hg	$J(^{199}Hg^{31}P)$ [c]	$J(^{119}Sn^{31}P)$ [c]	$^{2}J(^{199}Hg^{119}Sn)$ [d]
1. $[IrCl(SnCl_3)(HgCl)(CO)(PPh_3)_2]$	−21.7	−197	−2026	331	167	41479
2. $[IrCl(SnCl_3)(HgCl)(CO)(P(p\text{-}CH_3OC_6H_4)_3)_2]$	−26.5	−192	−2077	338	166	42688
3. $[IrCl(SnCl_3)(HgCl)(CO)(P(p\text{-}FC_6H_4)_3)_2]$	−24.9	−176	−2002	338	172	39916
4. $[IrCl(SnCl_3)(HgCl)(CO)(P(p\text{-}ClC_6H_4)_3)_2]$	−23.7			337	160	
5. $[IrBr(SnBr_3)(HgBr)(CO)(PPh_3)_2]$	−22.2	−170	−2387	314	148	39294
6. $[IrCl(OAc)(HgOAc)(CO)(PPh_3)_2]$	−0.6		−2584	329		
7. $[IrCl_2(HgCl)(CO)(PPh_3)_2]$	−18.2		−2645	321		
8. $[IrBr_2(HgBr)(CO)(PPh_3)_2]$	−23.9		−2814	289		
9. $[IrI_2(HgI)(CO)(PPh_3)_2]$	−31.1		−3093	244		
10. $[IrClBr(HgBr)(CO)(PPh_3)_2]$	−20.9			191		
11. $[IrClI(HgI)(CO)(PPh_3)_2]$	−29.9		−2964	284		
12. $[IrCl_2(HgCl)(CO)(P(p\text{-}CH_3OC_6H_4)_3)_2]$	−21.6		−2712	324		
13. $[IrCl_2(HgCl)(CO)(P(p\text{-}FC_6H_4)_3)_2]$	−20.4		−2595	322		

[a] 1–5 measured in $CDCl_3$; 6–13 in C_6D_6/CH_2Cl_2, 1/4 R.T. [b] ^{31}P, ^{119}Sn ^{199}Hg rel. to H_3PO_4, $(CH_3)_4Sn$ and $Hg(CH_3)_2$, respectively. [c] ±3 Hz. [d] ±12 Hz.

TABLE 2

OBSERVED RAMAN BANDS ($\Delta\nu < 650\ cm^{-1}$; L = vibration of PPh_3)

$[IrCl_3CO(PPh_3)_2]$	$[IrCl_2(HgCl)CO(PPh_3)_2]$	$[IrClBr(HgBr)(CO)(PPh_3)_2]$	$[IrClI(HgI)(CO)(PPh_3)_2]$	$[IrBr_2(HgBr)(CO)(PPh_3)_2]$	$[IrH(SnCl_3)Cl(CO)(PPh_3)_2]$		$[IrCl(SnCl_3)(HgCl)(CO)(PPh_3)_2]$
118 m def.	105 sh def.		92 def.		85 m (86) [b]	def.	107 s def.
157 s def.		142 s [a]	115 s [a]	140 s [a]			155 s [a]
	167 w def.	162 s def.	161 s [a]	159 m def.	166 s (165)	def.	
	179 s [a]			193 m [a]			
198 w Ir-P	202 w Ir–P	195 m Ir–P	198 w Ir–P		189 w (188)	Ir–P	
		204 m [a]		204 m [a]	208 m (208)	[a]	
225 w L		231 m L	232 m [a]	229 w L			232 m [a]
241 w L	238 w L	242 m [a]	245 w L	241 m [a]	241 m (239)	L	
261 w L	260 w L	261 w L	262 w L	258 w L	255 m (254)	L	259 w L
284 w L		279 w L	278 w L	277 w L	277 w (276)	L	
	294 w [a]						
303 m [a]	300 sh [a]						290 s [a]
320 s [a]	324 m [a]	316 w [a]	308 m [a]		319 m (316)	[a]	312 m [a]
		367 w [a]	367 w [a]		337 s (335)	[a]	339 s [a]
433 m L	436 m L	430 m L	435 m L	427 m L	434 w (432)	L	434 m L
	460 w [a]	458 w [a]			459 w [a]		459 w [a]
			521 w L		512 w (523)	L	508 w L
534 m L	534 m L	540 s L	537 m L	539 m L	536 m (476)	δ(Ir–H)	543 m L
			548 w L				547 m L
618 m L	618 m L	617 m L	619 m L	619 m L	617 m (617)	L	618 m L
					782 m (582)	δ(Ir–H)	

[a] See Table 4. [b] $[IrD(SnCl_3)Cl(CO)(PPh_3)_2]$.

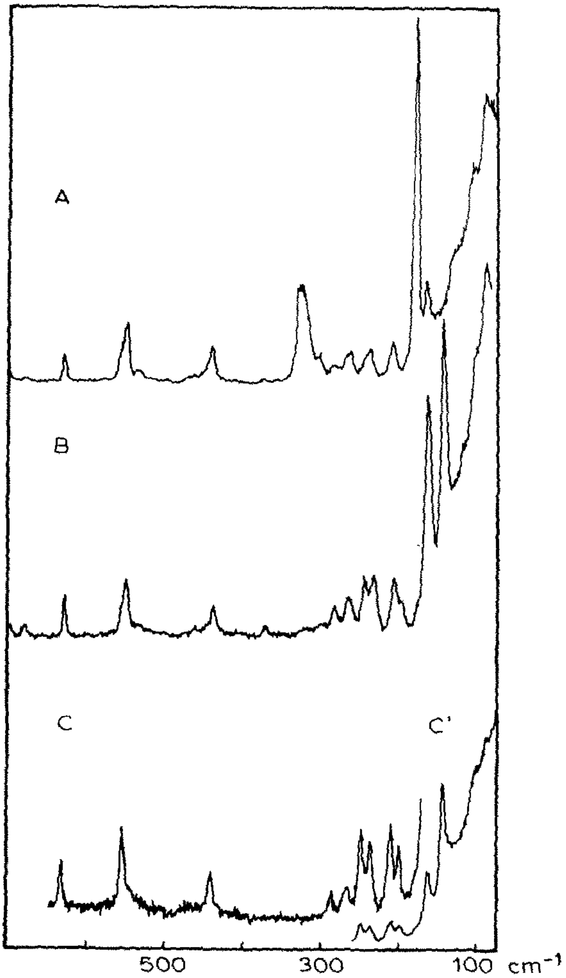


Fig. 1. Raman spectra of: (A) $[IrCl_2(HgCl)(CO)(PPh_3)_2]$, ν_0 19430 cm^{-1}, laser power 50 mW; (B) $[IrClBr(HgBr)(CO)(PPh_3)_2]$, ν_0 15867 cm^{-1}, laser power 100 mW; (C) $[IrBr_2(HgBr)(CO)(PPh_3)_2]$, ν_0 16259 cm^{-1}, laser power 100 mW; (C′) idem, intensity 0.25.

terms of localized vibrations. Rather the following three normal coordinates in order of decreasing energy can be used.

	X	Ir	Hg	X	X = Br	X = I
ν_1	←O	O→	←O	O→	252 cm^{-1}	232 cm^{-1}
ν_2	←O	O→	O→	←O	205 cm^{-1}	164 cm^{-1}
ν_3	O→	O→	←O	←O	141 cm^{-1}	108 cm^{-1}

Of these three vibrations ν_1 and ν_3 contribute significantly to the Ir–Hg stretching coordinate. The spectra for the tin chloride adducts IV and V are similar to that for the $HgCl_2$ adduct V. In IV, ν(H–Ir) (2159, 2196 cm^{-1}), ν(Sn–Cl) (330, 307 cm^{-1}) and ν(Ir–Sn) (208 cm^{-1}) are strongly localised. Hence the estimation of the Ir–Sn force constant is straightforward. The calculated and observed isotopic shifts upon

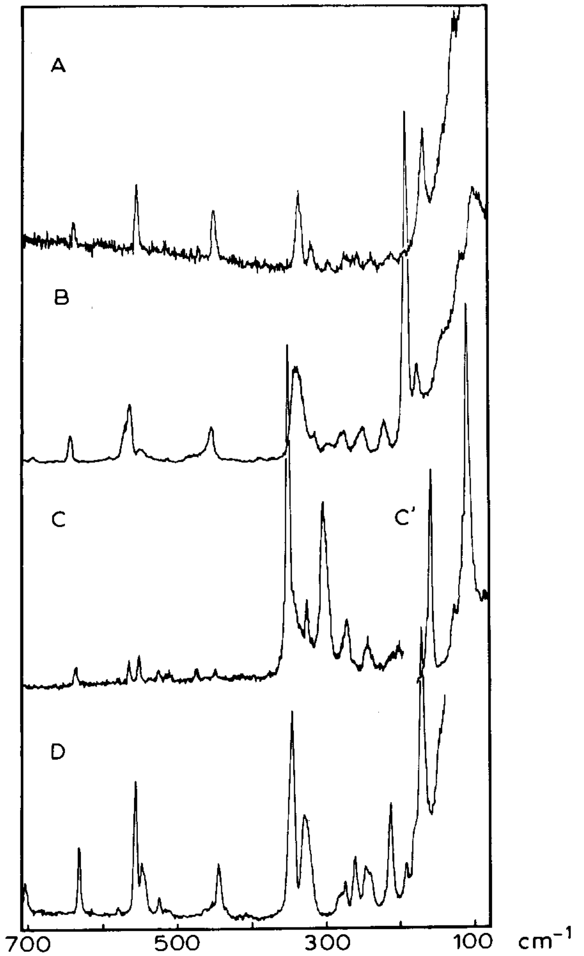


Fig. 2. Raman spectra of: (A) $[IrCl_3(CO)(PPh_3)_2]$, ν_0 16263 cm^{-1}, laser power 50 mW; (B) $[IrCl_2(HgCl)(CO)(PPh_3)_2]$, ν_0 19430 cm^{-1}, laser power 50 mW; (C) $[IrCl(HgCl)(SnCl_3)(CO)(PPh_3)_2]$, ν_0 17081 cm^{-1}, laser power 80 mW; (C') idem, intensity 0.25; (D) $[IrHCl(SnCl_3)(CO)(PPh_3)_2]$, ν_0 16266 cm^{-1}, laser power 100 mW.

deuteration are in good agreement, indicating that the set of force constants is reasonable. With the force field established in this manner (Table 4) we calculated the spectrum of V for the four different structures in Scheme 1. Structure A is the only one which leads to calculated frequencies which are in reasonable agreement with the experimental values. A Cl^- in *trans* position to Hg can be excluded, since no weak Raman band is observed in the region of 350 cm^{-1}. Configurations C and D do not allow any coupling between the Ir–Sn and Ir–Hg vibrations, which are perpendicular in these structures and consequently can be eliminated. To reproduce the observed splitting of these two vibrations would require a change in the Ir–Sn and Ir–Hg force constants. This decision against both C and D is supported by the NMR data cited above.

TABLE 3

STRUCTURAL PARAMETERS USED IN APPROXIMATE NORMAL COORDINATE CALCULATION

Distance (Å)	
Ir–Cl (*trans* CO)	2.41 [a]
Ir–Cl	2.453 [a]
Ir–Br (*trans* CO)	2.54 [a]
Ir–Br	2.586 [a]
Ir–Hg (–Cl)	2.57 [a]
Ir–Hg (–Br)	2.578 [a]
Hg–Cl	2.366 [a]
Hg–Br	2.499 [a]
Hg–I	2.71 [b]
Ir–I	2.80 [b]
Ir–Hg (–I)	2.58 [b]
Ir–C	2.00 [b]
Ir–Sn	2.50 [b]
Ir–Sn	2.50 [b]
Sn–Hg	2.70 [b]
Ir–H (D)	1.48 [b]
Sn–Cl	2.60 [b]
Angle (°)	
X–Ir–Y	90 [b]
Ir–Sn–Cl	109 [b]
Cl–Sn–Cl	109 [b]

[a] Ref. 3. [b] Estimated value; calculations for e.g. Sn–Cl 2.40 Å do not qualitatively change the results.

TABLE 4

FORCE CONSTANTS ($N\ m^{-1}$)

Ir–Hg	235	Ir–Cl	(*trans* Hg)	190
Hg–Cl	145	Ir–Cl	(*trans* CO)	169
Hg–Br	135	Ir–Cl	(*trans* Cl)	215
Hg–I	125	Ir–Br	(*trans* Hg)	150
Ir–Sn	195	Ir–Br	(*trans* CO)	130
Ir–CO	300	Ir–I	(*trans* Hg)	125
Ir–H (D)	278	Ir–I	(*trans* CO)	110
Hg–Sn	200	Sn–Cl		170

Discussion

The force constants in Table 4 give some insight into the metal–metal bonding and the electron distribution in these complexes. In Hg_2Cl_2 the Hg–Hg force constant is 213 $N\ m^{-1}$ [11], i.e., of the same magnitude as that for Ir–Hg in our complexes. In contrast, the Hg–Co force constant in $Hg[Co(CO)_4]_2$ is only 126 $N\ m^{-1}$ [12] so that we take our relatively large value for the Ir–Hg interaction as an indication of a strong covalent Ir–Hg bond. The Hg–Cl force constants are also informative. The value of 145 $N\ m^{-1}$ is similar to that found for Hg_2Cl_2 (121 $N\ m^{-1}$) [11] but about half of that for $HgCl_2$ (248 $N\ m^{-1}$) [13]. Consequently, we

(*Continued on p. 27*)

TABLE 5

NORMAL COORDINATES AND CALCULATED FREQUENCIES OF THE STRETCHING VIBRATIONS OF THE PLANAR FRAGMENT IrXYZCO

CO
|
Cl–Ir–Cl
|
Cl′

Obsd.	(calcd.)	Ass.
303m	(304)	Ir–Cl′
320s	(321)	Ir–Cl *sym*
–	(375)	Ir–Cl *asym*
–	(460)	Ir–CO

CO
|
Cl–Ir–Hg–Cl
|
Cl

Obsd.	(calcd.)	Ass.
179s	(177)	Ir–Hg
294w	(293)	Hg–Cl
300sh	(304)	Ir–Cl[t]
324m	(345)	Ir–Cl
460w	(464)	Ir–CO

CO
|
(Cl*)Br–Ir–Hg–Br
|
Cl(Br*)

Obsd.	(calcd.)	Ass. (PE distribution)		
142s	(141)	0.22 Ir–Br	0.52Ir–Hg	0.25Hg–Br
204m	(205)	0.41 Ir–Br	0.	0.58 Hg–Br
242m	(252)	0.36 Ir–Br	0.46Ir–Hg	0.17 Hg–Br
316w	(304)	Ir–Cl		
357w	(352)	Ir–Cl*		
458w	(460)	Ir–CO		

CO
|
Br–Ir–Hg–Br
|
Br*

Obsd.	(calcd.)	Ass. (PE distribution)		
140s	(137)	0.24 Ir–Br	0.51Ir–Hg	0.25Hg–Br
193m	(193)	Ir–Br*		
204m	(204)	0.44 Ir–Br		0.54Hg–Br
241m	(252)	0.31 Ir–Br	0.49Ir–Hg	0.20Hg–Br
	(461)	Ir–CO		

CO
|
(Cl*)I–Ir–HgI
|
Cl

Obsd.	(calcd.)	Ass. (PE distribution)		
105s	(108)	0.37 Ir–I	0.34Ir–Hg	0.29Hg–I
161s	(164)	0.44 Ir–I		0.54Hg–I
232m	(236)	0.17 Ir–I	0.66Ir–Hg	0.17Hg–I
308w	(304)	Ir–Cl		
367m	(352)	Ir–Cl*		
–	(462)	Ir–CO		

Table 5 (continued)

$H(D)-Ir(CO)(Cl)-SnCl_3$			$Cl_3Sn-Ir(CO)(Cl)-Hg-Cl$		
Obsd.	(calcd.)	Ass.	Obsd.	(calcd.)	Ass. (PE distribution)
208m (208)	(207(207))	Ir–Sn	155s	(147)	0.51 Ir–Hg 0.37Ir–Sn
319m (317)	(304(304))	Ir–Cl	232m	(236)	0.32 Ir–Hg 0.45Ir–Sn 0.10Hg–Cl
	(307(307))	Sn–Cl *sym*	290s	(294)	Hg–Cl
337s	(338)	Sn–Cl *asym*		(304)	Ir–Cl
459w	(460(460))	Ir–CO	312m	(309)	Sn–Cl *sym*
782m (582)	(785(562))	δ(Ir–H)	339s	(338)	Sn–Cl *asym*
2159w (1550)	(2169(1544))	Ir–H	459w	(460)	Ir–CO
2196w					

TABLE 6

$\nu(C\equiv O)$ AND ELECTRON AFFINITIES OF X AND Y IN OXIDATIVE ADDITION PRODUCTS OF $IrCl(CO)(PPh_3)_2$

Complex	$\nu(C\equiv O)$ (cm^{-1})	X	*EA* (eV)	Y	*EA* (eV)	ζEA
$IrCl_3(CO)(PPh_3)_2$	2075 [a]	Cl	3.61 [b]	Cl	3.61 [b]	7.22
$IrD_2Cl(CO)(PPh_3)_2$	2034 [a]	D	0.75 [b]	D	0.75 [b]	1.50
$IrHCl_2(CO)(PPh_3)_2$	2046 [a]	H	0.75 [b]	Cl	3.61	4.36
$IrCl_2(HgCl)(CO)(PPh_3)_2$	2044	Cl	3.61 [b]	HgCl	0.61	3.00 [c]
$IrH(SnCl_3)Cl(CO)(PPh_3)_2$	2068	H	0.75 [b]	$SnCl_3$	4.80	5.55 [c]
$IrCl(SnCl_3)(HgCl)(CO)(PPh_3)_2$	2055	HgCl	0.61	$SnCl_3$	4.80	4.40 [c]
						4.19

[a] Ref. 1. [b] F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 3rd Ed., Interscience Publishers 1972, p.57. [c] Estimated from Fig. 3.

believe that the effective oxidation state of mercury is rather low. This assumption is supported by the high field position of the ^{199}Hg resonances in our complexes *. Often there is a high field shift of the metal resonance with decreasing oxidation state [14].

The interaction of the $SnCl_3$ ligand with the transition metal ion is ambiguous. Formally, $SnCl_3$ can be regarded as a derivative of either Sn^{II} or Sn^{IV}. In the former, $SnCl_3$ is a nucleophile, in the latter an electrophile. Specifically, in the metal carbonyl complexes $[Cl_3SnCo(CO)_4]$, 123 N m^{-1}, [15], $[Cl_3SnFe(CO)_4]^-$, 133 N m^{-1}, [16] and $[Cl_3SnMn(CO)_5]$, 109 N m^{-1}, [17], we can view the M–Sn bond as resulting from the interaction either of the low valent anionic metal carbonyl with the electrophile $SnCl_3^+$ [18] or of the nucleophilic $SnCl_3^-$ with the metal cation. Our Ir–Sn force constant of ca. 195 N m^{-1} is considerably larger, so that the latter might be a more appropriate description of this bond for our derivatives.

A further characterisation of the coordinated $SnCl_3$ is the Sn–Cl force constant (170 N m^{-1}), which is between the values reported for $SnCl_4$ (255 N m^{-1}) and $SnCl^-$ (122 N m^{-1}) [19]. The interpretation of this constant is not straightforward, since it is influenced by the coordination number and the oxidation state of Sn [19]. However, the Sn–Cl force constant in the Ir^{III} complexes is smaller than those in $[Cl_3SnCo(CO)_4]$ [15], and $[Cl_3SnMn(CO)_5]$ [17]. This is an indication that the effective charge on Sn is lower, especially since a similar value is reported for $Cl_3SnFe(CO)_4^-$ [16], in which the lowering of the effective oxidation state is probably due to strong back donation from the low valent electron rich iron carbonyl group. This lower charge on Sn is consistent with our observation about the nature of the $SnCl_3$ ligand. Based on these observations it is probably reasonable to formulate complex V as the product of the oxidative addition of the hypothetical $Cl_3SnHgCl$ to Vaska's complex. This interpretation is also supported by a discussion of the (C≡O) frequencies (Table 6). Vaska [1] found two different types of behaviour of the C≡O frequency upon oxidative addition. Type A characterises the molecules X–Y, which form *cis*-adducts, with only partial breaking of the X–Y bond, whereas

* These are amongst the highest field ^{199}Hg signals observed to date see refs. [19,20,21].

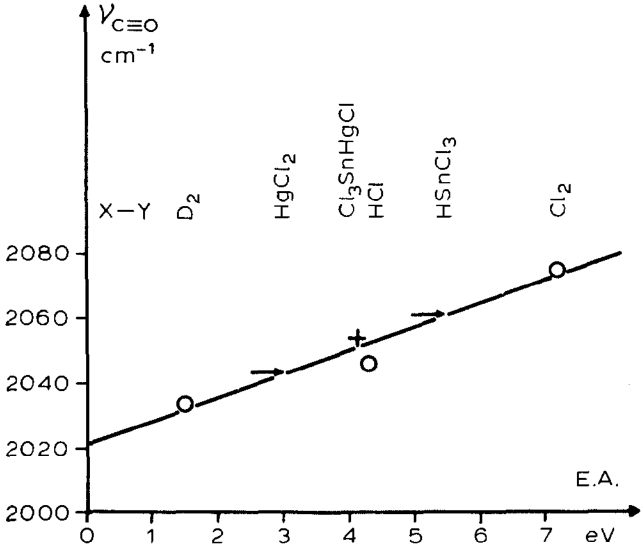


Fig. 3. Linear relation between ν(C≡O) and sum of the electron affinities of X–Y. The circles stem from ref. 1. The arrows show the positions from which the *E.A.*'s of $HgCl^+$ and $SnCl_3^-$ can be obtained. The cross indicates the sum of the *E.A.*'s of $SnCl_3^-$ and $HgCl^+$ for V.

type B molecules X–Y, form *trans* adducts. For type B one finds a linear correlation (Fig. 3) between the sum of the electron affinities (*E.A.*) of X and Y and the (C≡O) frequency [1]. Using this correlation we estimate the *E.A.*'s of $HgCl^+$ and $SnCl_3^-$ based on ν(C≡O) of VI and IV to be −0.61 and 4.80 eV, respectively. The sum of these values compares favourably with the value of 4.40 eV, estimated from CO frequencies of complex VI by the correlation in Fig. 3. This further supports the formulation of complex V as *trans* addition product of a hypothetical $ClHgSnCl_3$ molecule.

The information from the synthesis (see Introduction) suggests that the product stems from reaction of $[IrCl_2(HgCl)(CO)(PPh_3)_2]$ with $SnCl_2$ such that only the isomer with tin *trans* to Hg is formed. We attribute this specificity to the reluctance of $SnCl_3$ to be *trans* to CO, and will expand on this theme later.

Experimental

The Raman spectra were measured on a Spex Raman Ramalog 4 spectrometer equipped with a double monochromator Spex Ser. No 5421 and a digital photon counting unit Spex DPC 2. Either an Argon ion laser Spectra Physics 164 (19430 cm^{-1}) or a dye laser Spectra Physics 375 (Rhodamine G) pumped by an Argon ion laser Spectra Physics 175 was used as exciting source. $\tilde{\nu}_0$ was determined recording the Raman spectrum of CCl_4. The spectra of the solid samples in melting point tubes were measured under the following standard conditions: exciting power 50–100 mW, slit width 200 μ, sensitivity 5000 photons s^{-1}, integration time 0.5 s, scan speed 1 cm^{-1} s^{-1}.

NMR spectra were measured as solutions in either $CDCl_3$ or C_6D_6/CH_2Cl_2 (see

Table 1) in 10 mm tubes, using a Bruker WM 250. ^{31}P, ^{119}Sn and ^{199}Hg spectra were measured at 101.3, 93.3 and 44.7 MHz respectively. Acquisition times and pulse angles for the three nuclei were 0.8, 0.2 and 0.2 s, respectively. In view of the large spin–spin coupling constants 50 KHz spectral widths were routinely employed.

All synthetic operations were carried out using dry solvents under N_2. If H_2O is present oxidative addition to afford "Ir–H" complexes is often observed.

Synthesis of [IrCl$_2$(HgCl)(CO)(P(p-CH$_3$OC$_6$H$_4$)$_3$)$_2$]

Solid $HgCl_2$ (0.136 g, 0.50 mmol) was added to a solution of [IrCl(CO)(P(*p*-$CH_3OC_6H_4)_3)_2$] in ca. 3 ml $CHCl_3$. Ethanol was then added until all of the $HgCl_2$ dissolved. Stirring for 10 min was followed by concentration using a rotary evaporator. Extraction with 20 ml $CHCl_3$ and filtration through Celite was followed by concentration to ca. 3 ml. Addition of alcohol caused precipitation of the product (0.563 g, 92%).

Synthesis of [IrCl(SnCl$_3$)(HgCl)(P(p-CH$_3$OC$_6$H$_4$)$_3$)$_2$]

The following is representative: An excess of anhydrous $SnCl_2$ (0.040 g) was added to [$IrCl_2$(HgCl)(CO)(P(*p*-$CH_3OC_6H_4)_3)_2$] (0.154 g, 0.125 mmol) in 6 ml dry CH_2Cl_2. Stirring for 2 h was followed by decanting the solution (a pipette may be used) such that unreacted $SnCl_2$ remained behind. The CH_2Cl_2 solution was then covered with petroleum ether (30–60°) and allowed to stand for several days at room temperature. The yellow needles which precipitated were collected (0.133 g, 75%). The product crystallized with a molecule of CH_2Cl_2, and is light sensitive. Calcd.(found): C, 34.39 (34.18); H, 2.41 (2.30)%.

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