A coordinatively flexible ligand for carbonyl clusters: bridging and terminal SnCl$_3$ groups in the iridium clusters [Ir$_4$(CO)$_{11}$(μ-SnCl$_3$)]$^-$, [Ir$_4$(CO)$_{10}$(SnCl$_3$)(μ-SnCl$_3$)]$^{2-}$ and [Ir$_6$(CO)$_{15}$(μ$_3$-SnCl$_3$)]$^-$ †

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The carbonyl cluster [Ir$_4$(CO)$_{11}$(SnX$_3$)]$^-$ [X = Cl, (**1a**) or Br (**1b**)] can be formed in good yield by insertion of SnX$_2$ in the Ir–Br bond of [Ir$_4$(CO)$_{11}$Br]$^-$ or, much less efficiently, by substitution of bromine with [SnCl$_3$]$^-$, in THF at room temperature. The disubstituted cluster [Ir$_4$(CO)$_{10}$(SnCl$_3$)$_2$]$^{2-}$ (**2**) was obtained in 50% yields by double substitution on [Ir$_4$(CO)$_{11}$Br]$^-$, in THF at 60 °C, whereas [Ir$_6$(CO)$_{15}$(SnCl$_3$)]$^-$ (**3**) can be prepared by carbonyl substitution of the homoleptic complex [Ir$_6$(CO)$_{16}$] with an excess of [SnCl$_3$]$^-$ in refluxing THF. In the three compounds, the SnCl$_3$ units act as a one electron donor, displaying terminal (in **2**), edge-bridging (in **1** and **2**) and face-bridging (in **3**) coordination. In keeping with a reduced bond order, the Ir–Sn bond distances increase in the series, being 2.584(1) Å for a terminal group; 2.72 Å for edge-bringing units and 2.78 Å for the face-bridging SnCl$_3$. Regardless of the coordination mode, the geometry of the three chlorine atoms is always pyramidal, with Cl–Sn–Cl angles close to 90° and Sn–Cl bond distances close to 2.42 Å. Tin is always symmetrically bridging, with Ir–Sn–Ir close to 60°.

SnR$_2$ (stannylene) and [SnR$_3$]$^-$ (stannato) units are well known ligands for noble metal complexes, and have been largely used, both for synthetic purposes, and also for their important catalytic application. Trihalogenostannato groups have been widely employed in the chemistry of iridium, more frequently as ligands in mononuclear complexes of Ir in the positive oxidation states.[1] The Ir–Sn bond is usually formed after insertion of SnX$_2$ into pre-existent Ir–X bonds: the result is a terminal SnX$_3$ ligand, acting as a one-electron donor, with a conventional covalent bond between the two metals.

Conversely, SnR$_2$ groups (dialkylstannylene) have been used as ligands for carbonyl clusters of iridium, in the zero oxidation state. Having one lone pair and one empty low-lying molecular orbital, SnR$_2$ can have both σ-donors and π-acceptor properties, comparable with those of CO. As a matter of fact, the SnR$_2$ groups have been introduced in Ir cluster *via* carbonyl substitution. The result is invariably an edge-bridging μ-SnR$_2$ group.[2] However, when clusters of other metals are used, different coordination modes can be obtained, such as (in the case of [Os$_3$(CO)$_{11}${Sn{CH(Me$_3$Si)$_2$}$_2$}]^2) terminal. Also dihalogenostannylene can be used for clusters, and they can be used to stabilize unconventional structures: thus, if [Pt$_{15}$(CO)$_{30}$]$^{2-}$ reacts with SnCl$_2$, a deep structural rearrangement occurs, with multiply bridging μ$_4$-SnCl$_2$ sitting on a "butterfly" arrangement of platinum atoms.[3]

Beside these synthetic applications, the interest in M–Sn compounds stem from their catalytic application. Tin is an important modifier of noble metal catalysts in many reactions, involving hydrogen. Yet, its role is not fully clarified: in some

instances, it is thought to modify the electronic environment of the active sites, in some others it probably disperses the atoms of the noble metal, reducing the activity in hydrogenolysis reactions.[4] Anodes covered with mixed oxide layers of SnO$_2$–IrO$_2$ are studied for their ability to electrocatalyze O$_2$ evolution.[5] The use of bimetallic particles, prepared from preformed heterometallic clusters containing tin, has been already documented. For example, Ru–Sn clusters, can be supported to mesoporous material and used for solvent free hydrogenation (a nice example of a clean technology);[6] also Ir–Sn supported metal particles have been prepared and characterized by EDX (energy-dispersed X-ray analysis); TEM and TPRE (temperature-programmed reactions): the properties and the catalytic behavior of the particles are very dependent on the precursor used, and the supporting oxide.[7]

Iridium–tin complexes have been exploited for photocatalysis[8] and for hydrogen-transfer reactions.[9] In order to gather more information on the bonding ability of the SnCl$_2$ and SnCl$_3$ groups, and attempting to better characterize the nature of the Sn–Ir bond, we have investigated the synthesis of new heterometallic clusters, obtaining a series of compounds, in which the SnCl$_3$ ligand displays a unexpected coordinating flexibility.

Results

Synthesis and chemical characterization

In agreement with the synthesis of the mononuclear Ir derivatives, we tried to insert SnBr$_2$ into the preformed Ir–Br bond of the well known [Ir$_4$(CO)$_{11}$Br]$^-$ cluster.[10] The reaction is fast and clean, proceeding at room temperature in THF, with quantitative conversion. This is by far the best method to obtain the tribromostannato derivative [Ir$_4$(CO)$_{11}$(SnBr$_3$)]$^-$ (**1b**). However, owing to the instability of the chloro-substituted [Ir$_4$(CO)$_{11}$Cl]$^-$,

the trichlorostannato-substituted cluster $[Ir_4(CO)_{11}SnCl_3]^-$ (**1a**) could not be obtained in the same way. Since **1a**, together with **2** and **3**, would form a nice series of compounds, we had to find a different method to prepare it. As yet, the best synthesis of the trichlorostannato derivative is the direct substitution of the bromine atom of $[Ir_4(CO)_{11}Br]^-$ with $[SnCl_3]^-$. A sluggish reaction with low yields occurs, probably because $[SnCl_3]^-$ is a much poorer nucleophile than Br^-. If excess $[SnCl_3]^-$ is added, the disubstituted cluster $[Ir_4(CO)_{10}(SnCl_3)_2]^{2-}$ is obtained, providing evidence that the carbonyl groups in **1** are labilized toward further substitution. This behavior is typical for the polysubstitution on $Ir_4(CO)_{12}$ derivatives.[11] As a matter of fact the reaction between $[Ir_4(CO)_{11}Br]^-$ and $[SnCl_3]^-$ in 1 : 2 molar ratio (the double substitution of bromine and CO, performed in THF at 60 °C), is the simplest preparation of cluster **2**. However, a very large excess of $[SnCl_3]^-$ leads to complete cluster demolition.

The synthesis of $[Ir_6(CO)_{15}SnCl_3]^-$ was performed by reacting $Ir_6(CO)_{16}$ and $[SnCl_3]^-$ in THF, at refluxing temperature, for 8 h. Excess of free ligands, or longer times, did not give any evidences of further substitutions.

The monosubstituted cluster **1b** can be dehalogenated with $AgBF_4$ to yield a new product (**4**), presently under characterization. However, the IR spectrum (v_{max} in THF 2066s, 2027m, 1828m, 1780w cm^{-1}), the solubility, and the chemical behavior (**4** is converted back to **1b** if $[PPh_4]Br$ is added) strongly suggest for this product the formula $Ir_4(CO)_{11}SnBr_2$

Solid-state structures

The solid-state structures of **1a**, **2** and **3** are represented in Figs. 1, 2 and 3 respectively. The relevant bond distances for the two tetranuclear clusters **1a** and **2** are listed in Table S1 (ESI †), while Table S2 collects the bond distances of the octahedral cluster **3**.
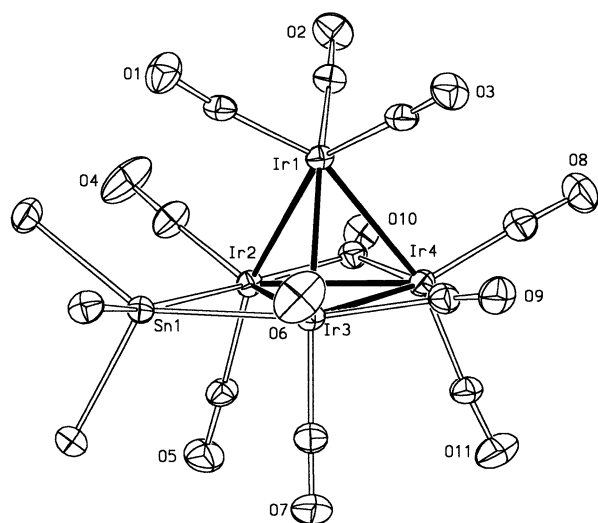

Fig. 1 Solid-state structure of $[Ir_4(CO)_{11}SnCl_3]^-$ (**1a**); ellipsoids are drawn at the 30% probability level. The carbon atoms are labeled as the oxygen to which they are attached.

Clusters **1a** and **2** display a tetrahedral arrangement of iridium atoms, with a basal plane defined by three bridging (two CO groups and one $SnCl_3$) group. To help comparisons identical numbering schemes were adopted.

The obvious difference between the two clusters is the substitution of CO11 (an axial carbonyl group of **1a**) with one terminal $SnCl_3$ unit. In order to find any trend attributable to the different coordination modes of the $SnCl_3$ groups, the average structural parameters for the three clusters are compared in Table 1.

All bond distances are extremely similar and no obvious effect can be observed. As a matter of fact the thrichlorostannato groups do not have any elongating effect on the
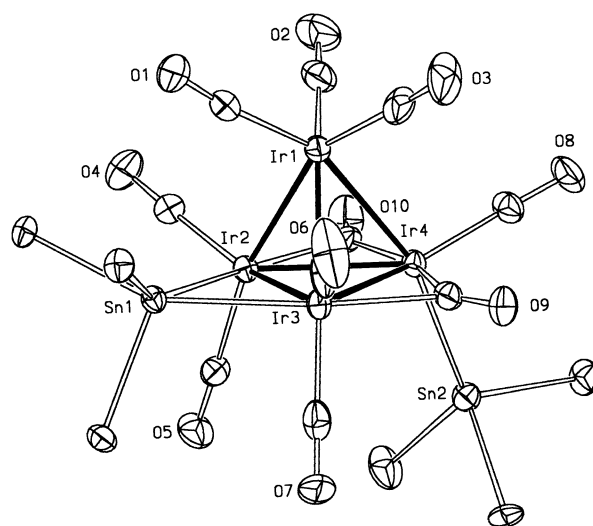

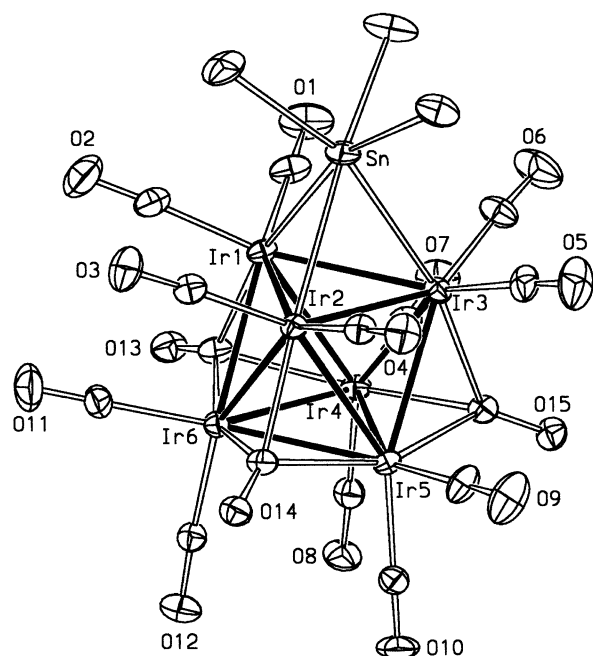**Fig. 2** Solid-state structure of $[Ir_4(CO)_{10}(SnCl_3)_2]^{2-}$ (**2**); other details as in Fig. 1.

Fig. 3 Solid-state structure of $[Ir_6(CO)_{15}SnCl_3]^-$ (**3**); other details as in Fig. 1.

bridged bonds. Even the negative charges brought about by the $SnCl_3$ units do not seem to be back-donated to the remaining carbonyl ligands, as both the Ir–C and the C–O bond distances are substantially identical. The "structural" *trans* effect is very similar for terminal $SnCl_3$ and CO ligands, as Ir1–Ir4 (the bond *trans* to tin in **2**) measures 2.725(1) Å, to be compared with an average Ir1–Ir$_{basal}$ separation of 2.723 Å (and an Ir1–Ir4 distance of 2.773(1) in **1a**). Also the geometry around of the three chlorine atoms are substantially identical in terminal and bridging moieties, with Sn–Cl distances close to 2.42 Å, and Cl–Sn–Cl close to 90°. These angles are comparable to those found in the "free" $SnCl_3^-$ ion,[12] whereas the Sn–Cl distances are shorter, as usually found in other iridium complexes.[1]

Cluster **3** has an octahedral metal cage with one face bridged by the $SnCl_3$ group. Three carbonyls are face-bridging ligands, the other (two for each iridium atom) are terminal. This distribution is reminiscent to that found in $Ir_6(CO)_{16}$ (red isomer)[13] and in the metal-substituted derivative $[Ir_6(CO)_{15}(HgCl)]^-$.[14]

In this case, an important structural variation brought about by the $SnCl_3$ ligand can be appreciated, since the three Ir–Ir

Table 1 Average distances (Å) and angles (°) in the clusters **1a**, **2** and **3**

	1a	**2**	**3**
Average distances			
Ir–Ir (unbridged)	2.724	2.727	–
Ir–Ir (bridged by Sn)	2.775(1)	2.763(1)	2.831
Ir–Ir (bridged by CO)	2.750	2.760	2.776
Ir–Sn$_{term}$	2.584(1)	–	–
Ir–Sn$_{br}$	2.738	2.718	2.775
Sn–Cl	2.425	2.426	2.417
Ir–C$_{term}$	1.90	1.89	1.88
Ir–(μ-C)	2.09	2.09	2.20
C–O$_{term}$	1.13	1.14	1.13
C–O$_{br}$	1.17	1.17	1.16
Average angles			
Ir–Sn–Ir	60.88(1)	61.12(1)	61.32
Cl–Sn–Cl	93.64	96.12	90.86

term = Terminal; br = edge bridging.

distances of the face bridged by SnCl₃ are definitely longer than the remaining nine, bridged by CO.

The asymmetry of the bridging carbonyl ligands is a very sensitive tool to measure different electron density at the metal atoms.[15] However, the bridging CO groups in **1**, **2** and **3** are essentially symmetric (the small differences in the Ir–C$_{bridging}$ bond lengths are less than 0.15 Å and comparable to experimental errors (±0.05 Å)) reinforcing the idea that CO and SnCl₃ have very similar donor ability.

Experimental

All the solvents were purified and dried by conventional methods and stored under nitrogen. All the reactions were carried out under oxygen-free nitrogen atmospheres using the Schlenk-tube technique.[16] Ir₄(CO)₁₂ [17] and ammonium and phosphonium salts of [SnCl₃]⁻ [18] were prepared by literature methods. Infrared spectra in solution were recorded on a Nicolet Avatar spectrophotometer, using calcium fluoride cells previously purged with N₂. Elemental analyses were carried out by the staff of Laboratorio di Analisi of the Dipartimento di Chimica Inorganica, Metallorganica e Analitica, at the University of Milano.

Synthesis of [PPh₄][Ir₄(CO)₁₁(SnCl₃)] ([PPh₄]1a)

[PPh₄][Ir₄(CO)₁₁Br] (0.41 g; 0.27 mmol) and [PPh₄][SnCl₃] (0.55 g, 0.27 mmol) were dissolved in THF and stirred at room temperature for 1 h. The mixture was decanted and the clear solution transferred by syringe. The solution was dried in vacuum and the product extracted with 2-propanol. Crystals (0.10 g, 23%) were obtained by slow evaporation.

v_{max}/cm⁻¹ (THF): 2088w, 2050s, 2027w, 2014m, 1839m, 1816m cm⁻¹.

Found: C, 25.0; H, 1.1. C₃₅H₂₀Cl₃Ir₄O₁₁PSn requires C, 25.6; H, 1.2%.

Synthesis of [PPh₄][Ir₄(CO)₁₁(SnBr₃)] (1b)

[PPh₄][Ir₄(CO)₁₁Br] (0.251 g; 0.17 mmol) and SnBr₂ (0.06 g, 0.21 mmol) were dissolved in THF (25 cm³) and stirred at room temperature for 2 h. After checking complete conversion by IR spectroscopy, the solvent was dried in vacuum, and the orange residue washed with hexane (2 × 10 cm³). According to the elemental analysis, the compound is sufficiently pure for synthetic purposes. Yield 0.30 g, 82%

v_{max}/cm⁻¹ (THF): 2087w, 2050vs, 2028m, 2010m, 1838w.

Found: C, 23.6; H, 1.15. C₃₅H₂₀Br₃Ir₄O₁₁PSn requires C, 23.69; H, 1.14%.

Synthesis of [N(PPh₃)₂]₂[Ir₄(CO)₁₀(SnCl₃)₂]·C₆H₁₂ ([N(PPh₃)₂]₂2·C₆H₁₂)

[N(PPh₃)₂][Ir₄(CO)₁₁Br] (0.33 g; 0.20 mmol) and [N(PPh₃)₂]-[SnCl₃] (0.76 g, 0.39 mmol) were dissolved in THF (15 cm³) and stirred at 60 °C for 2 h. The solution was filtered and then concentrated in vacuum. It was then layered with cyclohexane until well shaped crystals were formed. Yield 50%.

v_{max}/cm⁻¹ (THF): 2062m, 2035vs, 1998vs, 1835m, 1799m

Found: C, 39.3; H, 2.3; N 1.2. C₈₈H₇₂Cl₆Ir₄N₂O₁₀P₄Sn₂ requires C, 39.7; H, 2.7; N, 1.0%.

Synthesis of [NMe₂(CH₂Ph)₂][Ir₆(CO)₁₅(SnCl₃)] ([NMe₂(CH₂Ph)₂]3)

[Ir₆(CO)₁₆] (0.16 g; 0.10 mmol) and [NMe₂(CH₂Ph)₂][SnCl₃] (0.046 g, 0.10 mmol) were dissolved in THF (20 cm³) and stirred at the refluxing temperature for 8 h. The solution was filtered and dried in vacuum. The residue was dissolved in CH₂Cl₂ and layered with cyclohexane to yield 20 mg (10%) of crystalline product.

Table 2 Crystallographic data

	[PPh₄]**1a**	[N(PPh₃)₂]₂**2**·C₆H₁₂	[NMe₂(CH₂Ph)₂]**3**·CH₂Cl₂
Formula	C₃₅H₂₀Cl₃Ir₄O₁₁PSn	C₈₈H₇₂Cl₆Ir₄N₂O₁₀P₄Sn₂	C₃₂H₂₂Cl₅Ir₆NO₁₅Sn
M	1641.37	2660.36	2109.68
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a/Å	9.032(1)	11.096(1)	10.321(1)
b/Å	36.926(4)	15.007(1)	15.465(2)
c/Å	12.169(1)	27.976(3)	15.482(2)
a/°	90	104.69(1)	85.64(1)
β/°	91.83(1)	93.39(1)	81.15(1)
γ/°	90	90.39(1)	78.11(1)
U/Å³	4056.5(7)	4497.2(8)	2386.8(5)
Z	4	2	2
μ(Mo-Kα)/cm⁻¹	139.3	67.3	174.6
T/K	223	223	223
Total no. reflections	37426	46397	30518
Total independent	9786	21679	11832
R_{int}	0.0419	0.0404	0.0370
Final R_2 (F^2, all reflections)[a]	0.050	0.062	0.045
Final R_{2w} (F^2, all reflections)[a]	0.076	0.079	0.071
Conventional R_1 ($I > 2\sigma(I)$)	0.034	0.038	0.028

[a] $R_2 = [\Sigma(|F_o^2 - kF_c^2|)/\Sigma F_o^2]$, $R_{2w} = [\Sigma w(F_o^2 - kF_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

ν_{max}/cm^{-1} (THF): 2104w, 2064vs, 2026w, 1751m cm^{-1}.

Found: C, 19.0; H, 1.1; N 0.74. $C_{32}H_{22}Cl_5Ir_6NO_{15}Sn$ requires C, 18.2; H, 1.1; N 0.66%.

X-Ray data collection and structure determination

Crystal data and other experimental details are summarized in Table 2. The diffraction experiments were carried out on a Bruker SMART CCD area-detector at 223 K. The structures were solved by direct methods[19] and subsequent difference Fourier syntheses, and refined by full-matrix least squares on F^2.

In compound [PPh$_4$]**1a** atoms Ir(1), Ir(3) and Ir(4) show a minor disorder with three other Ir atoms forming the frequent "star of David" disposition.[20] The occupancy factors of Ir(1), Ir(3) and Ir(4) have been refined to 0.96, those of the other three Ir atoms to 0.04. In compound [NMe$_2$(CH$_2$Ph)$_2$]**3**·CH$_2$Cl$_2$ the chlorine atoms of the solvent molecule are disordered and appear to be split into four Cl atoms with occupancy factors of 0.50 each. Isotropic thermal factors were refined for the low-weighted Ir atoms and for solvent atoms. All the other non-hydrogen atoms were treated anisotropically. Hydrogen atoms of the solvent molecules were neglected, all the other hydrogen atoms were placed in their ideal positions (C–H = 0.97 Å, B 1.10 times that of the carbon atom to which they are attached) and not refined.

CCDC reference numbers 218972 (**1a**), 218973 (**2**) and 218974 (**3**).

See http://www.rsc.org/suppdata/dt/b3/b310790f/ for crystallographic data in CIF format.

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