

The mixed-metal carbonyl cluster anion $[\text{Os}_3\text{Ir}(\text{CO})_{13}]^-$: synthesis, structure, reactivity and catalytic activity in the carbonylation of methanol

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Abstract

The cluster anion $[\text{Os}_3\text{Ir}(\text{CO})_{13}]^-$ (**1**) was prepared in 50% yield by reaction of $\text{Os}_3(\text{CO})_{12}$ with $[\text{Ir}(\text{CO})_4]^-$. The single-crystal X-ray structure analysis of the bis(triphenylphosphoranylidene)ammonium salt shows **1** to consist of a tetrahedral metal core with one of the 13 carbonyl ligands being bridging. Protonation of **1** led to the neutral cluster $\text{HOs}_3\text{Ir}(\text{CO})_{13}$ (**2**), whereas the hydrogenation gave the cluster anion $[\text{H}_2\text{Os}_3\text{Ir}(\text{CO})_{12}]^-$ (**3**). The catalytic activity of **1** for the carbonylation of methanol was studied. Using CH_3I as co-catalyst, catalytic turnover numbers up to 1800 were obtained (140°C, 30 bar) within 14 h. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Mixed-metal carbonyl clusters have received increasing attention over the past 25 years, because of the possible synergistic effects of the different metal centres in catalytic reactions. The polarity of the mixed-metal bonds also favours the reactivity of heterometallic systems with respect to homometallic clusters [1,2].

The carbonylation of methanol to give acetic acid is performed on an industrial scale using

the mononuclear complex $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ as the catalyst (Monsanto process) [3]. In a recent patent, a series of iridium compounds have been reported to be catalytically active for this process in the presence of ruthenium or osmium promoters [4]. This prompted us to study the chemistry of mixed iridium–ruthenium and iridium–osmium clusters and to explore their catalytic potential for carbonylation reactions.

In this paper we report the synthesis and structure of the cluster anion $[\text{Os}_3\text{Ir}(\text{CO})_{13}]^-$ (**1**), its reactivity towards protons and molecular hydrogen, as well as its catalytic activity in the carbonylation of methanol.

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2. Experimental

2.1. Materials

All synthetic reactions were carried out under an atmosphere of pure N_2 using standard Schlenk techniques. Solvents for synthetic and catalytic reactions were purified, dried and deoxygenated by distillation under N_2 over appropriate drying agents. $IrCl_3 \cdot xH_2O$ (Pressure Chemical) and $[N(PPh_3)_2]Cl$ (Fluka) were purchased and used as received. The compounds $Os_3(CO)_{12}$ [5], $Ir_4(CO)_{12}$ [6] and $[N(PPh_3)_2][Ir(CO)_4]$ [7] were prepared by literature methods. Preparative thin-layer chromatography was performed using 20×20 cm plates coated with FLUKA silica gel G.

2.2. Physical measurements

Infrared spectra of solutions and KBr pastilles were recorded on a Perkin-Elmer 1720X FT-IR spectrometer. 1H NMR spectra were recorded with a Varian Gemini 200 BB instrument and referred to the residual proton of the deuterated solvents. Microanalyses were carried out by the Mikroelementaranalytisches Laboratorium of ETH Zürich, Switzerland. The gas chromatographic analysis and the calibration experiments were carried out using a DANI 86.10 gas chromatograph (capillary column $50 m \times 0.25 mm \times 0.25 \mu m$, Carbowax 20 M, SPB-1 Fused Silica, no packing).

2.3. Carbonylation of methanol

All catalytic reactions were performed in glass-lined steel autoclaves (total volume 100 ml), methanol being both solvent and substrate. In a typical experiment, the reaction mixture contained: CH_3OH , 369.85 mmol, 15.00 ml; CH_3I , 3.57 mmol, 223.0 μl ; $[N(PPh_3)_2][Os_3Ir(CO)_{13}]$, 0.0357 mmol, 59.4 mg. Then the autoclave was charged with 30 bar of CO and heated to $140^\circ C$ under vigorous stirring. At the end of the reaction, the autoclave was cooled to

room temperature, the solution volume was measured, and the reaction solution was analysed by gas chromatography (two injections per sample), after addition of 0.1000 g of toluene as internal standard to 2.00 ml of the solution. The yields of acetic acid and methyl acetate were determined with respect to the toluene standard, using separate calibration graphs for each of the products. The organometallic compounds found in the reaction solution were identified to be $Ir_4(CO)_{12}$ (yellow precipitate) and $[N(PPh_3)_2][Os(CO)_3I_3]$ (crystals obtained after concentration of the filtered reaction solution) by IR spectroscopy.

2.4. Preparations

2.4.1. $[N(PPh_3)_2][Os_3Ir(CO)_{13}]$ (anion 1)

A thf solution (50 ml) containing $Os_3(CO)_{12}$ (200 mg, 0.22 mmol) and $[N(PPh_3)_2][Ir(CO)_4]$ (190 mg, 0.225 mmol) was stirred at $100^\circ C$ in a pressure Schlenk tube for 4 h. The dark red solution was evaporated to dryness and treated with 30 ml of diethyl ether. Addition of an equal volume of hexane to the filtered solution under vigorous stirring gave an orange microcrystalline precipitate of $[N(PPh_3)_2][Os_3Ir(CO)_{13}]$; the product was isolated by decantation. A second crop of product was collected after slow evaporation of the decanted solution under reduced pressure. Yield: 197 mg (53.6%). Anal. Found: C, 35.32; H, 1.93; N, 0.85. Calc. for $C_{49}H_{30}NO_{13}P_2IrOs_3$: C, 35.34; H, 1.82; N, 0.84. IR (KBr, carbonyl region): 2072w, 2012vs, 1969s, 1780w, br cm^{-1} . 1H NMR ($CDCl_3$): δ 7.55 (m, 30 H, C_6H_5) ppm.

2.4.2. $HOs_3Ir(CO)_{13}$ (2)

To a stirred solution of **1** (100 mg, 0.06 mmol) in 15 ml of CH_2Cl_2 a slight excess of $HBF_4 \cdot OEt_2$ (54%, 31 μl) was added. After 15 min the dark orange solution was concentrated to 2 ml. The products were separated by TLC using CH_2Cl_2 and hexane (2:3) as eluent. The orange main band was extracted with CH_2Cl_2 ,

followed by evaporation to dryness, to give $\text{HOs}_3\text{Ir}(\text{CO})_{13}$ as a dark orange powder. The product was recrystallised from a mixture of CH_2Cl_2 and CH_3OH . Yield: 48 mg (70.8%). Anal. Found: C, 14.49; H, 0.18. Calc. for $\text{C}_{13}\text{HO}_{13}\text{IrOs}_3 \cdot \text{CH}_3\text{OH}$: C, 14.49; H, 0.43. IR (CH_2Cl_2 , carbonyl region): 2103vw, 2080m, 2059vs, 2018m, 2004m, 1838vw cm^{-1} . ^1H NMR (CDCl_3): δ 21.00 (s, 1 H) ppm.

2.4.3. $[\text{N}(\text{PPh}_3)_2][\text{H}_2\text{Os}_3\text{Ir}(\text{CO})_{12}]$ (anion 3)

A CH_2Cl_2 solution (30 ml) of $[\text{N}(\text{PPh}_3)_2][\text{Os}_3\text{Ir}(\text{CO})_{13}]$ (anion 1) (100 mg, 0.06 mmol) was placed in a pressure Schlenk tube under a pressure of 2 bar of hydrogen. The solution was stirred 5 h at 120°C. After evaporation of the solvent, the residue was dissolved in 20 ml of diethyl ether and filtered. The product $[\text{N}(\text{PPh}_3)_2][\text{H}_2\text{Os}_3\text{Ir}(\text{CO})_{12}]$ (anion 3) was iso-

lated by addition of an equal volume of hexane as a yellow micro-crystalline product. Yield: 82 mg (80.2%). Anal. Found: C, 34.98; H, 1.93; N, 0.84. Calc. for $\text{C}_{48}\text{H}_{32}\text{NO}_{12}\text{P}_2\text{IrOs}_3$: C, 35.16; H, 1.97; N, 0.85. IR (diethyl ether, carbonyl region): 2080vw, 2045m, 2012vs, 1968m, 1943w, 1924vw cm^{-1} . ^1H NMR (CDCl_3): δ -20.39 (s, 2 H), 7.55 (m, 30 H, C_6H_5) ppm.

2.4.4. $\text{H}_3\text{Os}_3\text{Ir}(\text{CO})_{12}$ (4)

A solution of $\text{HOs}_3\text{Ir}(\text{CO})_{13}$ (2) (50 mg, 0.044 mmol) in 25 ml of hexane was placed in a pressure Schlenk tube under a pressure of 2 bar of hydrogen. After stirring at 100°C for 10 min the colour of the solution changed from orange to yellow. Cooling the solution to room temperature caused the precipitation of $\text{H}_3\text{Os}_3\text{Ir}(\text{CO})_{12}$ (4) as a pale yellow powder. Yield: 41 mg (83.9%). IR (CH_2Cl_2 , carbonyl region): 2081vs,

Table 1
Crystallographic data for the $[\text{N}(\text{PPh}_3)_2]^+$ salt of 1

Formula	$\text{C}_{49}\text{H}_{30}\text{IrNO}_{13}\text{Os}_3\text{P}_2$
<i>M</i>	1665.48
Crystal system	Monoclinic
Space group	$P2_1/c$
<i>a</i> (Å)	18.003(6)
<i>b</i> (Å)	16.965(4)
<i>c</i> (Å)	18.237(7)
α (°)	90
β (°)	116.56(2)
γ (°)	90
<i>U</i> (Å ³)	4982(3)
<i>Z</i>	4
Crystal dimensions (mm)	$0.57 \times 0.418 \times 0.304$
Colour	orange
<i>D_c</i> (g cm^{-3})	2.220
μ (mm^{-1})	10.417
Transmission factors: minimum/maximum	0.0248/0.0538
<i>F</i> (000)	3080
θ limits (°)	2.24–25.48
<i>hkl</i> ranges	–21 to 19, 0 to 20, 0 to 22
Reflections measured	9240
Independent reflections	9240
Observed reflections	6643
$R1[I > 2\sigma(I)]/R1$ (all data) ^a	0.0682/0.1069
$wR2[I > 2\sigma(I)]/wR2$ (all data) ^b	0.1162/0.1359
Goodness of fit on F^{2c}	1.183

^a $R1 = \sum |F_o| - |F_c| / \sum |F_o|$.

^b $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^4]^{1/2}$.

^c $S = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ (*n*—number of reflections, *p*—number of parameters).

2050s, 2025m, 2011m cm^{-1} . $^1\text{H NMR}$ (CDCl_3): δ –20.65 (s, 3 H).

2.5. Crystallography

Single crystals (dark orange blocks) of the $[\text{N}(\text{PPh}_3)_2]^+$ salt of **1** were obtained by slow diffusion of hexane into a diethyl ether solution (Table 1). Single crystal X-ray data were collected at 20°C on a STOE AED2 4-circle diffractometer using Mo-K α graphite-monochromated radiation ($\lambda = 0.71073$ Å; ω - 2θ scans). The structure was solved by direct methods using SHELXS-97 program [8]. The structure refinement, using weighted full-matrix least-squares on F^2 , was carried out using the program SHELXL-97 [9] with anisotropic thermal parameters for all non-hydrogen atoms. An absorption correction was applied using psi scans. The hydrogen atoms in the $[\text{N}(\text{PPh}_3)_2]^+$ cation were placed in calculated positions and refined as riding atoms using the SHELXL-97 default parameters. Fig. 1 was drawn with Zortep [10] (thermal ellipsoids, 30% probability level). Full tables of atomic parameters, bond lengths and angles are deposited at the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ (UK).

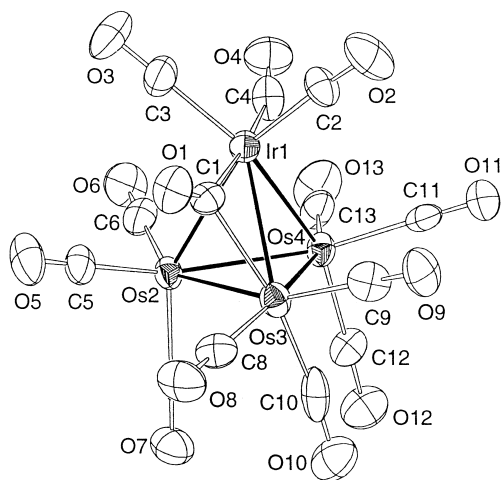
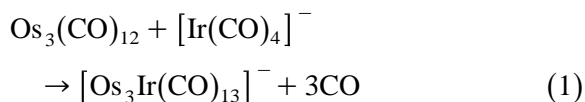


Fig. 1. Molecular structure of cluster anion **1**.

3. Results and discussion

3.1. Synthesis, characterisation and solid-state structure of $[\text{Os}_3\text{Ir}(\text{CO})_{13}]^-$ (**1**)

The reaction of $\text{Os}_3(\text{CO})_{12}$ and $[\text{Ir}(\text{CO})_4]^-$ in refluxing tetrahydrofuran (thf) leads to the mixed-metal anion of $[\text{Os}_3\text{Ir}(\text{CO})_{13}]^-$ (**1**), which is isolated as the bis(triphenylphosphoranylidene)ammonium salt from an ether-hexane mixture (Eq. (1)). The orange micro-crystalline product is air-stable and soluble in polar organic solvents such as methanol, THF, acetone or dichloromethane.



The IR spectrum of **1** is quite similar to that of the ruthenium homologue $[\text{Ru}_3\text{Ir}(\text{CO})_{13}]^-$ [11] with three bands in the region of terminal carbonyls and only one in the region of bridging carbonyls. In the $^1\text{H NMR}$ spectrum only the multiplet of the $[\text{N}(\text{PPh}_3)_2]^+$ cation, centred at δ 7.55 ppm, is observed.

In order to compare the molecular structure of **1** to that of the $[\text{Ru}_3\text{Ir}(\text{CO})_{13}]^-$ homologue, a single-crystal X-ray analysis of $[\text{N}(\text{PPh}_3)_2][\text{Os}_3\text{Ir}(\text{CO})_{13}]$ is undertaken. The crystal consists of discrete $[\text{N}(\text{PPh}_3)_2]^+$ cations and $[\text{Os}_3\text{Ir}(\text{CO})_{13}]^-$ anions, showing normal intermolecular contacts between the atoms of the ions. In contrast to $[\text{N}(\text{PPh}_3)_2][\text{Ru}_3\text{Ir}(\text{CO})_{13}]$ where the asymmetric unit contains three independent molecules (two of them being structural isomers) [11], the analysis of $[\text{N}(\text{PPh}_3)_2][\text{Os}_3\text{Ir}(\text{CO})_{13}]$ reveals only one molecule per asymmetric unit. This is in line with the higher stability of osmium clusters and indicates a lower mobility of the carbonyl ligands. The structure of **1** is depicted in Fig. 1, selected bond lengths and angles are given in Table 2.

The Os_3Ir core of **1** defines an almost regular tetrahedron with Os–Ir and Os–Os distances of 2.75 Å (average), only the Os(3)–Os(4) bond being with 2.821(1) Å longer. The envelope of

Table 2
Selected bond lengths (Å) and angles (°) for anion **1**

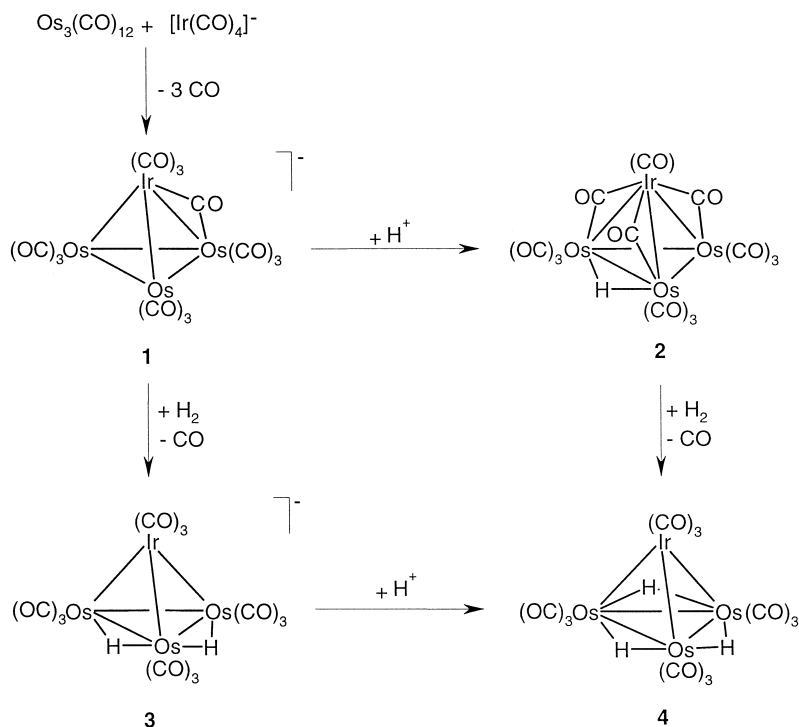
Ir(1)–Os(2)	2.7759(14)	Os(3)–Os(4)	2.8206(12)
Ir(1)–Os(3)	2.7672(14)	Ir(1)–C(1)	2.067(19)
Ir(1)–Os(4)	2.7853(11)	Os(3)–C(1)	2.266(17)
Os(2)–Os(3)	2.7597(13)	C(1)–O(1)	1.14(2)
Os(2)–Os(4)	2.7397(13)		
Os(3)–Ir(1)–Os(2)	59.72(4)	Os(2)–Os(3)–Os(4)	58.79(3)
Os(3)–Ir(1)–Os(4)	61.06(3)	Ir(1)–Os(3)–Os(4)	59.79(3)
Os(2)–Ir(1)–Os(4)	59.03(3)	Os(2)–Os(4)–Ir(1)	60.32(3)
Os(4)–Os(2)–Os(3)	61.71(3)	Os(2)–Os(4)–Os(3)	59.49(3)
Os(4)–Os(2)–Ir(1)	60.66(3)	Ir(1)–Os(4)–Os(3)	59.15(3)
Os(3)–Os(2)–Ir(1)	59.98(3)	Ir(1)–C(1)–O(1)	145.4(16)
Os(2)–Os(3)–Ir(1)	60.30(3)	Os(3)–C(1)–O(1)	135.3(15)

carbonyl ligands is different from those in the known homologues $[\text{Ru}_3\text{Ir}(\text{CO})_{13}]^-$ and $[\text{Os}_3\text{Co}(\text{CO})_{13}]^-$, where two or four (in the Ru_3Ir cluster) [11] and three (in the Ru_3Co cluster) [12] bridging CO groups have been found, respectively. In the structure of **1**, only the edge Ir(1)–Os(3) is bridged by a carbonyl

group, being in line with the metal–carbon distances Ir(1)–C(1) [2.067(19) Å] and Os(3)–C(1) [2.266(17) Å], the angles Ir(1)–C(1)–O(1) [145.4(16)°] and Os(3)–C(1)–O(1) [135.3(15)°] as well as with the IR spectrum. Each of the other metal atoms carries three terminal CO ligands. Contrary to the ruthenium analogue the bridged Ir(1)–Os(3) edge is not significantly shorter [2.767(1) Å] than the two non-bridged Ir–Os bonds with 2.776(1) Å for Ir(1)–Os(2) and 2.785(1) Å for Ir(1)–Os(4).

3.2. Reactions of $[\text{Os}_3\text{Ir}(\text{CO})_{13}]^-$ with H^+ and H_2

Treatment of **1** (Scheme 1) with an excess of $\text{HBF}_4 \cdot \text{OEt}_2$ in CH_2Cl_2 at ambient temperature leads quantitatively to the neutral orange cluster $\text{HOs}_3\text{Ir}(\text{CO})_{13}$ (**2**), which can be isolated by preparative thin-layer chromatography. Small crystals are obtained from a $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$



Scheme 1. Synthetic routes to clusters **1**–**4**.

mixture. In the IR spectrum of **2**, five bands in the region of terminal carbonyls are observed, a weak absorption band at 1838 cm^{-1} indicates bridging CO ligands. One singlet signal in the hydride region of the ^1H NMR spectrum is found at $\delta -21.00$ ppm. Based on these spectroscopic data, **2** should have the same ligand arrangement as $\text{HRu}_3\text{Co}(\text{CO})_{13}$, where the hydride ligand is found to bridge a Ru–Ru edge [13].

Anion **1** reacts with molecular hydrogen at 120°C to give the dihydrido cluster anion $[\text{H}_2\text{Os}_3\text{Ir}(\text{CO})_{12}]^-$ (**3**) in almost quantitative yield, which can be isolated as the bis(triphenylphosphoranyliden)ammonium salt from an ether/hexane mixture. The IR spectrum shows only six absorptions in the region of terminal carbonyl groups but no bands in the region of bridging CO groups, in contrast to the known homologues $[\text{H}_2\text{Ru}_3\text{Ir}(\text{CO})_{12}]^-$ [11] and $[\text{H}_2\text{Ru}_3\text{Co}(\text{CO})_{12}]^-$ [14]. The two equivalent hydride ligands give rise to a signal at $\delta -20.39$ ppm, in the same region as that observed for $[\text{H}_2\text{Ru}_3\text{Ir}(\text{CO})_{12}]^-$. We, therefore, believe that the two equivalent hydride ligands bridge two Os–Os edges in $[\text{H}_2\text{Os}_3\text{Ir}(\text{CO})_{12}]^-$.

The hydrogenation of $\text{HOs}_3\text{Ir}(\text{CO})_{13}$ (**2**) in hexane at 100°C affords the known cluster

$\text{H}_3\text{Os}_3\text{Ir}(\text{CO})_{12}$ (**4**), also accessible from the reaction of the anion $[\text{HOs}_3(\text{CO})_{11}]^-$ with the cyclooctadiene complex $[\text{Ir}(\text{cod})\text{Cl}]_2$ [15]. The air-stable cluster **4** precipitates as a pale yellow powder directly from the reaction solution. The four CO bands in the IR spectrum as well as the singlet at $\delta -20.65$ ppm in the ^1H NMR spectrum are in accordance with the spectroscopic data reported by Sundberg et al. [15]. By analogy to the trihydrido cluster homologues $\text{H}_3\text{Os}_3\text{Rh}(\text{CO})_{12}$ [15] or $\text{H}_3\text{Ru}_3\text{Ir}(\text{CO})_{12}$ [11], it can be assumed that in **4** the three hydride ligands bridge the metal–metal bonds of the Os_3 triangle, each metal atom of the Os_3Ir tetrahedron carrying three terminal carbonyl groups. The protonation of anion **3** with an excess of $\text{HBF}_4 \cdot \text{OEt}_2$ also leads to the formation of cluster **4**.

3.3. Catalytic activity of $[\text{Os}_3\text{Ir}(\text{CO})_{13}]^-$ in the carbonylation of methanol

The carbonylation of methanol is carried out using **1** as catalyst and CH_3I or HI as co-catalyst. The catalyst is tested at 140°C and CO pressure of 30 or 50 bar. The reactions are stopped after 2.5 or 14.5 h. Under the reaction conditions, the acetic acid formed undergoes

Table 3
Carbonylation of methanol catalysed by $[\text{Os}_3\text{Ir}(\text{CO})_{13}]^-$ **1**^a

Entry	Co-catalyst	Time (h)	p_{CO} (bar)	Yield (mmol) ^b		TON ^c	TOF (h^{-1}) ^d
				$\text{CH}_3\text{COOCH}_3$	CH_3COOH		
1	CH_3I	2.5	50	8.53	–	244	98
2	CH_3I	2.5	30	18.54	0.40	531	212
3	HI	2.5	50	19.76	3.09	640	256
4	HI	2.5	30	24.48	1.35	723	289
5	CH_3I	14.5	50	50.27	9.89	1685	116
6	CH_3I	14.5	30	52.79	11.98	1814	125
7	HI	14.5	50	42.90	7.34	1407	97
8	HI	14.5	30	44.69	6.65	1438	99

Effect of co-catalysts and CO pressure on the activity.

^aReactions conditions: $[\text{N}(\text{PPh}_3)_2][\text{Os}_3\text{Ir}(\text{CO})_{13}]$, 0.0357 mmol; CH_3OH , 369.85 mmol; co-catalyst, 3.57 mmol; temperature, 140°C ; agitation speed, 600 min^{-1} .

^bMeasured by gas chromatography.

^cTON (catalytic turnover number) = mol products formed ($\text{CH}_3\text{COOCH}_3$ and CH_3COOH) per mol catalyst.

^dTOF (catalytic turnover frequency) = mol products formed ($\text{CH}_3\text{COOCH}_3$ and CH_3COOH) per mol catalyst per hour.

Table 4
Carbonylation of methanol catalysed by $[\text{Ru}_3\text{Ir}(\text{CO})_{13}]^- \mathbf{1}^a$

Entry	Co-catalyst	Time (h)	p_{CO} (bar)	Yield (mmol) ^b		TON ^c	TOF (h^{-1}) ^d
				$\text{CH}_3\text{COOCH}_3$	CH_3COOH		
1	CH_3I	2.5	50	7.86	0.16	224	98
2	CH_3I	14.5	50	21.03	1.92	642	44
3	HI	2.5	50	14.87	0.43	429	172
4	HI	14.5	50	37.48	6.46	1231	85
5	HI	2.5	30	20.66	0.78	601	240
6	HI	14.5	30	47.67	9.23	1594	110

Effect of co-catalysts and CO pressure on the activity.

^aReactions conditions: $[\text{N}(\text{PPh}_3)_2][\text{Ru}_3\text{Ir}(\text{CO})_{13}]$, 0.0357 mmol; CH_3OH , 369.85 mmol; co-catalyst, 3.57 mmol; temperature, 140°C; agitation speed, 600 min^{-1} .

^bMeasured by gas chromatography.

^cTON (catalytic turnover number) = mol products formed ($\text{CH}_3\text{COOCH}_3$ and CH_3COOH) per mol catalyst.

^dTOF (catalytic turnover frequency) = mol products formed ($\text{CH}_3\text{COOCH}_3$ and CH_3COOH) per mol catalyst per hour.

partial esterification to give methyl acetate, due to the excess of methanol which is used as the solvent. After the catalytic reaction, the reaction mixture is analysed and shown to contain methyl acetate, acetic acid, methyl iodide, water, unreacted methanol and dimethylether. The yields of the products formed are determined by gas chromatography (Table 3).

The best conversion is observed after a reaction time of 14.5 h with CH_3I as co-catalyst under a CO pressure of 30 bar, the catalytic turnover number (TON) being 1814, corresponding to a catalytic turnover frequency (TOF) of 125 h^{-1} . With HI as the co-catalyst under the

same conditions, the yields of methyl acetate and acetic acid are slightly lower. Comparable reactions using the ruthenium homologue $[\text{Ru}_3\text{Ir}(\text{CO})_{13}]^-$, which we synthesised recently [11], as catalyst show an inverse effect (Table 4). It is noteworthy that in all cases a decrease in the catalytic activity is observed when the CO pressure is raised from 30 to 50 bars.

In all catalytic reactions the final volume of the reaction solution is found to have been reduced from 15 ml to 14–12 ml depending on the reaction time. It is assumed that some of the solution is lost by handling during the venting process, but most of the loss is due to a volatile

Table 5
Effect of variation of the catalyst in comparison to $[\text{Os}_3\text{Ir}(\text{CO})_{13}]^- \mathbf{1}^a$

Entry	Catalyst	n (mmol) of catalyst	Co-catalyst	Time (h)	Yield (mmol) ^b		TON ^c	TOF (h^{-1}) ^d
					$\text{CH}_3\text{COOCH}_3$	CH_3COOH		
1	$[\text{N}(\text{PPh}_3)_2][\text{Os}_3\text{Ir}(\text{CO})_{13}]$	0.0357	HI	2.5	24.48	1.35	723	289
2	$[\text{N}(\text{PPh}_3)_2][\text{Os}_3\text{Ir}(\text{CO})_{13}]$	0.0357	CH_3I	2.5	18.54	0.40	531	212
3	$[\text{N}(\text{PPh}_3)_2][\text{Os}_3\text{Ir}(\text{CO})_{13}]$	0.0357	CH_3I	14.5	52.79	11.98	1814	125
4	$[\text{N}(\text{PPh}_3)_2][\text{Os}(\text{CO})_3\text{I}_3]/\text{Ir}_4(\text{CO})_{12}$	0.1069/ 0.0357	HI	2.5	12.77	0.41	92	37
5	$[\text{N}(\text{PPh}_3)_2][\text{Os}(\text{CO})_3\text{I}_3]/\text{Ir}_4(\text{CO})_{12}$	0.1069/ 0.0357	CH_3I	2.5	11.52	0.19	82	33
6	$[\text{N}(\text{PPh}_3)_2][\text{Os}(\text{CO})_3\text{I}_3]/\text{Ir}_4(\text{CO})_{12}$	0.1069/ 0.00905	CH_3I	14.5	38.02	5.03	371	26
7	$[\text{N}(\text{PPh}_3)_2][\text{Os}(\text{CO})_3\text{I}_3]$	0.1069	HI	2.5	7.24	0.12	69	28

^aReaction conditions: CH_3OH , 369.85 mmol; temperature, 140°C; co-catalyst, 3.57 mmol; agitation speed, 600 min^{-1} .

^bMeasured by gas chromatography.

^cTON (catalytic turnover number) = mol products formed ($\text{CH}_3\text{COOCH}_3$ and CH_3COOH) per mol catalyst.

^dTOF (catalytic turnover frequency) = mol products formed ($\text{CH}_3\text{COOCH}_3$ and CH_3COOH) per mol catalyst per hour.

side-product which, according to its ^1H NMR spectrum ($\delta = 3.30$ ppm, s), is presumably dimethylether.

The catalyst $[\text{Os}_3\text{Ir}(\text{CO})_{13}]^-$ **1** undergoes fragmentation and re-organisation during the catalytic process. At the end of the reaction, no intact Os_3Ir cluster anion is found in the reaction solution, whatever the reaction conditions are. An organometallic product which precipitates from the solution is identified by IR spectroscopy as $\text{Ir}_4(\text{CO})_{12}$. By evaporation of the solution under reduced pressure a second organometallic compound crystallises and is identified to be $[\text{N}(\text{PPh}_3)_2][\text{Os}(\text{CO})_3\text{I}_3]$. This is in accordance with similar observations using $[\text{N}(\text{PPh}_3)_2][\text{Ru}_3\text{Ir}(\text{CO})_{13}]$ as the catalyst, where $\text{Ir}_4(\text{CO})_{12}$ and $[\text{N}(\text{PPh}_3)_2][\text{Ru}(\text{CO})_3\text{I}_3]$ are obtained after the catalytic reaction. In order to get an idea, if the catalytically active species could be a mixed-metal rather than a homometallic compound, experiments with a mixture of $\text{Ir}_4(\text{CO})_{12}$ and $[\text{N}(\text{PPh}_3)_2][\text{Os}(\text{CO})_3\text{I}_3]$ were tested for the catalytic reaction. The results show in all cases that the mixed-metal cluster $[\text{N}(\text{PPh}_3)_2][\text{Os}_3\text{Ir}(\text{CO})_{13}]$ is a better catalyst than the reaction mixture of $\text{Ir}_4(\text{CO})_{12}$ and $[\text{Os}(\text{CO})_3\text{I}_3]^-$ (Table 5).

Despite these results, catalysis by an intact mixed-metal cluster is not very likely, since the treatment of $[\text{Ru}_3\text{Ir}(\text{CO})_{13}]^-$ with an excess of HI in methanol at room temperature immediately leads to the formation of $\text{Ir}_4(\text{CO})_{12}$ and $[\text{N}(\text{PPh}_3)_2][\text{Ru}(\text{CO})_3\text{I}_3]$, as found in the catalytic reaction mixture. Therefore, the question of cluster catalysis remains a debatable point.

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