Journal of Organometallic Chemistry, 94 (1975) 99—106

THE REACTION OF $Ir_4(CO)_{12}$ WITH BASES

M. ANGOLETTA, L. MALATESTA and G. CAGLIO

Istituto di Chimica Generale e Inorganica dell' Università e Centro del C.N.R., Via G. Venezian 21, 20133 Milano (Italy)

(Received February 10th, 1975)

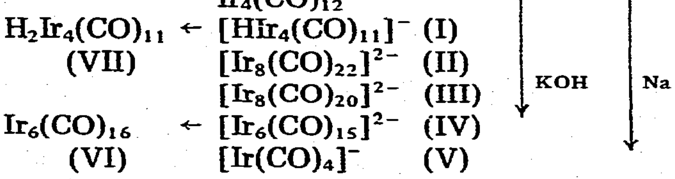
Summary

The reaction of $Ir_4(CO)_{12}$ with potassium hydroxide in methanol and/or with sodium in tetrahydrofuran leads to the carbonyliridate anions $[HIr_4(CO)_{11}]^-$, $[Ir_8(CO)_{22}]^{2-}$, $[Ir_8(CO)_{20}]^{2-}$, $[Ir_6(CO)_{15}]^{2-}$ and $[Ir(CO)_4]^-$ obtained as salts with bulky cations. From these, the tetranuclear carbonyl hydride $H_2Ir_4(CO)_{11}$ and the hexanuclear carbonyl compound $Ir_6(CO)_{16}$ are also obtained.

In a brief communication [1] we reported the preparation of the cluster carbonyl anions $[HIr_4(CO)_{11}]^-$, $[Ir_8(CO)_{20}]^{2-}$, $[Ir_6(CO)_{15}]^{2-}$ and also the neutral $Ir_6(CO)_{16}$. We now report in more detail the reactions of $Ir_4(CO)_{12}$ with potassium hydroxide in methanol, and with sodium in tetrahydrofuran which lead to these and other cluster carbonyl compounds.

Results and discussion

The reaction between $Ir_4(CO)_{12}$ and potassium hydroxide or carbonate, in methanol, and that between $Ir_4(CO)_{12}$ and sodium or sodium amalgam in tetrahydrofuran give rise to the same series of anions from I to IV:



In the presence of alcohol, successive nucleophilic attacks on the carbonyl groups take place:

$$Ir_4(CO)_{12} + OR^- \rightarrow [Ir_4(CO)_{11}COOR]^{-}*$$

followed either by disproportionation, with reduction of the metal and oxidation of a carbon monoxide ligand to carbon dioxide, or by elimination of a CO group as formate. The first reaction takes place in, for example, passage from I to II:

$$Ir_4(CO)_{12} \xrightarrow{OR^-} [Ir_4(CO)_{11}COOR]^- \xrightarrow{2OH^-} [HIr_4(CO)_{11}]^- + CO_3^{2-} + ROH$$

whilst the second reaction, which merely reduces the number of CO groups attached to the cluster, takes place in the passage from I to III. Both reactions must occur simultaneously in the passage from III to IV. This explains why the reaction which converts IV to V occurs only with sodium and THF. The reactions from I to III, with sodium in THF, are probably indirect, and brought about by the hydroxide formed by traces of water: in fact they do not take place in thoroughly dry THF. On the other hand, the reaction from IV to V implies a transfer of electrons from sodium metal to the cluster, followed by addition of CO and depolymerisation:

$$[Ir_6(CO)_{15}]^{2-} \xrightarrow[Na]{CO} Na[Ir(CO)_4] + \text{products}$$

The reaction rates of the different steps between I and V are very different in the two cases. Hence, to allow isolation of each of the intermediate compounds, it is preferable, and sometimes necessary, to follow either reaction sequence. Anion V can be obtained only by reaction with sodium. The anion I is readily obtained from $Ir_4(CO)_{12}$ suspended in a methanol solution of K_2CO_3, or KOH, under carbon monoxide and can be isolated as the benzyltrimethylammonium salt, Ia. Under the same conditions, but in a nitrogen atmosphere, the reaction leads directly to anion III. Since carbon monoxide does not appear in the hypothetical reaction $2\ I \rightarrow II + H_2$ and since the anion II has never been obtained under these conditions, we suggest that I gives III directly via the equilibrium reaction $2\,I \rightarrow III + H_2 + 2\,CO$.

The effect of the presence of CO may hence be explained, expecially if we consider that the carbonyliridate anions catalyse the formation of formate from carbon monoxide**, so that the concentration of the latter in the solution becomes very low unless an excess is continuously supplied. The salt Ia is stable enough in aprotic solvents to allow determination of its molar conductivity, which is as expected for a uni-unielectrolyte, and of the IR and NMR spectra, which indicate the presence of a hydride hydrogen and of terminal and bridging CO's. Hence, we suggest that I has a structure derived from that of the parent carbonyl $Ir_4(CO)_{12}$ with a hydrido ion substituting a CO group. Ethanol solutions of Ia are unstable in a nitrogen atmosphere and impure $Ir_4(CO)_{12}$ slowly separates. By contrast, the same reaction in a CO atmosphere

---

* This ester has been isolated as the tetraalkylammonium salt by Paolo Chini and coworkers (personal communication).

** Unpublished results from this laboratory.

gives very pure $Ir_4(CO)_{12}$ in almost quantitative yield, probably via the reaction:

$$[HIr_4(CO)_{11}]^- + H_2O + 2\,CO = Ir_4(CO)_{12} + H_2 + HCO_2^-$$

When Ia is treated directly with dilute acetic acid in a nitrogen atmosphere, it gives the crystalline dihydride $H_2Ir_4(CO)_{11}$ (VII), which shows a hydride signal in the NMR at τ 25.53 (against TMS) and in the IR at 2130 cm^{-1}. The anion II is easily obtained by reducing a suspension of $Ir_4(CO)_{12}$ in THF with sodium, and can be precipitated as the tetramethyl- (IIa) or tetraethyl-ammonium (IIb) salt. These do not show any signal ascribable to hydride hydrogen in the NMR or IR spectra, and have the expected conductivity (Λ 30.4 and 35.4 in nitrobenzene). IIb can also be obtained directly from the solid Ia by leaving it for several days in a nitrogen or carbon monoxide atmosphere. The proposed structure of II follows from the assumption that the loss of hydrogen from I is accompanied by a link between two tetrahedra. The ν(CO) IR stretching bands in anion II are at practically the same frequencies as those in anion I, as expected, since the ratio between the number of the iridium atoms in the cluster and its charge are the same in I and II. On the other hand, the bistetrameric structure is in agreement with the diamagnetism of the compound.

The anion III is considered to have two CO groups less than the anion II, in agreement with the analytical data for oxygen of its tetraethylammonium salt, IIIa. Unfortunately, it is not possible to measure the CO set free in the reaction II → III + 2 CO because the gas is not evolved but, rather, is transformed into formate ion. Moreover, the addition of excess triphenylphosphine (L) to IIa and IIIa gives $Ir_4L_3(CO)_9$ whilst with Ia it gives $Ir_4L_2(CO)_{10}$. IIIa is stable in an inert atmosphere and has Λ 43.2 in nitrobenzene. Solutions of IIIa in ethanol are stable under a CO atmosphere (in contrast to solutions of Ia) and on addition of acetic acid give only 20% of $Ir_4(CO)_{12}$.

By carrying out the reduction of III with sodium in THF (or, less conveniently, with potassium hydroxide in methanol) a new IR band at 1980 cm^{-1} gradually appears, accompanied by the gradual disappearance of that at 2020 cm^{-1}. When this latter band has just disappeared, addition of an aqueous solution of tetraethylammonium chloride gives a brown precipitate, IVa. A full crystal structure analysis on IVa has not been performed, but it is isomorphous with $[NEt_4][Co_6(CO)_{15}]$. The analytical data of IVa, the virtual identity of its IR spectrum with those of the corresponding rhodium and cobalt compounds, and, finally, its easy conversion into $Ir_6(CO)_{16}$, are also in accordance with this structure. The anion IV can also be obtained easily from $Ir_4(CO)_{12}$ and $[Ir(CO)_4]^-$ added in a ratio corresponding to 6 iridium atoms per 2 negative charges:

$$Ir_4(CO)_{12} + 2[Ir(CO)_4]^- \rightarrow [Ir_6(CO)_{15}]^{2-} + 5\,CO$$

Compound IVa suspended in acetic acid under a CO atmosphere gives slowly the neutral compound $Ir_6(CO)_{16}$ which has been shown by X ray analysis to be isostructural with $Co_6(CO)_{16}$ and $Rh_6(CO)_{16}$ [2].

When the reaction with ethanol and potassium hydroxide is carried on beyond the stage where IV is observed, other brown anions are formed, which can be precipitated as a mixture of tetraalkylammonium compounds. The Ir/CO

(continued on p. 104)

TABLE 1

ANALYTICAL AND IR DATA

No.	Formula	Found (calcd.) (%)					Colour	Λ	IR ν(Ir—H) and ν(CO)
		C	H	N	O	Ir		(Ω^{-1}cm^{2}mol^{-1})	
I	$[Na][HIr_4(CO)_{11}]$								2020-1795s (THF)
Ia	$[N(CH_2C_6H_5)Me_3)][HIr_4(CO)_{11}]$	20.28	1.25	1.15	14.8	62.4	yellow	22.1	2010s-1790s (nujol)
		(20.48)	(1.39)	(1.14)	(14.36)	(62.6)			
Ib	$[NBu_4][HIr_4(CO)_{11}]$	24.3	2.67	0.50	14.25	56.2			2065(sh), 2015s, 1965s, 1800s (THF)
		24.62	2.82			58.1			
						59.5			
		(24.6)	(2.81)	(1.06)	(13.35)	(58.3)	yellow		
					58.1				
Ic	$[NEt_4][HIr_4(CO)_{11}]$	18.8	1.60		14.36		yellow		2010-1790s (nujol), 2065w, 2025(sh),
					15.05				
		(18.95)	(1.74)		(14.60)				2015s, 1970(sh), 1800s (THF)
II	$Na_2[Ir_8(CO)_{22}]$						red		2020-1800s (THF)
IIa	$[NMe_4]_2[Ir_8(CO)_{22}]$	15.11	1.26	1.00			red		2060w, 2025(sh), 2015s, 1970(sh), 1800s
		(15.64)	(1.04)	(1.22)					
IIb	$[NEt_4]_2[Ir_8(CO)_{22}]$	19.52	1.83	1.10			red		2020-1780s (nujol)
		18.64	1.75	1.04	15.05				2020-1800s (THF)
		(18.90)	(1.66)	(1.16)	(14.6)				
III	$Na_2[Ir_8(CO)_{20}]$						brown		2020-1795s (THF)
IIIa	$[NEt_4]_2(Ir_8(CO)_{20}]$	18.72	1.94	1.15	12.52		brown	30.4	2010-1790s (nujol)
					12.96				2020-1780s (CH_2Cl_2)
		(18.35)	(1.70)	(1.19)	(13.6)				2020-1800s (THF)
IIIb	$[N(CH_2C_6H_5)Me_3]_2[Ir_8(CO)_{20}]$	20.68	1.18	1.30	13.04	62.4	brown		2010-1780s (nujol)
		(20.02)	(1.34)	(1.17)	(13.35)	(64.2)			

IIIc	$[NMe_4]_2[Ir_8(CO)_{20}]$	15.6 (14.95)	0.78 (1.07)	1.31 (1.25)			34.5	2010-1780s (nujol)
IVa	$[NEt_4]_2[Ir_6(CO)_{15}]$	20.50 20.46 20.74 (20.30)	2.35 2.21 2.03 (2.18)	1.65 1.53 1.54 (1.53)	14.03 (13.10)	brown	53.2	2020(sh), 1970s, 1910(sh), 1770s, 1745s (THF)
IVb	$[NMe_4]_2[Ir_6(CO)_{15}]$	16.29 (16.05)	1.57 (1.4)	1.61 (1.63)		brown		2030(sh), 1970s, 1910(sh), 1775s, 1735s (THF)
IVc	$[Ph_3PCH_2CH_2PPh_3][Ir_6(CO)_{15}]$	29.19 (28.80)	1.48 (1.41)					
V	$Na[Ir(CO)_4]$						white	2000w, 1898s, 1868(sh) (THF)
Va	$[Ni(fen)_3][Ir(CO)_4]_2$	42.79 44.20 (43.80)	2.30 2.25 (2.0)	6.30 6.58 (6.97)			pale-pink	1880s (THF) 1868s (nujol) 2000w, 1898s, 1868(sh) (THF)
Vb	$[Ph_3P{=}N{=}Ph_3][Ir(CO)_4]$	57.03 (57.0)	3.47 (3.56)	1.45 (1.66)			white	1890s (THF)
VI	$Ir_6(CO)_{16}$	10.99 (12.0)				red-brown		2115w, 2070s, 2057(sh), 2047w, 2034vw, 2009vw, 1800w, 1765s (nujol)
VII	$Ir_4(CO)_{11}H_2$	12.67 12.88 (12.28)	0.19 0.13 (0.18)					2130s, 2055s, 2020m, 2010m [742-728 δ(Ir—H)] (nujol)
VIII	$Ir_4L_2(CO)_{10} \cdot C_6H_6$	37.90 (37.8)	1.82 (2.18)		9.86 (9.7)	orange	PF = 215 PM = 1740	2064s, 2036s, 1992s, 1965m, 1862w, 1827s, 1790s (CS_2)
IX	$Ir_4L_3(CO)_9$	41.87 (41.9)	2.38 (2.5)		8.16 (7.97)	orange	PF = 170 PM = 2090	2063m, 2042s, 1998s, 1985s, 1964m, 1815w, 1778s, 1777s, 1711w (CS_2)

ratio in these compounds is very high, and becomes higher the longer the reaction time. The IR spectra do not show any difference in the CO stretching bands compared to those of IV. This suggests that these compounds are cluster anions containing many iridium atoms, in which, as in IV, there is one negative charge per 3 metal atoms. Hence, it appears that the hydroxide, from this point on, no longer acts as a reducing agent but only as a decarboxylating agent, the nucleophilic attack on carbon monoxide giving potassium formate and not potassium carbonate.

On the other hand, when the reaction with sodium in THF is carried beyond the stage at which IV is formed, a brown solid is observed and the mother liquor becomes colorless. If the reaction is carried out under CO, the solid contains only 20% of the iridium present in solution, but if the reaction is carried out under N_2 it contains about 80%. This solid is a sodium salt, probably a mixture of cluster carbonylpolyiridates with a very low CO/Ir ratio. It is soluble in ethanol, from which it can be precipitated as the tetraalkylammonium salt, a pyrophoric black powder of varying composition, having CO stretching bands at 1950 and 1720 cm^{-1}. The colourless solution contains the tetracarbonyliridate anion V, which could be isolated either as the tris(phenantroline)nickel salt Va or as the bis(triphenylphosphine)immonium salt Vb.

The anion V is a very strong base which is protonated by ethanol to give $Ir_4(CO)_{12}$:

$$[Ir(CO)_4]^- \xrightarrow{C_2H_5OH} Ir(CO)_4H \rightarrow Ir_4(CO)_{12}$$

It is a very strong reducing agent, as shown by its reaction with bis(triphenylphosphonium)ethane dichloride with which it gives $[Ir(PPh_3)(CO)_3]_2$ [3] instead of the corresponding salt.

Analytical and infrared data are presented in Table 1.

Experimental

When more than one alkylammonium salt was obtained, the preparation of only one is reported. When using a CO or N_2 atmosphere the solvents were first saturated with the gas.

$[NCH_2C_6H_5Me_3][HIr_4(CO)_{11}]$ *(Ia)*

From $Ir_4(CO)_{12}$ (420 mg) in MeOH with K_2CO_3 (160 mg) by stirring under CO at room temperature for 2 h. The yellow solution was treated with excess aqueous $N(CH_2C_6H_5)Me_3Cl$ (150 mg) solution (40 ml). The yellow powder which separated was filtered under CO, washed with water and dried in vacuum (256 mg, yield 55%).

Compound Ia may also be obtained, as described below, by stopping the reaction as soon as the $Ir_4(CO)_{12}$ was dissolved and the solution became yellow.

$[NEt_4]_2[Ir_8(CO)_{22}]$ *(IIb)*

From $Ir_4(CO)_{12}$ (819 mg) in THF (50 ml) with Na (478 mg) by stirring under CO at room temperature until the colour turned yellow and then red.

After decanting, 45 ml of clear solution were transferred to a flask and treated with a small excess of NEt_4Cl in water (50 ml). The red powder was then filtered under CO, washed with water and dried in vacuum (380 mg, yield 42%).

$[N(CH_2C_6H_5)Et_3]_2[Ir_8(CO)_{22}]$ from Ia

When 450 mg of Ia were stored under high vacuum for a week, the solid became red, without any change in the analyses. In the IR and NMR spectrum the IrH absorptions were no longer present.

$[NEt_4]_2[Ir_8(CO)_{20}]$ (IIIa)

From $Ir_4(CO)_{12}$ (668 mg) in methanol (20 ml) with KOH (290 mg) by stirring under N_2 at room temperature for 15 min. The brown solution was then treated with excess NEt_4Cl in water (20 ml), the brown powder filtered under N_2, washed with water and dried in vacuum (430 mg, yield 60%).

From $Ir_4(CO)_{12}$ (819 mg) and Na (478 mg) in THF, as for compound II, but carrying out the reaction until the colour turned brown. Care must be taken to stop the reaction as early as possible. The IR CO stretching band must be at 2020 cm^{-1}. A peak at 1980 cm^{-1} indicates the presence of the anion IV.

$[NEt_4]_2[Ir_6(CO)_{15}]$ (IVa)

From $Ir_4(CO)_{12}$ (810 mg) and Na (478 mg) in THF, as for compound II, but carrying on the reaction until the solution turned brown and the terminal stretching CO was 1980 cm^{-1}. The brown powder obtained by addition of an ethanol solution of NEt_4Cl was recrystallised from THF—EtOH, giving brown crystals of IVa (35%).

From $Ir_4(CO)_{12}$ (668 mg) and KOH (290 mg) in methanol (20 ml), as for III, but until the IR terminal CO stretching was 1980 cm^{-1}.

From $Ir_4(CO)_{12}$ (350 mg) and 5 ml of a THF solution of $NaIr(CO)_4$ containing 122 mg of iridium by stirring under CO for 10 h. Addition of NEt_4Cl in ethanol (10 ml) to the brown solution and leaving to stand for a day gave brown crystals of IVa (250 mg, yield 43%).

Uncharacterized brown tetraethylammonium polycarbonylpolyiridates

The reaction of $Ir_4(CO)_{12}$ (334 mg) with KOH (145 mg) in methanol (10 ml) was allowed to proceed in three different runs, for 30 min, 1 h and 2 h, respectively, beyond the point at which compound IV is formed. The brown solutions were then treated with NEt_4Br and the precipitates obtained filtered in a N_2 atmosphere and dried. The analyses indicated very low and variable Ir/CO ratios, and also variable Ir/N ratios. Pure substances could not be obtained by recrystallisation.

$[Niphen_3][Ir(CO)_4]_2$ (Va)

From $Ir_4(CO)_{12}$ (400 mg) in THF (30 ml) with Na (400 mg) by stirring under CO at room temperature for 16 h. After decanting, the clear colourless solution was treated with $[Niphen_3]Cl_2$ (500 mg) in water (150 ml). The white powder was filtered under CO, washed with degassed water and dried in vacuum (346 mg, 40%).

$[(Ph_3P)_2N][Ir(CO)_4]$ (Vb)

As above with sodium amalgam (0.98 g in 7 ml mercury) by addition of $(Ph_3P)_2NCl$ to the clear solution.

$Ir_6(CO)_{16}$ (VI)

From $[NEt_4]_2[Ir_6(CO)_{15}]$ (170 mg) in acetic acid under CO (30 ml) at room temperature for 2 days. The red-brown crystals were filtered, washed with ethanol and dried in vacuum (130 mg, yield 87%).

$Ir_4(CO)_{11}H_2$ (VII)

A methanol solution of $[NMe_4][HIr_4(CO)_{11}]$ (320 mg) was treated with acetic acid under nitrogen. The white powder was filtered under N_2, washed with a N_2-saturated water solution and dried in vacuum (150 mg, yield 52%).

$Ir_4(PPh_3)_2(CO)_{10}$ (VIII)

From $Ir_4(CO)_{12}$ (480 mg) in ethanol (20 ml) with K_2CO_3 (150 mg), by stirring under CO at room temperature for 2 h. The yellow solution was treated with PPh_3 (350 mg) in 50 ml benzene. The orange precipitate was filtered under CO, washed with water, ethanol and then hexane (420 mg, yield 61%).

$Ir_4(PPh_3)_3(CO)_9$ (IX)

As for compound VIII by stirring at 50°C for 6 h. The brown solution was treated with PPh_3 (350 mg). The orange precipitate was filtered under CO, washed with water, ethanol, and then hexane (510 mg, yield 65%). From $Ir_4(CO)_{12}$ (730 mg) in THF (40 ml) with Na (460 mg) by stirring under CO at room temperature until the solution became red in colour. After decanting, 35 ml of clear solution were treated with PPh_3 (520 mg) in benzene. Concentration of the mixture gave an orange precipitate (770 mg, yield 70%).

References

1 L. Malatesta, G. Caglio, Chem. Commun., (1967) 420;
L. Malatesta, G. Caglio, M. Angoletta, Chem. Commun., (1970) 532.
2 P. Chini, Inorg. Chim. Acta, (1968) 31.
3 L. Malatesta, M. Angoletta, G. Caglio, J. Organometal. Chem., 73 (1974) 265.